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Certification for Trace Elements and Methyl Mercury Mass Fractions in IAEA-452 Scallop (*Pecten maximus*) Sample

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CERTIFICATION FOR TRACE ELEMENTS AND METHYL MERCURY MASS FRACTIONS IN IAEA-452 SCALLOP (*Pecten maximus*) SAMPLE

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FOREWORD

The primary goal of the IAEA Environment Laboratories (NAEL) is to help Member States understand, monitor and protect the marine environment. The major impact exerted by large coastal cities on marine ecosystems is therefore of great concern to the IAEA, particularly to its Environment Laboratories. The marine pollution assessments needed to understand such impacts depend on accurate knowledge of contaminant concentrations in various environmental compartments. Two fundamental requirements to ensure the reliability of analytical results are quality control (QC) and quality assurance (QA). Since the early 1970s, NAEL has been assisting national laboratories and regional laboratory networks through its reference material programme for the analysis of radionuclides, trace elements and organic compounds in marine samples. Relevant activities include global interlaboratory comparison exercises and regional proficiency tests, the production of marine reference materials, and the development of reference methods for analysis of trace elements and organic pollutants in marine samples.

QA, QC and associated good laboratory practice should be essential components of all marine environmental monitoring. QC procedures are commonly based on the analysis of reference materials to assess reproducibility and measurement bias. QA can be realized by participation in externally organized laboratory performance studies, also known as interlaboratory comparison exercises, which compare and evaluate the analytical performance and measurement capabilities of participating laboratories.

The need for good QA/QC in the chemical analysis of marine environmental samples is widely recognized and has been tested in a number of international QA exercises. Such diligence also needs to be applied to other components of the monitoring exercise, since these may represent a greater source of error in many instances. Data that are not based on adequate QA/QC can be erroneous, and their misuse can lead to poor environmental management decisions. The IAEA has a long history of organizing interlaboratory studies, which have evolved to include an increasing array of potential contaminants in the marine environment.

A marine certified reference material (CRM), IAEA-452, prepared with a scallop (*Pecten maximus*) sample, was recently produced by the IAEA and certified for trace elements and methylmercury (MeHg). This species of scallop is a common, widely consumed seafood that is also used as a bioindicator for trace metal contamination in marine pollution studies.

This publication presents the sample preparation methodology, material homogeneity and stability studies, evaluation of certification campaign results, and assignment of property values and their associated uncertainty. The reference values and associated expanded uncertainty for nine trace elements (As, Cd, Cr, Cu, Fe, Hg, Mn, Pb and Zn) and MeHg in the scallop sample are established. The informative value for one more element (Ni) is also given. The new CRM can be used for the development and validation of analytical methods in the determination of trace elements and MeHg in seafood *Pecten maximus* as well as for QA/QC purposes.

The IAEA officers responsible for this publication were E. Vasileva and S. Azemard of the IAEA Environment Laboratories.

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CONTENTS

1. INTRODUCTION

The society’s growing interest in environmental issues requires the production of reliable information for policy makers, stakeholders and public in general. This information must be based on accurate and comparable results produced by qualified laboratories. National and international marine monitoring programmes have been initiated worldwide to assess the quality of the marine environment. In monitoring programme it is considered essential to ensure that the data produced from different laboratories over a number of years can be compared. If results are to be comparable, it is essential that they are based on reliable measurement standards whose values are linked to a stated reference. The difficulties inherent to traceability are generally recognised, but this task can be considerably simplified by the use of a suitable certified reference material (CRM). CRMs are key tools to establish traceability of measurement results. Indeed the best reference material should be of a matrix similar to the analysed sample and should contain comparable mass fraction of analytes of interest. Regular use of CRM by laboratories is essential also for the performance evaluation of analytical techniques and for the validation of analytical methods used in environmental monitoring programmes.

The Marine Environmental Studies Laboratory (MESL) of the International Atomic Energy Agency’s Environment Laboratories (IAEA-NAEL) has the programmatic responsibility to provide assistance to its Member States’ laboratories, in maintaining and improving the reliability of analytical measurement results, both in trace elements and organic pollutants. This is accomplished through the provision of CRMs of marine origin, validated analytical procedures, training in the implementation of internal quality control, and through the evaluation of measurement performance by the organization of worldwide and regional interlaboratory comparison (ILC) exercises. IAEA’s analytical quality control service (AQCS), now named reference products for environment and trades represents important benchmark in upgrading the quality of laboratory performances and assessing the validity of the analytical methods used for marine monitoring studies in the Member States.

One of the outcomes from the IAEA’s coordinated research project on seafood safety was the identification of the need of producing seafood matrix CRM with elevated level of toxic elements. The species selected was scallop (*Pecten maximus*), which is popular seafood in many countries and is used to assess the potential transfer of toxic elements through the food chain.

The CRM IAEA-452 will assist laboratories in validating their analytical methods and controlling the quality of produced analytical results for the determination of trace elements and methyl mercury in marine biota samples.

2. METHODOLOGY

2.1. COLLECTION AND PREPARATION OF THE MATERIAL

Two hundred kilograms of scallop (*Pecten maximus*) was collected in December 2007 and January 2008 by scuba diving in Pertuis Breton, western France. Organisms were immediately dissected. Soft tissues (the gills, mantle and digestive glands) were thawed overnight in a refrigerator, and lyophilised in a Labconco Freeze Dry System 4.5 (Labconco, Kansas City, USA). The freeze dried matter was grinded to a powder in a grinder Retsch SM 200 (Retsch, Haan, Germany). The powder was then sieved through a 250 µm sieve (Fritsch, Idar Oberstein, Germany). Biota particles retained in the sieve were collected, milled and sieved again. The sieved material with a particle size of less than 250 µm was further homogenized. The homogeneity was performed by mixing the material in a stainless steel rotating homogeniser Moritz ERM-BB124 (Moritz, Chatou, France) for 14 days in a clean atmosphere at a temperature of 20°C (+/-2) and relative humidity of 50%. After checking for the homogeneity of sample material, aliquots of about 8 g were packed into pre-cleaned brown borosilicate glass bottles with polyethylene screw caps and then sealed in plastic bags. The sample material was labelled as the IAEA-452 sample. The average moisture content of the sample after bottling was determined by drying to a constant weight at 85°C.

2.2. SELECTION OF LABORATORIES FOR THE CERTIFICATION CAMPAIGN

The selection of participants for this certification exercise was based on the measurement performances, demonstrated by laboratories in the previous IAEA's ILC. Each laboratory received one bottle of scallop (*Pecten maximus*) sample, accompanied by an information sheet and a report form. Participants were requested to analyse as many trace elements as possible, using a validated analytical method. They were asked to report the measurement results (six replicates and average value) along with the expanded uncertainty in addition to the information about the applied quality control procedure. The second request was to report results for the trace elements in CRM with similar to the candidate reference material matrix. Moisture determination method was prescribed.

Sixteen of the 23 invited laboratories sent the requested information/measurement results (value and expended uncertainty), description of the method used, results from the analysis of CRM and results for moisture determination.

The reference value for MeHg was obtained from the results of the worldwide ILC run on the same matrix in 2009 [1].

List of laboratories participating in the certification exercise is presented in Table 1.

TABLE 1. LIST OF LABORATORIES PARTICIPATING IN THE IAEA-452 CERTIFICATION

LABORATORIES	COUNTRY
International Atomic Energy Agency, IAEA	
Brooks Rand Labs, BRL	USA
University of Plymouth, UP	UK
Finnish Customs Laboratory, FCL	FINLAND
Centro de Energia Nuclear na Agricultura, CENA	BRAZIL
Comisión Chilena de Energía Nuclear, CCEN	CHILE
Institute for Environmental Protection and Research, ISPRA	ITALY
Laboratory of Environmental Chemistry, NKUA	GREECE
Flett Research Ltd., FRLtd	CANADA
Ukranian Scientific Center of the Ecology of the Sea, UkSCES	UKRAINE
Trent University, TU	CANADA
Laboratory of Public Health, Department of Health, LPH	MACAO
National Agency for New Technologies, Energy and Sustainable Economic Development, ENEA	ITALY
Institute of Nuclear Chemistry and Technology, INCT	POLAND
Israel Oceanographic & Limnological Research, IO-LR	ISRAEL
Institute of Public Health, IPH	CROATIA

2.3. HOMOGENEITY TESTING

Extensive homogeneity tests were carried out on this material in order to ensure its suitability as a candidate reference material and to estimate the uncertainty associated with homogeneity of the sample. Between bottle homogeneity was tested by the determination of the mass fraction of some typical elements (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn and MeHg). In total, 10 bottles were selected using random stratified sampling of the whole batch. Care was taken to ensure that the order of measurements did not correspond to the filling sequence of the bottles, which enable the differentiation between potential trend in the filling sequence and analytical drift. Three subsamples from each bottle were analysed for their total element mass fractions. The within bottle homogeneity was assessed by 15 replicate determinations of the content of investigated trace elements in one bottle. Subsamples of 0.2 g were mineralised with 5 ml conc. HNO_3 and digested in a microwave oven by adding 2 ml conc. HF according to the protocol described earlier [1]. The final measurements were performed by graphite furnace atomic absorption spectrometry under repeatability conditions and in a randomised way in order to be able to separate a potential analytical drift from a trend in the filling sequence. The determination of the total mercury was done in solid subsamples with solid mercury analyser. The method used for homogeneity study of MeHg was based on alkaline digestion and aqueous phase ethylation followed by gas chromatography separation, thermal desorption of Hg species and atomic fluorescence spectrometry (AFS) detection. All methods used for homogeneity studies were previously validated by MESL, IAEA.

2.4. STABILITY STUDY

Three sets of five bottles each were stored in the dark at different temperature, -20°C, +20°C and +60°C, just after bottling process and kept at described conditions over a period of two years. One isochronous study over 8 weeks was applied to evaluate stability of the materials during transport and one isochronous study over 12 months and 24 months, respectively, to evaluate stability during storage. Obtained results were compared with the results from samples kept at -20°C during this period (-20°C is considered the reference temperature). The stability investigation for the evaluation of long term stability is still ongoing.

2.5. CHARACTERIZATION

Characterization refers to the process of determining the reference values. The candidate reference material was initially analysed by MESL. The final characterization was based on the results delivered by selected laboratories with demonstrated measurement capabilities, based on criteria that comprised both technical and quality management aspects. Characterization of the trace element mass fraction in the IAEA-452 scallop (*Pecten maximus*) sample was based on the application of different analytical techniques as summarised in Figure 1. All participating laboratories have used validated methods for determination of trace elements in marine samples. In addition they provided results from the analysed CRM with similar matrix composition and the information on standard calibration solutions, used for every trace metal and MeHg. The results of laboratories that did not report any quality assurance information were excluded from the further evaluation.

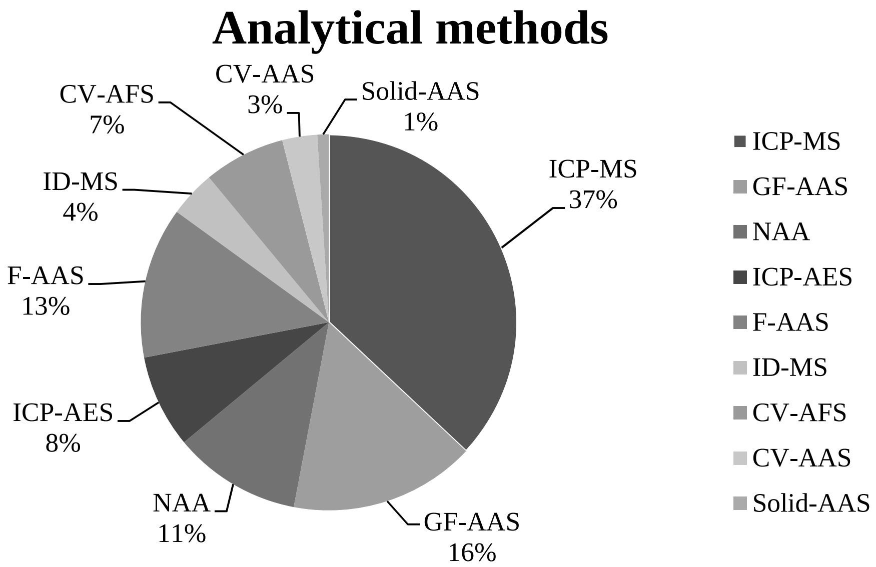


FIG. 1. Analytical methods used for the certification of trace elements in the IAEA-452 biota sample.

Combined uncertainties were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [3], including uncertainties due to possible heterogeneity and instability.

All participating laboratories claimed traceability of provided results to the International System of Units (SI) via standard calibration solutions and CRM applied as a part of their analytical procedures.

2.6. MOISTURE DETERMINATION

The determination of the moisture content of the samples is to some extent operationally defined. In view of the comparability of results, the protocol for the correction of the moisture was developed at NAEL and prescribed to other participants. The drying procedure at 85^{o}C (+/-2) was established after experimental evaluation of sample stability. Correction for dry mass was obtained from separate portions of the material of minimum mass of 0.5 g (10 sub samples from 5 bottles). The weighing and repeated drying were performed until constant mass was attained. Moisture, determined at 85°C was found to be 6.5% ± 0.4% for bottles kept at 20°C.

3. RESULTS AND DISCUSSION

3.1. RESULTS OF THE HOMOGENEITY STUDY

For the homogeneity study, 10 samples (about 2% of the total batch) of the IAEA-452 were chosen using a random stratified sample picking scheme and analysed for their trace elements and MeHg contents in triplicate. The results were combined and evaluated to detect any trends regarding filling or analysis sequence and to estimate the uncertainty contribution from possible heterogeneity. Grubbs tests were performed to identify potentially outlying individual results as well as outlying bottles means. Two individual results for Ni, Cr and Pb respectively were detected as outlier. These results were excluded as they were outliers at 95% but also at 99% confidence level.

The retained individual results and bottle means were checked whether they follow a normal distribution or are unimodally distributed. The series of results for investigated trace elements and MeHg were normally distributed. The distribution of Cr, Ni and Pb were skewed, but unimodal. One way analysis of variance ANOVA [2] was then applied to assess the between bottles and within bottles homogeneities. The ANOVA allowed the calculation of within unit standard deviation S_{wb} and also between bottles standard deviation S_{bb}:

$$s_{wb} = u_{wb} = \sqrt{MS_{wb}} \tag{1}$$

$$s_{bb} = u_{bb} = \sqrt{\frac{MS_{bb} - MS_{wb}}{n}} \tag{2}$$

For several elements (As, Fe, Zn, MeHg) MS_{bb} (ANOVA mean square between bottles) was smaller than MS_{wb} (ANOVA mean square within bottles) and $S_{bb.}$ could not be calculated. Instead u^*_{bb}, the heterogeneity that can be hidden by the method repeatability was calculated, as described by Linsinger et al. [4]:

$$u^*_{bb} = \frac{s_{wb}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwb}}} \tag{3}$$

where:

n is number of replicate subsamples per bottle;

V_{MSwb} is the degrees of freedom of MS_{wb}.

Heterogeneity could be quantified due to the good repeatability of the method used. The between bottles variations/heterogeneity were between 2.0 and 6.1%, small enough to ensure the homogeneity of the material. The uncertainty contributions due to the inhomogeneity were estimated according to ISO Guide 35 [2] as the maximum values obtained with Equation 2 or Equation 3. The results for sample size 0.2 g are presented in Table 2.

TABLE 2. THE ESTIMATE OF INHOMOGENEITY CONTRIBUTIONS TO THE TOTAL UNCERTAINTY FOR THE CERTIFIED TRACE ELEMENTS

Element	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	MeHg
u_{bb}%		2.3	6.1	1.2		1.2	1.8	4.5	5.9		
u^*_{bb}%	2.2				1.6					0.9	3.2

The conclusion from the presented results for the tested trace elements was that the homogeneity of the candidate reference material complied with the provisions given by the ISO 35 at the range of weights used. A minimum sample intake of 0.2 g was set, based on the smallest sample intake used in the characterization study.

3.2. RESULTS FROM THE STABILITY STUDY

Samples selected for stability study were analyzed and each of the elements was evaluated individually. No outliers were detected on 95% confidence level in any study. The evaluation of data was further carried out by performing a linear regression on the determined mass fractions vs. time.

The test material showed no significant trend to degradation over the time frame at different temperature -20°C, +20°C and +60°C. Significant impact of storage conditions on the stability of the certified properties could be detected, neither of storage time nor of temperature (up to +60°C). In all cases the slope of the linear regression did not significantly differ from zero. No significant slope at 95% level of confidence was detected for any of investigated analytes, neither in the short term study nor in the long term study. As no degradation could be observed under any conditions neither, in the short term nor in the long term study, it was concluded that no special precautions regarding temperature control during shipment were necessary. The uncertainty of the short term stability (u_{sts}) was assumed to be negligible since no degradation is expected to happen during this short time. Nevertheless, 20°C was chosen as the storage temperature.

Failure to detect degradation does, however, not prove stability. The uncertainty of stability u_{stab} describes the potential degradation which still can be reconciled with the data, even if the slope is not statistically significantly different from zero. Although under these conditions, an expansion of the total uncertainty of the certified values is generally not encouraged, but in this case the approach of ISO Guide 35 was followed, mainly due to the lack of sound alternatives. An uncertainty contribution related with stability of the candidate reference material was estimated as uncertainty of the regression line with a slope of 0 multiplied with the chosen shelf life, as described by Linsinger et al. [5]. Factor of 3 was selected, taking into account a minimum shelf life of 3 years. Stability during storage period was chosen as 1%, which ensured the validity of the certificate for at least 3 years. Results for MeHg mass fractions in the IAEA-452 scallop (*Pecten maximus*) sample found in bottles kept at different storage conditions over 3 years period are presented in Table 3. Each result is obtained as a mean value for MeHg mass fractions for three different bottles (three replicates from each one).

TABLE 3. MASS FRACTIONS OF MeHg IN THE IAEA-452 SCALLOP (*Pecten maximus*) SAMPLE FOUND IN BOTTLES KEPT FOR DIFFERENT TIMES IN DIFFERENT STORAGE CONDITIONS

Temperature	-20°C	20°C	60°C
1 week	0.022±0.03	0.023±0.04	0.021±0.04
1 year	0.021±0.02	0.020±0.03	0.021±0.04
2 years	0.022±0.03	0.022±0.03	0.020±0.03
3 years	0.022±0.03	0.023±0.02	0.021±0.04

Obtained results from short term and long term studies provide evidence to a good stability of all analytes under consideration, including MeHg.

3.3. DETERMINATION OF CERTIFIED VALUES AND UNCERTAINTIES

The characterization campaign resulted in 7 to 14 results per element and 16 results for MeHg. The obtained data were first checked for compliance with the certification requirements and then for their validity based on technical reasons. All accepted set of results were submitted to the following statistical tests: Grubbs test to detect single and double outliers, Dixon’s test to detect outlying lab means and Kolmogorov–Smirnov test for normal distribution.

Four outlying values (two for Zn, one for Cr and one for Cu) were detected in the received data sets. These results were outliers at 95%, but not at 99% confidence level. The outlying values were scrutinised but no technical reason for exclusion was found, therefore the results were accepted for further evaluation. The normal distribution at 95% level of confidence was found for the sample means of all studied elements except for Zn. At 99% level of confidence Zn means were also normally distributed. All laboratories reported combined standard and expended uncertainties. As more important contributors to the combined uncertainty they stated recovery, within lab reproducibility and uncertainty of the reference value of the CRM applied.

The IAEA-452 reference values were calculated as a median of the accepted dataset, rounded off to the most significant number of the uncertainty, as described in ISO 13528 [5]. The robust mean and unweighted mean of the means were also calculated and compared with the respective medians. As no differences were observed, the reference values obtained with the median approach were further used. These values are considered to be the most reliable estimates of the property values.

The uncertainties associated with the reference values were calculated according to the ISO standard 35 [2]. The relative combined uncertainty of the certified value of the CRM consists of uncertainty related to characterization u_{char}, between bottle heterogeneity (u_{bb}) and long term stability (u_{stab}). These different contributions were combined to estimate the expanded, relative uncertainty.

$$U^2_{CRM,rel} = 2^*(u^2_{char} + u^2_{hom} + u^2_{stab}) \tag{4}$$

where

k: coverage factor equalling 2, representing a level of confidence of about 95%;

u_{hom} was estimated as a larger value of the standard deviation between bottles (u_{bb}) or the maximum heterogeneity potentially hidden by the method repeatability (u_{bb}*) as previously shown in Table 2;

u_{stab} was the stability during storage period chosen as 1%, which as described before, ensured the validity of the certificate for at least 3 years;

u_{char} was estimated using an approach described by Pauwels, J., et al. [6]. In this approach, the uncertainty of characterization is separated into laboratory dependent uncertainty u(I), uncertainty common to all laboratories u(II) and uncertainty common to a groups of laboratories u(III).

$$u(I) = \frac{\sqrt{\sum_1^n u_i^2}}{n} \tag{5}$$

where

u_i is the combined standard uncertainty for the mean value given by each laboratory;

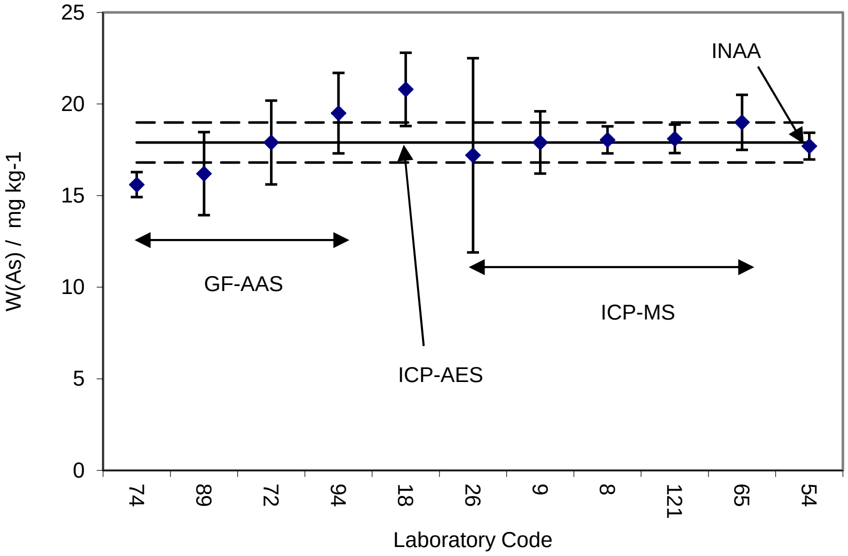
n is the number of laboratories. For this study u(II) and u(III) were set to zero.

As it can be seen from the Figure 1, methods with different quantification steps (AAS, GF-AAS, AFS, ICP-OES, ICP-MS — see Table 4 for list of instrumental techniques) as well as methods without sample preparation step (NAA) were used for characterization of the material. The agreement between results confirms the absence of any significant method bias and demonstrates the identity of the analyte.

TABLE 4. INSTRUMENTAL TECHNIQUES

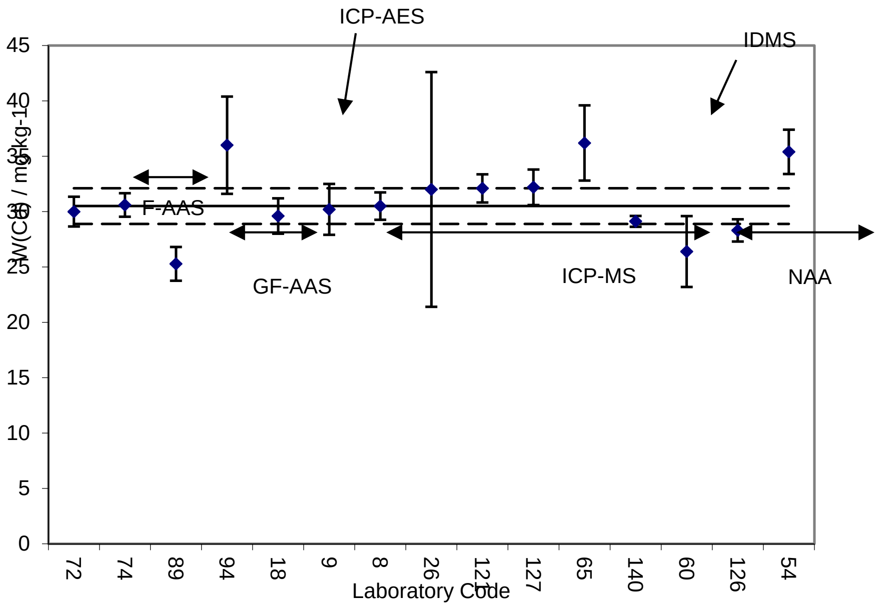
Method code	Instrumental technique
AAS	Atomic absorption spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ID-MS	Isotope dilution ICP-MS
ICP-AES	Inductively coupled plasma atomic emission spectrometry
AFS	Atomic fluorescence spectrometry
CV	Cold vapour
GF	Graphite furnace

Provided by participants, results for trace elements and MeHg mass fractions grouped by methods are displayed in Figures 2 to 11. Detailed results as they were reported by participants are shown in Appendix II. In all figures the reported results are plotted versus the reference values, which are denoted by a bold line, while the dashed lines represent the expended uncertainty (*k=2*) associated with the reference value. Error bars represent expanded uncertainty as reported by participants.



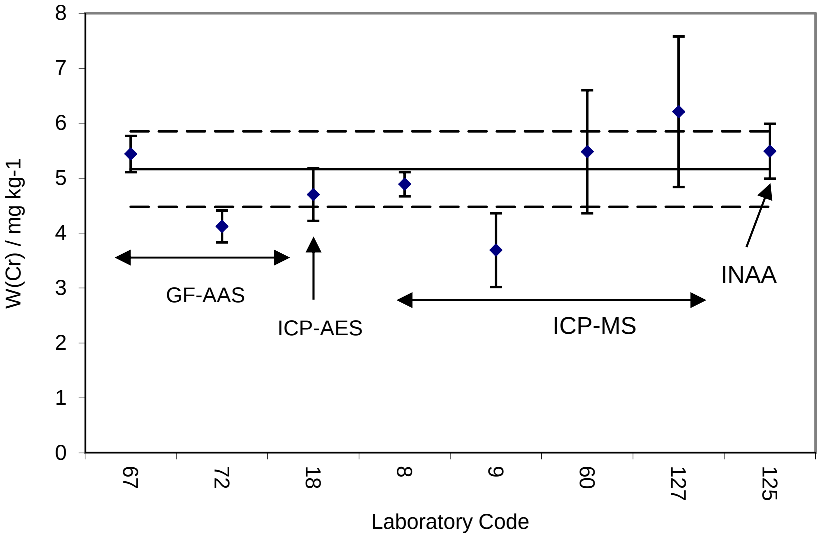
The median (solid line) and corresponding expanded uncertainty (k=2) (dashed line) are shown. The error bars correspond to the expanded uncertainty reported by each laboratory.

FIG. 2. Laboratory results for arsenic mass fraction (mg kg^{-1}).



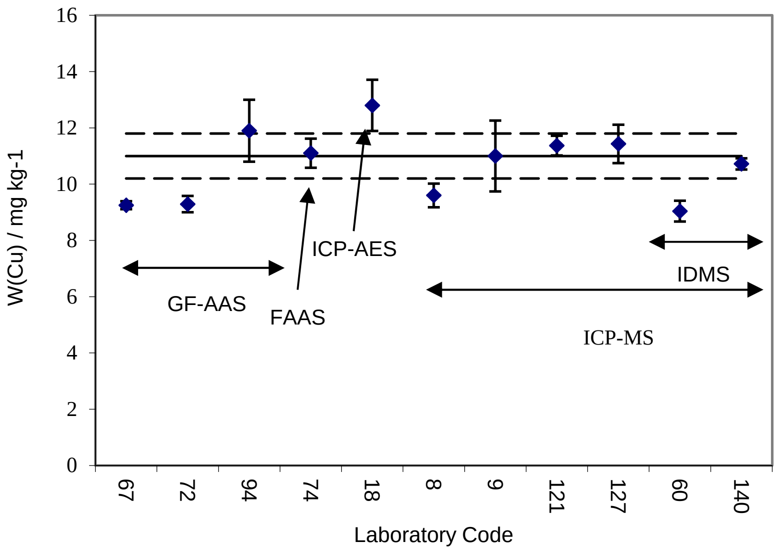
The median (solid line) and corresponding expanded uncertainty (k=2) (dashed line) are shown. The error bars correspond to the expanded uncertainty reported by each laboratory.

FIG. 3. Laboratory results for cadmium (Cd) mass fraction (mg kg^{-1}).



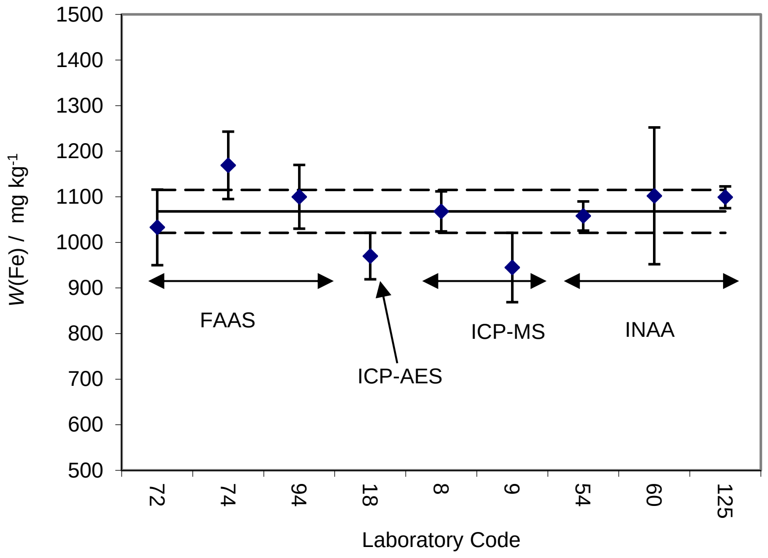
The median (solid line) and corresponding expanded uncertainty (k=2) (dashed line) are shown. The error bars correspond to the expanded uncertainty reported by each laboratory.

FIG. 4. Laboratory results for chromium mass fraction (mg kg^{-1}).



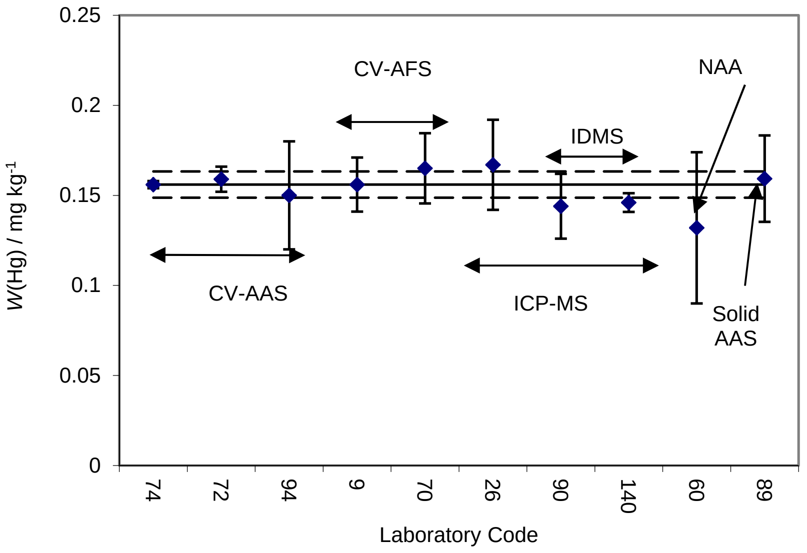
The median (solid line) and corresponding expanded uncertainty (k=2) (dashed line) are shown. The error bars correspond to the expanded uncertainty reported by each laboratory.

FIG. 5. Laboratory results for copper mass fraction (mg kg^{-1}).



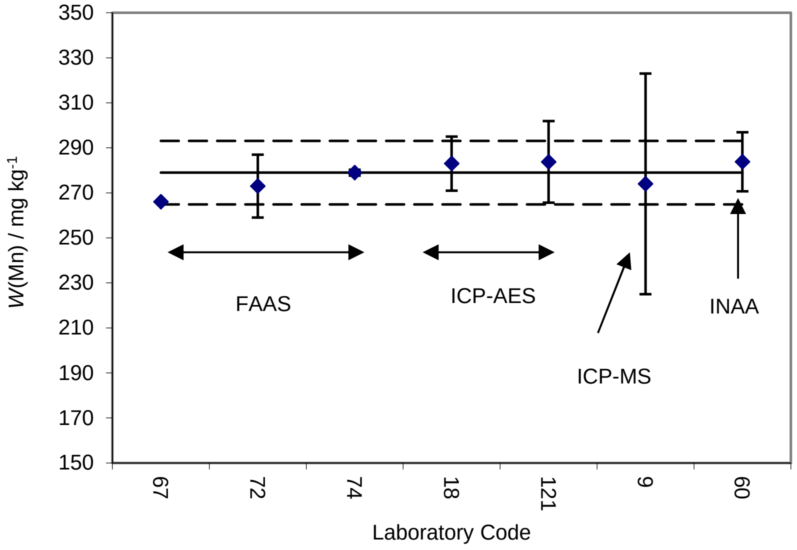
The median (solid line) and corresponding expanded uncertainty (k=2) (dashed line) are shown. The error bars correspond to the expanded uncertainty reported by each laboratory.

FIG. 6. Laboratory results for iron mass fraction (mg kg^{-1}).



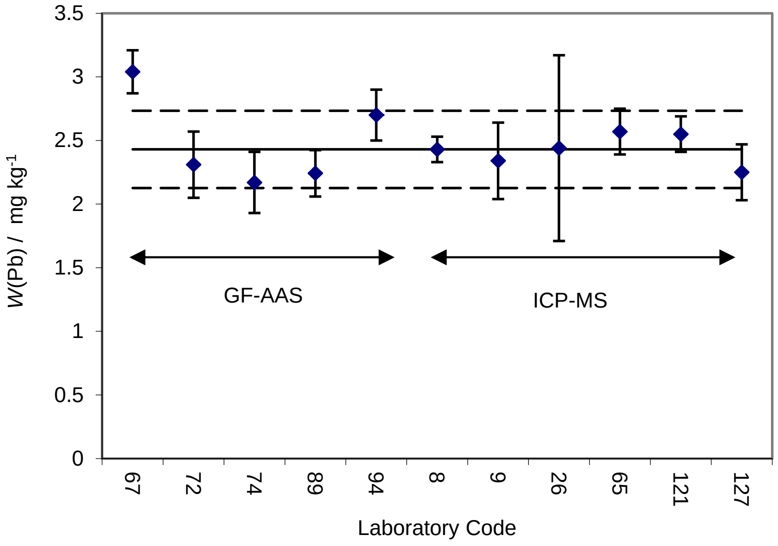
The median (solid line) and corresponding expanded uncertainty (k=2) (dashed line) are shown. The error bars correspond to the expanded uncertainty reported by each laboratory.

FIG. 7. Laboratory results for mercury mass fraction (mg kg^{-1}).



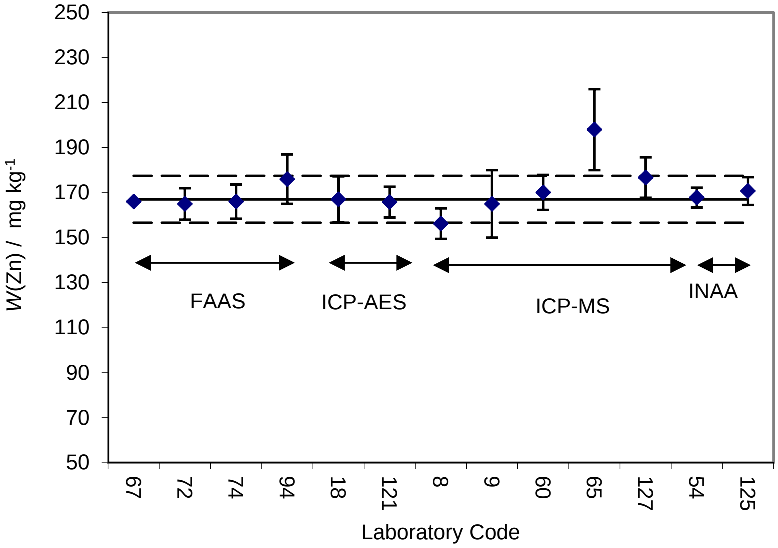
The median (solid line) and corresponding expanded uncertainty (k=2) (dashed line) are shown. The error bars correspond to the expanded uncertainty reported by each laboratory.

FIG.8. Laboratory results for manganese mass fraction (mg kg^{-1}).



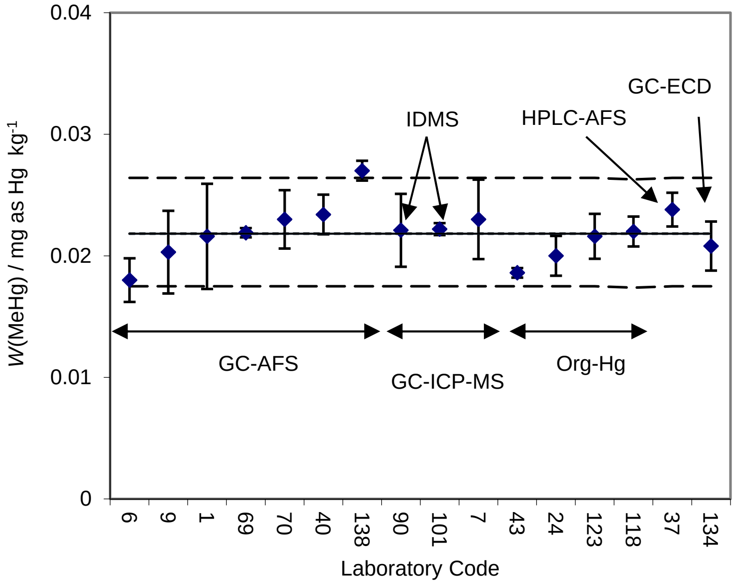
The median (solid line) and corresponding expanded uncertainty (k=2) (dashed line) are shown. The error bars correspond to the expanded uncertainty reported by each laboratory.

FIG. 9. Laboratory results for lead (Pb) mass fraction (mg kg^{-1}).



The median (solid line) and corresponding expanded uncertainty (k=2) (dashed line) are shown. The error bars correspond to the expanded uncertainty reported by each laboratory.

FIG. 10. Laboratory results for zinc mass fraction (mg kg^{-1}).



The median (solid line) and corresponding expanded uncertainty (k=2) (dashed line) are shown. The error bars correspond to the expanded uncertainty reported by each laboratory.

FIG. 11. Laboratory results for methyl mercury mass fraction (mg kg^{-1}).

A good agreement within the stated uncertainty was observed for results obtained with different methods. Therefore, all of them were considered in the deriving of reference values.

The reference values for As, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Zn and MeHg are presented in Table 5, together with their expanded uncertainty (*k=2*). Due to the limited number of provided results, the information value was assigned to Ni – see Figure 12.

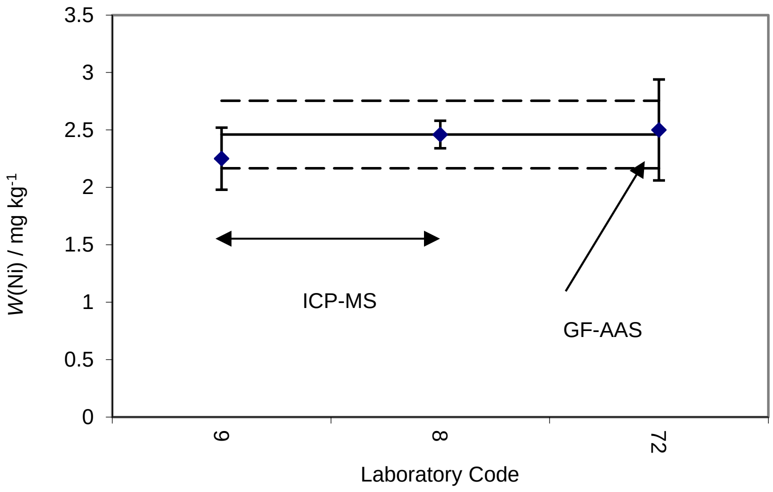
TABLE 5. REFERENCE VALUES FOR TRACE ELEMENTS AND MeHg MASS FRACTIONS AND THEIR EXPANDED UNCERTAINTY (*k=2*) IN THE IAEA-452 BIOTA SAMPLE

Element	Reference value[1] mg kg^{-1}	Expanded uncertainty [2] mg kg^{-1}	Number of accepted datasets
As	17.9	1.1	11
Cd	30.5	1.6	15
Cr	5.2	0.7	8
Cu	11.0	0.8	11
Fe	1068	47	9
Hg	0.16	0.02	10
Mn	279	14	7
Pb	2.4	0.3	11
Zn	167	10	13
MeHg	0.022	0.004	16

---

[1] The value is the median of accepted sets of data, each set being obtained by different laboratory. The certified values are reported on dry mass basis and are traceable to the SI.

[2] Expanded uncertainty with a coverage factor *k=2* according to the guide to the Expression of Uncertainty of Measurement (GUM), corresponding to the level of confidence of about 95%.



The median (solid line) and corresponding expanded uncertainty (k=2) (dashed line) are shown. The error bars correspond to the expanded uncertainty reported by each laboratory.

FIG. 12. Laboratory results for nickel mass fraction (mg kg^{-1}).

3.4. METHYL MERCURY (MeHg) CERTIFICATION

In total, 16 laboratories sent results for MeHg in the frame of the IAEA-452 ILC [1]. The sixteen results for MeHg were obtained using a variety of methodologies as described in Table 6. In the first step — release of MeHg from the binding sites, three techniques were mainly used: distillation, alkaline digestion and acid leaching. Further steps included separation of organic and inorganic mercury by ion exchange, solvent extraction or gas chromatography after appropriate derivatisation. The following methods were then applied for the detection of MeHg: atomic fluorescence spectrometry, gas chromatography with electron capture detector, inductively coupled plasma mass spectrometry and cold vapour atomic absorption spectrometry. Two laboratories used species specific isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS).

ID-ICP-MS method is considered as potentially primary method of measurement and gives the results with highest metrological quality. As it can be seen in Figure 11, the results within uncertainty obtained with other methods are in good agreement with those obtained after application of species specific ID-ICP-MS. Therefore the reference value for MeHg in the IAEA-452 sample was calculated taking into account the results provided by all sixteen laboratories participating in the IAEA's ILC study.

TABLE 6. METHODS FOR DETERMINATION OF MeHg, USED BY THE LABORATORIES PARTICIPATING IN THE IAEA-452 WORLDWIDE ILC

Sample preparation	Detection	Number of Laboratories
Alkaline digestion aqueous phase ethylation ($NaBEt_4$), GC separation, thermal desorption of Hg species at 600°C	AFS	7
Alkaline digestion, solvent extraction, derivatisation ($NaBEt_4$), GC separation	ICP-MS	1
Alkaline digestion, solvent extraction, derivatisation ($NaBEt_4$), GC separation	ID-ICP-MS	1
Distillation — aqueous phase ethylation ($NaBEt_4$), GC separation	ID-ICP-MS	1
Alkaline digestion, separation by HPLC	AFS	1
Dithizone–toluene extraction, GC separation	GC-ECD	1
Distillation, BrCl oxidation	CV-AAS	1
Toluene extraction, L-cysteine back extraction	CV-AFS	1
Leaching 10N HCl	CV-AAS	1
$H_2SO_4/CuSO_4/KBr$ leaching followed by toluene extraction, back extraction in aqueous thiosulfate solution	Solid AAS	1

Note: AFS: atomic fluorescence spectrometry; CV-AAS: cold vapour atomic absorption spectrometry; Solid AAS: solid Mercury analyser; ICP-AES: inductively coupled plasma atomic emission spectrometry; CV-AFS: cold vapour atomic fluorescence spectrometry; ICP-MS: inductively coupled plasma mass spectrometry; ID-ICP-MS: isotope dilution inductively coupled plasma mass spectrometry, GC-ECD: gas chromatography with electron capture detector.

4. METROLOGICAL TRACEABILITY AND COMMUTABILITY

If results obtained by different laboratories are to be comparable it is essential that all results are based on reliable measurement standards whose values are linked to a stated reference.

Only validated methods applied within stated scope were used by participating in the certification exercise laboratories. Matrix CRMs with stated SI traceability purchased from NIST, EC JRC IRMM, NRC-CNRC were used for validation of the applied in this study methods [1].

Pure metal standard solutions (CRM) with stated purity were employed for calibration from all laboratories participating in the certification campaign. As stated in the respective certificates of all CRM producers the mass fractions of the trace element and MeHg in the respective standard solutions were measured against another CRM (i.e. NIST, BAM or EMPA) with demonstrated SI traceability followed by gravimetric preparation using balances calibrated with SI-traceable weights. Consequently the value calculated by this unbroken chain of comparison is traceable to the reference to which the starting material is compared.

In addition, the agreement between the results confirms absence of any significant method bias and demonstrates the identity of the analytes.

Commutable CRMs should exhibit a similar analytical behaviour for given method as a real laboratory sample. Characterization study has been selected such as to provide variety of analytical methods, regarding sample preparation, calibration and detection. The good agreement between the results obtained indicates commutability of the material. However CRMs might show behaviour different from that of real samples, in particular during digestion, due to their small particle size in contrast to the possible larger particle size for real laboratory samples. The commutability was also confirmed in the frame of the IAEA worldwide ILC for trace elements with the same sample material, in which 143 laboratories took part [1].

5. CONCLUSIONS

This exercise allows assignment of reference values for As, Cd, Cr, Cu Fe, Hg, Mn, Pb, Zn and MeHg with associated uncertainties following ISO guidelines. The certified values are derived from measurement results provided by the laboratories participating in the certification campaign. Only validated methods were applied in the certification of the IAEA-452 scallop (*Pecten maximus*) sample. As the certified values are the combination of SI traceable individual results, they are themselves traceable to SI. The obtained results are in excellent agreement with the results from the IAEA-452 worldwide ILC exercise.

The produced matrix CRM is suitable for QC purposes of environment and food laboratories, and has a high level Cd as requested by experts in food safety. As any certified reference material, it can be used for validation studies.

6. ACKNOWLEDGEMENTS

We highly acknowledge the participants and laboratories that took part in this interlaboratory comparison exercise and contributed their time and facilities to the present work.

The International Atomic Energy Agency is grateful to the Government of the Principality of Monaco for the support provided to its Environment Laboratories.

Appendix I

REFERENCE SHEET
CERTIFIED REFERENCE MATERIAL

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REFERENCE SHEET

CERTIFIED REFERENCE MATERIAL

IAEA-452

MASS FRACTIONS OF TRACE ELEMENTS AND METHYL MERCURY IN BIOTA SCALLOP (*Pecten maximus*)

Analyte	Reference value[1] [mg kg^{-1}]	Expanded uncertainty[2] [mg kg^{-1}]
As	17.9	1.1
Cd	30.5	1.6
Cr	5.2	0.7
Cu	11.0	0.8
Fe	1068	47.0
Hg	0.16	0.02
Mn	279	14.0
Pb	2.4	0.3
Zn	167	10.0
MeHg	0.022	0.004

(1) Median of the accepted data sets, each set being obtained by a different laboratory and/or a different method of determination.
(2) Estimated expanded uncertainty with a coverage factor k=2, correponding to a level of confidence of approximately 95%, as defined in the Evaluation of measurement data — Guide to the expression of uncertainty in measurement JCGM100:2008 [7].

Origin and preparation of the material

200 kg of Scallop (*Pecten maximus*) were collected in December 2007 and January 2008 by scuba diving in the "Pertuis Breton", western France. Organisms were dissected and soft tissues (the gills, mantle and digestive glands) lyophilized. The freeze dried matter was milled to a powder in a grinder, then sieved through a 250 µm sieve. The sieved material with a particle size of less than 250 µm was further homogenized.

Homogeneity was achieved by mixing the material in a stainless steel rotating homogenizer for 14 days in a clean atmosphere at a temperature of (20 +/-2)° C and relative humidity of 50 %. After checking for the homogeneity of sample material, aliquots of about 8 g were packed into pre-cleaned brown borosilicate glass bottles and then sealed in plastic bags. The sample material was labelled IAEA-452.

Homogeneity of the material, dry mass determination and recommended minimum test portion

Homogeneity of the material

Between bottle homogeneity was tested by the determination of the mass fraction of all certified elements (As, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Zn and MeHg). In total, 10 bottles were selected using random stratified sampling of the whole batch. Three subsamples from each bottle were analysed for their total element mass fractions. The within bottle homogeneity was assessed by 15 replicate determinations of mass fraction of trace elements in one bottle. The final measurements were performed by Graphite Furnace Atomic Absorption Spectrometry after microwave acid digestion. The determination of the total mercury was done in solid subsamples with solid mercury analyser. The method used for homogeneity study of MeHg was based on alkaline digestion and aqueous phase ethylation, followed by gas chromatography separation, thermal desorption of Hg species and Atomic Fluorescence Spectrometry detection. All analytical procedures used for homogeneity studies were previously validated in the IAEA's Marine Environmental Studies Laboratory (MESL), Monaco.

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 were attained and the uncertainty due to between and within bottles heterogeneity was within acceptable limits.

Dry mass determination

The average moisture content of the material was determined by drying several test portions of 1 g in an oven at 85±2°C until constant weight and was found to be approximately 6.5±0.8% (k=2). Since the moisture content can vary with ambient humidity and temperature, it is recommended that it should be checked prior to analysis and that all results should be corrected on a dry mass basis.

Recommended minimum test portion

Based on results obtained for within and between bottles homogeneity, the minimum test portion was set to be 0.2 g.

Characterization study

Twenty laboratories from Austria, Brasil, Canada, Chile, Croatia, Finland, Greece, Italy, Israel, Macao, Poland, UK, USA, including the IAEA Monaco Laboratory, participated in the characterization study.

Laboratories were requested to determine as many trace elements as possible by their analytical method of choice. The following methods were used: Atomic absorption spectrometry (flame and graphite furnace), inductively coupled optical emission spectrometry, inductively coupled mass spectrometry, neutron activation analysis and atomic fluorescence spectrometry.

Assignment of values — certification procedure

The assigned property values were established on the basis of results reported by participating laboratories to the IAEA Environment Laboratories in Monaco. The median concentrations for the sets of individual data were chosen as the best estimate of the property values [8]. Certified values are assigned when at least 7 laboratory means were available, and at least 4 different analytical methods applied.

The details concerning all reported results as well as the criteria for certification may be found in "Certification for trace elements and methyl mercury mass fractions in IAEA-452 scallop (*Pecten maximus*) sample"[8]. The paper is available free of charge upon request.

Based on the evidence on calibrators used, quality control procedures applied by the participating laboratories and their generally high quality performance in the IAEA interlaboratory comparisons, the Certification Committee decided to accept these assigned values as certified.

Statement on metrological traceability and uncertainty of assigned values

Expanded uncertainties with a coverage factor of k=2, corresponding to a level of confidence of about 95%, were calculated according to the JCGM100:2008 Evaluation of measurement data — guide to the expression of uncertainty in measurement [7].

The quantity values assigned to the IAEA-452 certified reference material are mass fractions of specified trace elements, expressed in the derived SI unit mg kg^{-1}. Evidence on metrological traceability to the SI Units of reference materials and calibrators used in the characterization process was provided by all laboratories in their reports. More details can be found in the reference [8].

Intended use

This certified reference material (CRM) is intended to be used in the development, validation and quality control of analytical methods for the determination of trace elements in marine biota samples. Based on the above metrological traceability statement, this material is not to be used as calibrator.

Instructions for use

The reference material is supplied in 8 g units. The minimum sample volume (mass) laboratories should take when using the IAEA-452 is 0.2 g.

Handling and storage

The original unopened bottle should be stored securely at ambient temperature in a dark and dry place. Analysts are reminded to take appropriate precaution in order to avoid contamination of the material during handling.

Issue and expiry date

The issue date of this reference material is **March 2012**. The expiry date is **March 2017**. 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 31:2000

The content of this this IAEA Reference Sheet is in compliance with the ISO Guide 31:2000: Reference materials — content of certificates and labels [9].

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-453, 'Trace elements and methyl mercury in biota'. IAEA, Vienna, 4 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 can be found in the IAEA's Reference Materials online catalogue:

http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials

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Appendix II

DATA REPORT OF RESULTS SORTED BY ELEMENTS

TABLE II.1. ARSENIC: RESULTS AS REPORTED BY PARTICIPANTS (in mg kg^{-1})

Lab code	Mean	Combined uncertainty (u)	Expanded uncertainty (U)
8	18.04	0.37	0.74
9	17.9	0.86	1.7
18	20.8	0.98	2
26	17.2	2.7	5.3
54	17.7	0.36	0.73
65	19	0.8	1.5
72	17.9	0.86	2.29
74	15.6	0.34	0.68
89	16.2	1.135	2.27
94	19.5	1.1	2.2
121	18.1	0.39	0.78

TABLE II.2. CADMIUM: RESULTS AS REPORTED BY PARTICIPANTS (in mg kg^{-1})

Lab code	Mean	Combined uncertainty (u)	Expanded uncertainty (U)
8	30.5	0.62	1.24
9	30.2	1.15	2.3
18	29.6	0.79	1.6
26	32	5.3	10.6
54	35.4	1	2
60	26.4	1.6	3.2
65	36.2	1.7	3.4
67	23.6	0.124	0.247
72	30	0.5	1.34
74	30.6	0.53	1.06
89	25.28	0.765	1.53
94	36	2.2	4.4
121	32.1	0.63	1.27
126	28.3	0.5	1
127	32.2	0.8	1.6

TABLE II.3. CHROMIUM: RESULTS AS REPORTED BY PARTICIPANTS (in mg kg^{-1})

Lab code	Mean	Combined uncertainty (u)	Expanded uncertainty (U)
8	4.89	0.11	0.22
9	3.69	0.333	0.67
18	4.7	0.24	0.48
60	5.48	0.56	1.12
67	5.44	0.164	0.329
72	4.12	0.11	0.29
125	5.49	0.24	0.5
127	6.21	0.68	1.37

TABLE II.4. COPPER: RESULTS AS REPORTED BY PARTICIPANTS (in mg kg^{-1})

Lab code	Mean	Combined uncertainty (u)	Expanded uncertainty (U)
8	9.6	0.21	0.42
9	11	0.632	1.26
18	12.8	0.46	0.91
60	9.04	0.19	0.37
67	9.25	0.07	0.141
72	9.29	0.11	0.29
74	11.1	0.26	0.52
94	11.9	0.55	1.1
121	11.37	0.18	0.35
127	11.43	0.34	0.68

TABLE II.5. IRON: RESULTS AS REPORTED BY PARTICIPANTS (in mg kg^{-1})

Lab code	Mean	Combined uncertainty (u)	Expanded uncertainty (U)
8	1068	22	44
9	945	38	76
18	970	26	51
54	1058	16	32
60	1102	75	150
72	1033	31	83
74	1169	37	74
94	1100	34.8	70
125	1099	12	24

TABLE II.6. MERCURY: RESULTS AS REPORTED BY PARTICIPANTS (in mg kg^{-1})

Lab code	Mean	Combined uncertainty (u)	Expanded uncertainty (U)
9	0.156	0.0077	0.015
26	0.167	0.013	0.025
60	0.132	0.021	0.042
70	0.165	0.0097	0.0195
72	0.159	0.003	0.007
74	0.156	0.001	0.002
89	0.1593	0.012	0.024
90	0.144	0.009	0.018
94	0.15	0.013	0.03

TABLE II.7. MANGANESE: RESULTS AS REPORTED BY PARTICIPANTS (in mg kg^{-1})

Lab code	Mean	Combined uncertainty (u)	Expanded uncertainty (U)
9	274	24.4	49
18	283	5.9	12
60	283.8	6.5	13.1
67	266	0.04	0.09
72	273	5	14
74	279	6.6	1.32
121	283.76	9.07	18.14

TABLE II.8. LEAD: RESULTS AS REPORTED BY PARTICIPANTS (in mg kg^{-1})

Lab code	Mean	Combined uncertainty (u)	Expanded uncertainty (U)
8	2.43	0.05	0.1
9	2.34	0.15	0.3
26	2.44	0.37	0.73
65	2.57	0.09	0.18
67	3.04	0.084	0.169
72	2.31	0.1	0.26
74	2.17	0.12	0.24
89	2.242	0.091	0.182
94	2.7	0.095	0.2
121	2.55	0.07	0.14
127	2.25	0.11	0.22

TABLE II.9. ZINC: RESULTS AS REPORTED BY PARTICIPANTS (in mg kg^{-1})

Lab code	Mean	Combined uncertainty (u)	Expanded uncertainty (U)
8	156.2	3.4	6.8
9	165	7.5	15
18	167	5.1	10.2
54	167.8	2.2	4.4
60	170.1	3.9	7.8
65	198	9	18
67	166	0.077	0.155
72	165	3	7
74	166	3.8	7.6
94	176	5.2	11
121	165.8	3.42	6.84
125	170.7	3.1	6.2
127	176.7	4.5	9

TABLE II.10. NICKEL: RESULTS AS REPORTED BY PARTICIPANTS (in mg kg^{-1})

Lab code	Mean	Combined uncertainty (u)	Expanded uncertainty (U)
8	2.46	0.06	0.12
9	2.25	0.135	0.27
72	2.5	0.05	0.44

TABLE II.11. METHYL MERCURY: RESULTS AS REPORTED BY PARTICIPANTS (in mg kg^{-1})

Lab code	Mean	Combined uncertainty (u)	Expanded uncertainty (U)
1	0.0216	0.0009	0.0018
6	0.018	0.0017	0.0034
7	0.023	0.0022	0.0043
9	0.0203	0.0002	0.0004
24	0.020	0.0012	0.0024
37	0.0238	0.0008	0.0016
40	0.0234	0.0004	0.0008
43	0.0186	0.0015	0.0030
69	0.0219	0.0002	0.0005
70	0.0230	0.0016	0.0033
90	0.0221	0.0002	0.0004
101	0.0222	0.0008	0.0016
118	0.022	0.0009	0.0018
123	0.0216	0.0006	0.0012
134	0.0208	0.0007	0.0014
138	0.027	0.0010	0.0020

REFERENCES

[1] INTERNATIONAL ATOMIC ENERGY AGENCY, Worldwide Laboratory Comparison on the Determination of Trace Elements in IAEA-452 Biota Sample, IAEA/AQ/23, IAEA, Vienna (2012).

[2] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide 35:2006 (E), Reference Materials — General and Statistical Principals for Certification, ISO, Geneva, Switzerland.

[3] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide to the Expression of Uncertainty of Measurements: (1995) ISO, Geneva, Switzerland.

[4] LINSINGER, T., et al., Accreditation and quality assurance, **6** (2005) pp. 20–25.

[5] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide 13528:2005 (E), Statistics Methods for Use in Proficiency Testing by Inter-Laboratory Comparisons, ISO, Geneva, Switzerland.

[6] PAUWELS, J., LAMBERTY, A., SCHIMMEL, H., Accreditation and quality assurance, **3** (1998) pp. 180–181.

[7] JOINT COMMITTEE FOR GUIDES IN METROLOGY (JGCM), Evaluation ofmeasurement data — Guide to the Expression of Uncertainty in Measurement, JGCM 100:2008 (GUM with minor corrections) (2008), http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf

[8] VASILEVA, E., AZEMARD, S., OH, J., BUSTAMANTE, P., BETTI, M., Certification for Trace Elements and Methyl Mercury Mass Fractions in IAEA-452 Scallop (Pecten maximus) Sample, Accreditation and Quality Assurance. **16** (2011) 439–447.

[9] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION (ISO), Reference materials —– content of certificates and labels, ISO Guide 31: 2000, ISO, Geneva (2000).

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