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IMEP-30: Total arsenic, cadmium, lead, and mercury, as well as methylmercury and inorganic arsenic in seafood

Interlaboratory Comparison Report

Ines Baer, Beatriz de la Calle, Inge Verbist, Håkan Emteborg, Piotr Robouch

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The mission of the JRC-IRMM is to promote a common and reliable European measurement system in support of EU policies.

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Contents

1 Summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme® IMEP. It organises interlaboratory comparisons (ILC's) in support to EU policies. This report presents the results of an ILC which focussed on the determination of total As, Cd, Pb, and Hg, as well as methylmercury and inorganic arsenic in seafood.

The test material used in this exercise was the Certified Reference Material (CRM) DOLT-4, dogfish liver of the National Research Council of Canada (NRC). The material was relabelled and dispatched end of May 2010. Each participant received one bottle containing approximately 20 g of test material. Fifty-seven laboratories from 29 countries registered to the exercise and all of them reported results.

The assigned values and their associated uncertainties for total As, Cd, Pb, Hg and methylmercury are the certified values taken from the DOLT-4 certificate. An attempt was made to establish an assigned value for inorganic As (iAs) using the results provided by a group of five laboratories expert in the field, following a similar approach to that used in IMEP-107 [1], an ILC on total and inorganic arsenic in rice. Unfortunately, contrary to what was observed in IMEP-107, the results obtained by the expert laboratories for iAs showed a large spread and no assigned value could be established.

Participants were invited to report the uncertainty of their measurements. This was done by the majority of the laboratories taking part in this exercise. Laboratory results were rated with z- and ζ-scores (zeta-scores) in accordance with ISO 13528 [2]. No scoring was provided to laboratories for submitted results of iAs. The standard deviation for proficiency assessment (also called target standard deviation) was fixed to 15 % by the advisory board of this ILC, on the basis of the outcome of previous ILCs organised by IMEP and on the state-of-the-art in this field of analysis.

The outcome of the exercise was in general positive, the share of satisfactory z-scores ranging between 80 and 96 %. Results for total As, and to a lesser extent for total Cd, showed a tendency for underestimation. As for iAs, the same spread of results as for the certifiers could be observed with the participants' results. No method influence could be detected, but the matrix seems to have a major impact.

2 IMEP support to EU policy

The International Measurement Evaluation Programme® (IMEP) is owned by the JRC - IRMM. IMEP provides support to the European measurement infrastructure in the following ways:

- IMEP **distributes metrological traceability** from the highest level down to the routine laboratories. These laboratories can benchmark their measurement result against the IMEP reference value. This value is established according to metrological best practice.

- IMEP helps laboratories to assess their estimate of **measurement uncertainty**. The participants are invited to report the uncertainty on their measurement result. IMEP integrates the estimate into the scoring, and provides assistance for the interpretation.

IMEP supports EU policies by organising intercomparisons in the frame of specific EU legislation, or on request of a specific Directorate-General. IMEP-30 provided specific support to the following stakeholders:

- To the European Co-operation for Accreditation (EA) in the frame of a formal collaboration on a number of metrological issues, including the organisation of intercomparisons. National accreditation bodies were invited to nominate a limited number of laboratories for free participation in IMEP-30. Mr. Paul Greenwood from the United Kingdom Accreditation Service (UKAS) liaised between EA and IMEP for this intercomparison. This report does not discern the EA nominees from the other participants. Their results are however summarised in a separate report to EA.

- To the Asia Pacific Laboratory Accreditation Cooperation (APLAC), in the frame of the collaboration with EA. The chair of the APLAC Proficiency Testing Committee, Mr. Dan Tholen, was invited to register a limited number of laboratories for this collaboration.

- To the European Union Reference Laboratory for Heavy Metals in Feed and Food (EU-RL-HM) in the frame of the support to the National Reference Laboratories (NRLs). The exercise was announced to the network of NRLs and they were invited to distribute the information between routine laboratories in their respective countries.

3 Introduction

From a toxicological point of view metal speciation is of paramount importance since in most cases different species have different toxicologies. For instance, methylmercury is more toxic than the inorganic mercury compounds [3] while inorganic arsenic is more toxic than the organic species of arsenic, with arsenosugars and arsenobetaine not being toxic [1]. The mentioned differences in toxicology, depending on the species in which a metal is present in food, should be taken into consideration when fixing maximum levels in legislation.

In the EU, maximum levels for total mercury in food are given in legislation, varying from 0.5 to 1 mg kg^{-1} for different seafood, but no maximum level exists for methylmercury. The U.S. Food and Drug Administration established a guideline for methylmercury in seafood at a level of 1 mg kg^{-1}.

No maximum levels have been settled, so far, for arsenic in European legislation, due to a lack of information about reliable analytical methods for the determination of iAs in different food commodities and to the general belief among scientists that the results for iAs are method dependent.

Methylmercury was for the first time considered by IMEP in 2004 in the IMEP-20 exercise [4]. However, only 3 % of the participants (8) reported a result and no scorings were given at that time. The EU-RL-HM has started investigating laboratories' performance in the determination of methylmercury and iAs in the IMEP-104 [3] and IMEP-107 [1]. In support to this investigation, IMEP-30 was carried out in parallel with the EU-RL-HM / IMEP-109. The same test material was used in both exercises. IMEP-30 was open to all laboratories involved in this type of analysis.

4 Scope

The scope of this ILC is to test the competence of the participating laboratories to determine the total mass fractions of As, Cd, Pb, and Hg, as well as those of methylmercury and iAs. The assessment of the measurement results is undertaken on the basis of requirements laid down in EU legislation [5, 6] and follows the administrative and logistics procedures of IMEP (IRMM). This programme is accredited according to ISO Guide 43-1.

5 Time frame

The interlaboratory comparison was agreed upon by the NRL network at the fourth EU-RL-HM workshop held on 1-2 October 2009. The ILC was announced to EA and APLAC on 19 April 2010. The NRL network was informed on 17 May 2010, when the exercise was also made public on the IMEP webpage [7].

Initially the registration deadline was set on 6 June 2010. However, the registration interface had to be closed prematurely on 25 May 2010, since all available samples were allocated. Samples were sent out to the laboratories on 27 – 28 May 2010. For all laboratories the deadline for reporting results was 16 July 2010. This deadline was extended for one laboratory by one week, after getting confirmation that they would be able to submit results in time. Another laboratory was allowed to submit its result for methylmercury one month later, as not many results were received for this measurand and under condition that the other values were submitted in time.

6 Invitation, registration and distribution

Invitations for participation were sent to the EA coordinator (Annex 1) and APLAC responsible (Annex 2) for distribution to nominated and interested laboratories. NRLs were informed via email (Annex 3) about this parallel exercise to give them the opportunity to invite laboratories from their respective countries. The web announcement on the IRMM website can be found in Annex 4.

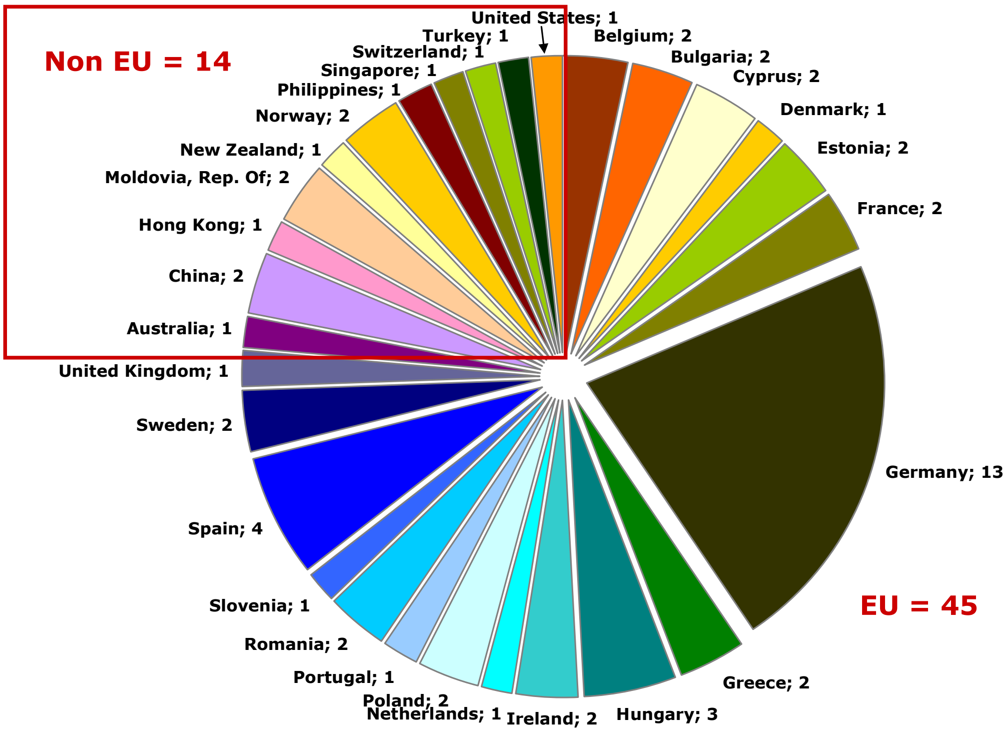
A letter containing instructions on measurands, sample storage conditions, water content determination, measurements, the individual access code for the result reporting website and further details on the envisaged time frame was sent to the participants together with the samples (Annex 5).

The participants received the reference values two weeks after the reporting interface was closed, except for methylmercury where it was sent on 23 August 2010. Fig 1 shows the participating countries and the number of participants having reported results.

6.1 Confidentiality

EA was invited to nominate laboratories for participation. The following confidentiality statement was made to EA: "*Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing. The EA accreditation bodies may wish to inform the nominees of this disclosure.*"

Fig 1- Country distribution in IMEP-30 based on number of participants having submitted results



6.2 Distribution

The ILC sample was dispatched by IRMM on 27 – 28 May 2010 to the participants. Each participant received one bottle containing approximately 20 g of test material, an accompanying letter with instructions on sample handling and reporting (Annex 5) and a form that had to be sent after receipt of the test material to confirm its arrival (Annex 6).

The dispatch was followed by the messenger's parcel tracking system on the internet and in all cases the sample was delivered within a week.

6.3 Procedure to apply

Concrete instructions were given to all participants in a letter that accompanied the test material. The measurands and matrix were defined as "Total As, Cd, Pb, and Hg, as well as methylmercury and inorganic As". Laboratories were asked to perform two or three independent measurements and to report the mean of the results, the uncertainty associated to the mean, the coverage factor and the technique that has been used to perform the measurements. The measurement results were to be corrected for recovery and for water content (following a procedure described in the accompanying letter which has been optimised at IRMM by the Reference Materials Unit). Participants were asked to follow their routine procedures. The results were to be reported in the same manner (e.g. number of significant figures) as those normally reported to customers.

The results were to be reported in a special on-line form for which each participant received an individual access code. A special questionnaire was attached to this on-line form. The questionnaire was intended to provide further information on the measurements and the laboratories (Annex 7).

7 Test material

7.1 Preparation

The commercially available CRM DOLT-4 (Dogfish Liver Certified Reference Material for Trace Metals) was used for this proficiency test (PT). The material was relabelled to avoid identification by the participants as an existing CRM. Comprehensive information on the preparation of the CRM can be found in the certification report (Annex 8) and on the NRC website [8].

The NRC dispatched about 60 bottles of test material at room temperature by courier to IRMM.

7.2 Homogeneity and stability

Information on the homogeneity and stability of the test material was gathered from the certificate of the CRM (Annex 8). According to the latter, uncertainties related to possible between-bottle variation (u_{hom}) are included in the overall uncertainty of the certified value. In the experience of the CRM producer, uncertainty components for long and short term stability were considered negligible and are thus not included in the uncertainty budget. As Total arsenic is homogenous and stable, it was assumed that this is also the case for iAs, as also confirmed from previous experience on the two measurands [1].

8 Reference values and their uncertainties

The CRM certificate provided certified values for all the measurands in this study except for iAs. The certified values were used as assigned values (X_{ref}) for this intercomparison. The certificate is valid until April 2014. The uncertainties provided in the certificate of the CRM represent the expanded uncertainties (U_{ref}) with a coverage factor k= 2, corresponding to a level of confidence of about 95 %.

In order to establish the assigned value for iAs, a group of five laboratories expert in the field performed analysis on the test material. The expert laboratories involved in the establishment of the assigned values were:

- Instituto de Agroquímica y Tecnología de Alimentos, Consejo Superior de Investigaciones Científicas (IATA-CSIC) (ES)
- Institute of Chemistry, Karl-Franzens University Graz (AT)
- The Food and Environment Research Agency (FERA) (UK)
- Technical University of Denmark (DTU)
- Department of Analytical Chemistry, University of Barcelona (ES)

The experts were asked to use the method of their choice without further requirements. The experts were also asked to report their results together with the measurement result uncertainty and a description of the method they have used. The means reported by the expert laboratories and their associated standard uncertainties (u_{exp}) for iAs are shown in Table 1, while the methods applied are summarised in Table 2.

Table 1 - Values for iAs and their associated uncertainties as reported by the expert laboratories.

Certifier	X_{exp} (mg kg^{-1})	u_{exp} (mg kg^{-1})	U_{exp} (mg kg^{-1})^{a}
1	< 0.040^{b}		
2	n.d.^{c}		
3	0.047	0.006	0.012
4	0.075	0.005	0.010
5	0.152	0.010	0.020

^{a} $U_{exp}= k \cdot u_{exp}$ is the estimated expanded uncertainty; with a coverage factor k= 2 corresponding to a level of confidence of about 95 %.
^{b} this is the LoQ (on dry matter content basis) of the method used.
^{c} not detected – the LoQ of the method used is 0.031 mg kg^{-1} for arsenite and 0.084 mg kg^{-1} for arsenate

Table 2 - Methods used by the expert laboratories for the determination of inorganic As.

Certifier	Sample treatment	Detection
1	0.2 g of sample and 10 mL 0.07 mol L^{-1} HCl in 3 % H_2O_2 were placed in µ-wave digestion vessels. Microwaves were applied for 20 min keeping the temperature at 90 °C. The extract was centrifuged and filtered (0.45 µm) prior to analysis with anion-exchange chromatography HPLC-ICP-MS	HPLC-ICP-MS
2	The inorganic arsenic (As(III) + As(V)) was evaluated from the speciation carried out after application of suitable extraction method. A sample of seafood (0.2 g from freeze-dried sample) and 20 ml of a methanol/water solution (1:1, v/v) were placed in the digestion vessels. 40 W of focused microwaves was applied for 10 min. After decanting, the extract was centrifuged at 2500 rpm for 10 min and the liquid phase was evaporated to remove the methanol under an IR lamp (T<40 °C) for approximately 4 h. The extract was then diluted in water up to 20 mL and filtered through a nylon membrane of 0.2 µm porosity. The filtrate was then defatted by clean-up with a C18 cartridge, which had been previously conditioned by passing methanol (5 mL) and water (5 mL) at 1 mL min^{-1}. The extract was passed through the cartridge (1 mL min^{-1}). The first 2–3 mL, mainly arising from conditioning solutions, were discarded. Finally, an aliquot of the cleaned up extract was made up to a fixed volume. Two chromatographic modes were used for separation of the As species. Arsenite, arsenate, DMA, MA, PO_4-sug, SO_4-sug and SO_3-sug were analyzed by anionexchange chromatography on the Hamilton PRP-X100 column using an aqueous solution of 20 mM $NH_4H_2PO_4$ at pH 5.6 as mobile phase. AB, AC, TMAO and Gly-sug were analysed in the extracts by cation-exchange chromatography on the Zorbax 300-SCX column with a mobile phase (1.5 mL min^{-1}) of 20 mM pyridine (pH=2.6, adjusted with formic acid).	HPLC-ICP-MS
3	0.250 g + 5 mL 1 mol L^{-1} trifluoracetic acid. Sonicate for 10 min and let stand overnight. Add 50 µL H_2O_2 to reduce arsenite to arsenate. Microwave in an argon atmosphere (max temp. 95 °C)	HPLC-ICP-MS
4	1 g of sample + 4.1 mL of H_2O + 18.4 mL of HCl agitated for 15 hours, let stand overnight. Add a reducing agent (2 mL HBr + 1 mL of hydrazine sulphate). Add 10 mL of chloroform and shake for 3 min. Separate the two phases centrifuging at 2000 rpm for 5 min. Repeat the extraction another two times. Eliminate remnants of organic As with a Whatman GD/X syringe filters with 25 mm PTFE membrane. Back extract into 10 mL of 1 mol L^{-1} HCl. Add 2.5 mL of 20 % w/v $Mg(NO_3).6H_2O$ and 2 % w/v MgO + 10 mL of 14 mol L^{-1} HNO_3. Evaporate to dryness at 425 °C for 12 h. Dissolve the ash in 5 mL of 6 mol L^{-1} HCl reduce with 5 mL reducing solution (5 % w/v KI + 5 % w/v ascorbic acid). After 30 min, filter the solution through Whatman No. 1 filter paper and dilute with 6 mol L^{-1} HCl.	FI-HG-AAS
5	Same approach as certifier 4 with some modifications, namely: No filtration through Whatman GD/X syringe filters was done before extracting into 1 mol L^{-1} HCl and no ashing step was applied; the 1 mol L^{-1} HCl was directly introduced in the HR-ICP-MS tuned to a resolution of at least 12,000.	HR-ICP-MS

Table 1 presents strong discrepancies among the results reported by the expert laboratories, contrary to what was observed in IMEP-107 (total and inorganic As in rice). For this reason, it was not possible to establish externally an assigned value for this measurand and it was decided not to score laboratories that reported results for iAs. The assigned reference values (X_{ref}) for the remaining measurands, total As, Cd, Pb, Hg and methylmercury, and their respective estimated uncertainties are summarised in Table 3.

Table 3 - Assigned values and their associated expanded uncertainties for the measurands of this ILC.

Measurand	X_{ref} (mg kg^{-1})	u_{ref} (mg kg^{-1})	U_{ref} (mg kg^{-1})
Total As	9.66	0.31	0.62
Total Cd	24.3	0.4	0.8
Total Pb	0.16	0.02	0.04
Total Hg	2.58	0.11	0.22
Methylmercury	1.33	0.06	0.12
iAs	Not available	Not available	Not available

X_{ref} is the reference value and $U_{ref}= k \cdot u_{ref}$ is the estimated associated expanded uncertainty; with a coverage factor k= 2 corresponding to a level of confidence of about 95 %.

9 Evaluation of results

9.1 General observations

All the 57 laboratories that registered for participation submitted results and completed the associated questionnaire. Of the 57 participants, 52 gave results for total Cd, Pb and Hg, 47 for total As, 13 for inorganic As and 9 for methylmercury. From these results, those reporting "less than" values were not included in the evaluation. This was the case for 4 laboratories for iAs, 3 for total Pb and 1 laboratory for total Cd.

L061 forgot to apply a correction factor for dilution to its results for total Cd and Hg, so that corrected results and uncertainties are actually 10 x higher. However, being informed about the mistake after the reference values were revealed, the corrected results were not taken into account for the evaluation.

L006 and L048 reported "less than" values for total Cd and total Pb, respectively, which were lower than the corresponding $X_{ref} - U_{ref}$ value. This was considered as an incorrect statement since they should have detected the respective element.

9.2 Uncertainties and coverage factor

A positive observation was that all except two participants reported an uncertainty associated to their results (~ 96 %). Of the 55 participants who submitted an uncertainty with their results, 5 (~ 9 %) did not give a value for the coverage factor. Furthermore, it was observed that some participants mixed up the coverage factor *k* and the recovery factor R. The following information regarding coverage factors can be found in the web page of the National Institute of Standards and Technology (NIST): *"In general, the value of the coverage factor k is chosen on the basis of the desired level of confidence to be associated with the interval defined by* $U = ku_c$*. Typically, k is in the range 2 to 3. When the normal distribution applies and* u_c *is a reliable estimate of the standard deviation of a measurement,* $U = 2\,u_c$ *(i.e., k = 2) defines an interval having a level of confidence of approximately 95 %, and* $U = 3\,u_c$ *(i.e., k = 3) defines an interval having a level of confidence greater than 99 %"*[9]. Participants who are not familiar with this term are advised to read the EURACHEM / CITAC Guide CG 4 [10].

9.3 Scores and evaluation criteria

Individual laboratory performance is expressed in terms of z- and ζ-scores in accordance with ISO 13528 [2].

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \qquad \text{and} \qquad \zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}}$$

where:

- x_{lab} is the measurement result reported by a participant
- X_{ref} is the reference value (assigned value)
- u_{ref} is the standard uncertainty of the reference value
- u_{lab} is the standard uncertainty reported by a participant
- $\hat{\sigma}$ is the standard deviation for proficiency assessment

Both scores can be interpreted as: satisfactory result for |score| ≤ 2, questionable result for 2 < |score| ≤ 3 and unsatisfactory result for |score| > 3.

z-score

The z-score compares the participant's deviation from the reference value with the target standard deviation for the proficiency assessment, $\hat{\sigma}$, used as common quality criterion.

$\hat{\sigma}$ is defined by the PT organiser as the maximum acceptable standard uncertainty. Based on feedback from experts, on the state-of-the-art and on discussions among the members of the advisory board of this PT, values for $\hat{\sigma}$ were set as 15 % of the assigned value for all measurands.

Should participants feel that these $\hat{\sigma}$ values are not fit for their purpose they can recalculate their scorings with a standard deviation matching their requirements.

ζ-score

The ζ-score states if the laboratory result agrees with the assigned value within the respective uncertainties. The denominator of its equation is the combined uncertainty of the assigned value and the measurement uncertainty as stated by the laboratory. The ζ-score is therefore the most relevant evaluation parameter, as it includes the measurement result, the expected value (assigned value), its uncertainty as well as the uncertainty of the reported values. An unsatisfactory ζ-score can either be caused by an inappropriate estimation of the concentration or of its uncertainty.

Uncertainty evaluation

It is a well-established fact that uncertainty estimation is not trivial. Therefore an additional assessment was given as an indication of the plausibility of its uncertainty estimate for each laboratory providing an uncertainty. The standard uncertainty (u_{lab}) is most likely to fall in a range between a minimum uncertainty (u_{min}), and maximum allowed uncertainty (u_{max}). u_{min} is set to the standard uncertainty of the reference value. It is unlikely that a laboratory carrying out the analysis on a routine basis would measure the measurand with a smaller uncertainty than the expert laboratories chosen to establish the assigned value. u_{max} is set to the target standard deviation accepted for the PT, $\hat{\sigma}$. If u_{lab} is smaller than u_{min}, the laboratory might have underestimated its uncertainty. However, such a statement has to be taken with care as each laboratory reported only measurement uncertainty, whereas the uncertainty of the reference value also includes contributions of homogeneity and stability. If those are large, measurement uncertainties smaller than u_{min} are possible and plausible. If $u_{lab} > u_{max}$, the laboratory might have overestimated the uncertainty. An evaluation of this statement can be made when looking at the difference of the reported value and the assigned value: if the difference is small and the uncertainty is large, then overestimation is likely. If, however, the deviation is large but it is covered by the uncertainty, then the uncertainty is properly assessed even if large. It should be pointed out that u_{max} is not a normative criterion. It is up to the customer of the respective result to decide which uncertainty is acceptable for a certain measurement.

The standard uncertainty of the laboratory (u_{lab}) was calculated by dividing the reported expanded uncertainty by the reported coverage factor (k). When k was not specified, the reported expanded uncertainty was considered as the half-width of a rectangular distribution; u_{lab} was then calculated by dividing this half-width by $\sqrt{3}$, as recommended by Eurachem / CITAC [10]. When no uncertainty was reported, it was set to zero (u_{lab} = 0).

9.4 Laboratory results and scorings

The results as reported by the participants are summarised in Annex 9 - 14. A table of the results and their graphical representation are provided. The tables also contain z-, ζ-scores and the uncertainty evaluation, except for iAs. Laboratory codes were given randomly.

The results were also represented as Kernel density plots, which are an alternative to histograms and a useful method to represent the overall structure of a data group and to highlight sub-populations. These plots can be found in Annex 15. The software used to calculate Kernel densities was provided by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry [11].

Regarding the z- and ζ-scores, the results are summarised in Fig 2. The laboratories' performances appear to be good for all evaluated measurands, the percentage of satisfying z-scores ranging between 80 % and 96 %. The share of satisfactory ζ-scores is slightly smaller than for the z-score and range between 56 % and 82 %. Shares of unsatisfactory ζ-scores range between 11 % and 22 %. Furthermore, the share of participants having a satisfying z- and ζ-score is between 56 and 78 %. The 56 % share was obtained for methylmercury – for this measurand only few results were submitted (9) and thus the percentages should be considered with caution. One single value more or less has a much higher impact on the percentages here than on those of the other measurands. Annex 16 summarises all scorings per laboratory and element.

Fig 2 - Overview of scores

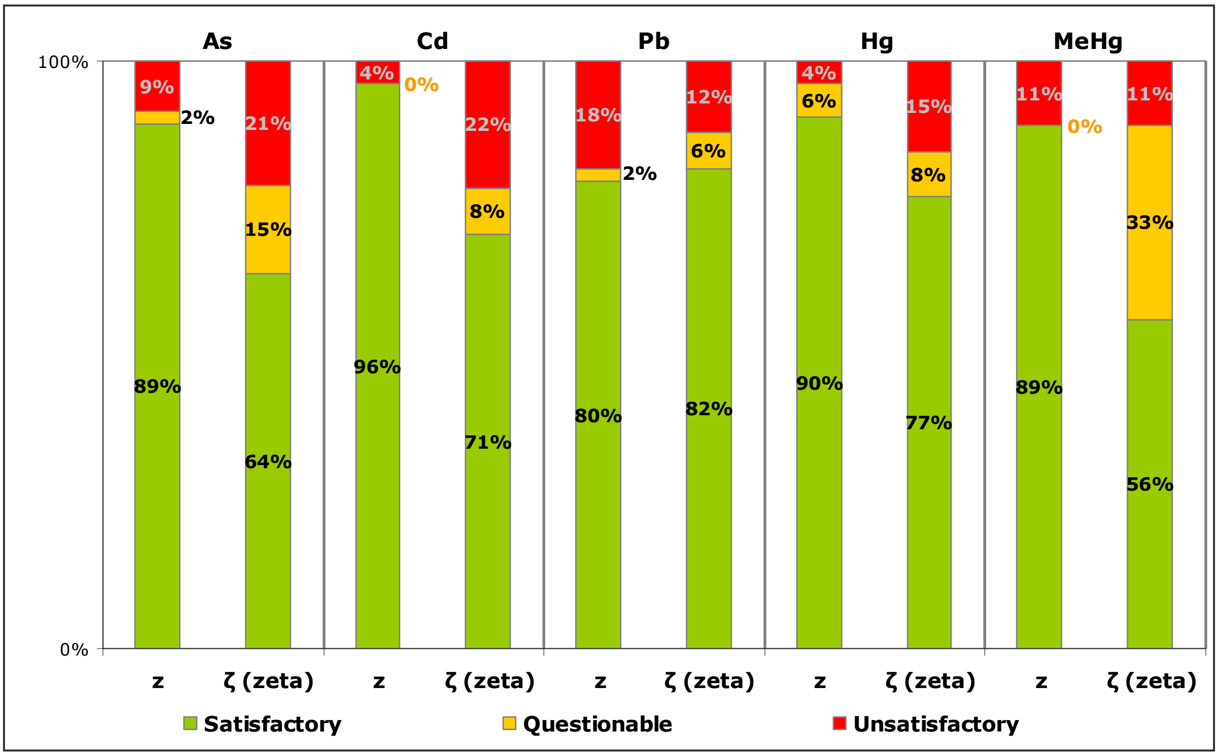


Table 4 shows that for total Pb most participants' uncertainties were out of range, the share of uncertainties between u_{min} and u_{max} being 12 %. This is most probably due to the high uncertainty of the reference value resulting in a narrow range $u_{min} – u_{max}$. When considering all shares for (b) and (c), it appears that participants tend to underestimate the uncertainty (b), rather than to overestimate it (c).

Table 4 – Uncertainty evaluation where $a = u_{min} \leq u_{lab} \leq u_{max}$, $b = u_{lab} < u_{min}$ *and* $c = u_{lab} > u_{max}$

		$u_{min} \leq u_{lab} \leq u_{max}$		$u_{lab} < u_{min}$		$u_{lab} > u_{max}$	
	n	**a (#)**	**a (%)**	**b (#)**	**b (%)**	**c (#)**	**c (%)**
Total As	47	24	51 %	16	34 %	7	15 %
Total Cd	51	30	59 %	14	27 %	7	14 %
Total Pb	49	6	12 %	29	59 %	14	29 %
Total Hg	52	23	44 %	19	37 %	10	19 %
Methylmercury	9	4	44 %	4	44 %	1	11 %

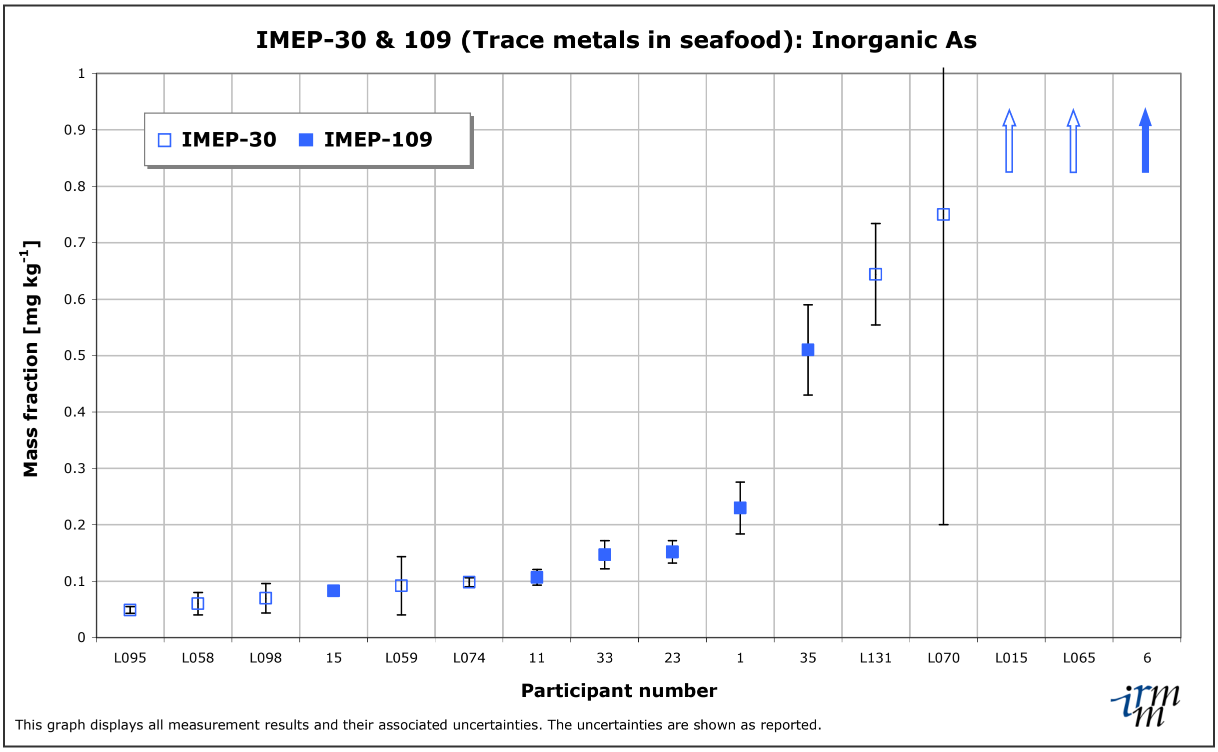
n – total number of laboratories having submitted results, # - number of laboratories

For total As there seems to be a tendency to underestimation which is visible on the result graph and the Kernel density graph (Annex 9; 15). According to the information obtained from the expert laboratories having performed speciation analyses on the test material, most of the arsenic is present in the form of arsenobetaine. It is known that digestion of arsenobetaine is difficult and requires high temperatures (more than 280 °C). Such a difficulty should not be a problem for laboratories using ICP-MS because the temperature in the plasma is high enough to mineralise arsenobetaine, but it could explain some of the unsatisfactory results obtained by laboratories having used HG-AAS. The same tendency of underestimation is observed for total Cd (Annex 10; 15), but less pronounced and cannot be explained.

The distribution of results for total Pb (Annex 11) is characterised by some very high values and also by being the measurand with the highest share of unsatisfactory z-scores (18 %). This could be due to the low mass fraction of lead in the test material in comparison to the other measurands. The results for total Hg and methylmercury (Annex 12; 14) are quite satisfying with most of the participants being inside the $X_{ref} \pm 2\sigma$ range.

Thirteen participants submitted results for iAs, 4 of them giving "less than" values. No scoring could be given as no reference value was established. The result graph (Annex 13) confirms what has been observed with the certifiers – there is a large spread of mass fractions. The results were pooled together with those of the IMEP-109 exercise run in parallel, in order to get a higher number and detect eventual tendencies. They are represented in Fig 3.

Fig 3 – Results reported for iAs by participants of the IMEP-30 & IMEP-109 exercises



Of the total of 24 results reported for iAs in the two ILCs, 3 laboratories (2 in IMEP-30, 1 in IMEP-109) reported values higher than 1 mg kg^{-1} and 8 laboratories reported "less than" values (4 in IMEP-30 and 4 in IMEP-109). With such a scattering of results it is not possible to derive any conclusion about the concentration of iAs in this test material. It seems however, that 18 laboratories agree on the fact that the percentage of iAs in this seafood material is very low (below 2.5 %). No method dependence could be determined as almost half of the participants of the two exercises reporting evaluable results (16) followed the procedure given in the European Standard EN 15517, but no clusters could be observed. The matrix might be one reason for the unexpected spread of results, as this spread was not observed in the IMEP-107 exercise, where rice was used as test material [1]. Furthermore, the EN 15517 is designed for the determination of inorganic arsenic in seaweed, a method that might not be suitable for the dogfish liver used in this IMEP-30 exercise.

The 5 certifiers for iAs have discussed the outcome of the results and some explanations were brought forward for the discrepancies observed. The matrix of the test material being rather complex, "less than" values could be explained by an insufficient amount of oxidant added, H_2O_2 to oxidize As(III) to As(V), which is the species of As measured when using HPLC-based methods. Furthermore, the use of MeOH/water and diluted HCl as extracting reagents might not have provided quantitative extraction of iAs. On the other hand, when applying extraction of iAs with chloroform and concentrated HCl, a cleaning step of the chloroform phase should be carried out to eliminate all traces of HCl and with it the there present arsenobetaine. Remains of the concentrated HCl in the chloroform phase might introduce a high contamination of the sample in organic species. Finally, it appears that when analysing complex matrices by HPLC-ICP-MS the retention time of the iAs shifts and it cannot be detected because of possible co-elution with minor organic species. This can be remedied by introducing an extra step of hydride generation between the HPLC and the ICP-MS.

One IMEP-30 participant commented having had problems analysing the sample with HG-AAS, such as foreseen in EN 15517, and analysed it with ICP-MS instead. This problem resulted from the matrix, as the sample ignited. No other participant reported such a problem.

9.5 Further information extracted from the questionnaire

Additional information was gathered from the questionnaire that participants were asked to fill in (Annex 7). Most of the answers are summarised in Annex 17 & 18 (recovery factors, uncertainty related questions, water content, method related questions, experience and use of reference material), or is otherwise highlighted in the following paragraphs.

Forty-four participants reported recovery factors, which are shown in a graph in Annex 17. How they were determined is summarised in Table 5 below. Of the 44 laboratories, three declared not to correct for recovery (R) and submitted a factor R of 100 %. The justification given for not applying a recovery factor was that the participant usually doesn't do it.

Table 5 – Determination of the recovery factors

Recovery factor R determined by:	Number of participants
a) adding a known amount of the same analyte to be measured (spiking)	14
b) using a certified reference material	18*
c) other	4
a) & b)	8
b) & c)	1
a) & c)	1
Reported as "Others": - using reference material from another interlaboratory comparison - total and inorganic As: material obtained when taking part in a former interlaboratory comparison - results not corrected for recovery - accuracy checked with CRM - matrix calibration - no recovery correction	

* 2 of these laboratories did not report any recovery factors

For uncertainty estimates, various combinations of one or more options were given (Q3, Annex 17). Five laboratories gave a third method to base their uncertainty on: "*DIN ISO 5725*", "*fitness-for-purpose approach of 333/2007*", "*data from in-house analytical quality control sample*", "*Nordtest TR537*" and "*estimation based on publication by National Health Inspection*".

Twelve participants have not corrected for the water content and gave the reasons listed in Table 6. The way in which the water content of the test material was to be determined was described in detail in the sample accompanying letter. This procedure has been established and tested by the Reference Material Unit at IRMM specifically for this test material to avoid loosing material other than water.

Some participants were pointing out the difference to the "usual" procedure – involving generally heating the sample for a number of hours – but the test material appeared to be heat-sensitive and even the drying procedure described in the certificate uses vacuum drying.

Table 6 – Reasons for not applying water correction as reported in the questionnaire

Part Nr	Reasons
L006	My habitual samples are humid
L017	We have obtained negative values
L054	Because the sample was dry, 98.5%. This will not be reflected in the results.
L086	Negligible factor (0.7 %)
L100	
L101	Water content was <1%
L108	To low water level (0.26%)
L113	
L125	Dry mass 98,9%
L131	It was not stated to do so in the accompanying letter, and for foodstuff the limits are applicable to fresh stuff
L145	We are using ultrapure water
L153	We correct for the water content if the order requires for this.

Annex 18 gives information reported by the laboratories about their method of analysis.

All participants but three have a quality system in place based on ISO 17025. Three have it combined with ISO 9000, and two have it combined with another quality system – "*NATA*" and "*Verordnung (EG) 882/2004*". Two laboratories have the ISO 9000 series in place and one did not answer the question.

Table 7 summarises the reference materials used for this type of analysis as reported by the participants.

Table 7 – Reference materials used by the participants as reported in the questionnaire

Part Nr	Which reference material ?
L002	only certified standard solutions for AAS e.g Fluka
L004	BCR 191/NIST 2976
L006	ERM-CE278 mussel tissue
L010	FAPAS T0774, FAPAS T0797
L013	GBW 08571
L015	we use the rest of material of interlaboratory comp. (in prev. year) as reference
L016	BCR, TORT-2
L018	Reference material from other interlaboratory comparisons
L021	TORT-2
L025	INCT-MPH-2, NCSZC73012-cabbage
L026	DOLT-4
L028	FAPAS RMs
L042	BCR 422, CRM 150, CRM 185R, BCR 184, BCR 151, NCZS 78005
L047	NIST 8414
L048	FAPAS Canned Crab Met
L050	GBW 10024 shell
L052	DORM-3 (Fish protein)
L054	NRC and NIST, different matrix.
L055	various
L057	AGAL 3
L058	BCR 422, BCR 279, BCR 627

Part Nr	Which reference material ?
L059	TORT-2-Lobster Hepatopancreas, SRM 1577a-bovine liver
L061	BCR 414
L065	e.g. BCR 279 (sea lettuce) // material of a former interlaboratory comparison in 2009 (algae)
L069	Oriental Tobacco Leaves, Powder Milk, Mix Polish Herbs
L074	SRM 1947
L085	Standard CNRC, TORT 2 - Lobster Hepatopancreas
L086	DORM-2 /National Research Council Canada
L090	Shrimp Powder, S/N 1106261, Tuna fish, hair CRM NCS, Hair DC73347,Level 1,2 & 3 Trace elements whole blood,serum, Seronorm; urine CRM , Medisafe Metalle U Level 2
L097	FAPAS reference materials
L098	ILC material algae from §64 LFGB: 25.06-1; SRM 1575; NBS 1577a; NIST 1643e
L099	Dogfish muscle (DORM-2;NRC-CNRC)
L100	BCR-463, RM 8414
L108	FAPAS 07109, 07120
L109	ERM CE 278 Mussel Tissue, BCR 627 Tuna Fish
L112	DOLT 4
L113	Internal Reference Material validated by the lab with ERM
L117	CE278, 1566b, DORM2
L125	oyster tissue, kidney, muscle
L130	Nist, BCR
L131	NIST 1643e
L136	DORM-3
L137	FAPAS T 07112 Canned Crab Meat; FAPAS T07120 Milk Powder
L141	ERM CE-278 mussel tissue
L142	1. National Research Council Canada DORM-2 and 2. BCR CRM 463
L148	several CRM, SRM, local RM
L153	LGC

Final comments made by participants are listed in Table 8. Most relate to preceding questions in the questionnaire. One participant complained about insufficient amount of test material. It is often said that the outcome of proficiency tests does not reflect the real situation in analytical laboratories because participants do not treat PT test materials as they would treat normal samples. For instance participants in a PT would perform more replicates than in routine analysis. In order to avoid this, IMEP sent out an amount of test material considered sufficient for this type of analysis. As noticed by another participant, concentrations for some elements were indeed high, but as IMEP did not produce the test material, the choice of the sample was a compromise between measurands of interest and available material. As for those interested in acquiring the material, it can be ordered at the NRC.

Table 8 – Comments as taken from the questionnaire

Part Nr	Comments
L002	Sample amount was insufficient for more measurements. Result was calculated from 2 replicates for each metal.
L004	Uncertainty reported as expanded uncertainty !
L010	This is the first analysis we perform for metals in food

Part Nr	Comments
L018	We normally do not correct for recovery, according to VO (EG) 333/2007 Nr. D.1.2
L048	No, thanks
L050	Thank you, we've learned a lot from this PT, it will greatly improve our ability in the following work.
L057	Our results have not been recovery corrected. A matrix spike was prepared and analysed and was within our acceptance criteria
L058	Determination of water content is very suspicious and not needed in the way as mentioned. You will get different values depending in the type of oven (circulation air or thermal convection only - the latter will give no loss of weight !!). I state that a normal glass container will need 5-10 min to reach 80 °C. The values you get with this procedure are in no relation to any volatile content.
L065	We tried to measure the inorganic arsine content of the hydrochloric acid extract with Hydride-GFAAS, which was quite good for our reference material. However, when we tried to measure the IMEP 30 sample, the liquid was burning while heating up in the graphite tube and we didn't get any signals. Therefore, we measured the IMEP 30 sample and our reference material with ICP-MS.
L085	For the calibration we use the solution of standard.
L101	we want to use IMEP-30 as reference material
L105	We run an in-house AQC but validation of this material is carried out with CRMs
L108	No, thanks
L125	As, Pb were not detected because there is an instrument defect (injection system) and there is no short repair in holidays
L136	Please let me know if it is possible to request for additional sample for QC from this and previous studies.
L141	Concentration levels are very high especially for cadmium and mercury. These values exceed the established legislation levels considerably and may not be of interest to our laboratory.

10 Conclusion

In the IMEP-30 exercise, 57 participants registered and all of them reported results. Between 80 % and 96 % satisfactory z-scores were achieved for all measurands except for iAs for which no reference value could be established and thus no scoring was possible. It is reassuring to observe that around 96 % of the participants reported an uncertainty with their results and the obtained ζ-scores were almost as good as the z-scores.

Unfortunately, only few participants reported values for methylmercury (9) and iAs (14). However, for methylmercury the reported results were satisfactory. The determination of iAs appears to be more problematic, as was noticed already with the results of the certifiers. Inorganic arsenic was added as a measurand to the certified components in the test material in order to continue the study initiated with the IMEP-107 (Total and inorganic As in rice) exercise and to extend it to a new type of food matrix, such as seafood, known to be one of the main contributors of As to the human diet. It seems that this change in matrix has a major influence on the analytical determination of its mass fraction, as results here show a large spread which could not be attributed to any method influence. However, potential sources of error in the different applied sample preparation procedures and analysis could be proposed.

Most of the laboratories tend to underestimate the total As content, and to a lesser extent the total Cd content. Concerning As, the hypothesis of the large presence of arsenobetaine, known to be difficult to digest, was put forward explaining to some extent low results when applying HG-AAS. However, only few results obtained with this technique are unsatisfactory. Generally, for total As and Cd no method influence could be detected.

11 Acknowledgements

The Reference Materials Unit of IRMM is acknowledged for relabeling the test material and the development of the drying procedure. The IMEP-group, Anne-Mette Jensen and Franz Ulberth are thanked for revising the manuscript.

The laboratories participating in this exercise, listed below, are also kindly acknowledged.

ORGANISATION	COUNTRY
Advanced Analytical Australia P/L	Australia
Executive Environment Agency at MOEW	Bulgaria
SGS Bulgaria Ltd.	Bulgaria
Fujian institute of testing technology	China
Guangzhou Center for Disease Prevention and Control (Guangzhou Center for Health Laboratory Technology)	China
GEMANALYSIS LTD	Cyprus
Panchris Animal Premix ltd	Cyprus
Danish Veterinary and Food Administration, Region West	Denmark
Tallinn University of Technology	Estonia
Estonian Environmental Research Centre Ltd	Estonia
LASAT	France
Eurofins Scientific Analytics Nantes	France
Landesbetrieb Hessisches Landeslabor	Germany
Bayer. Landesamt für Gesundheit+Lebensmittelsicherheit	Germany
Chemisches und Veterinäruntersuchungsamt	Germany
Institut Dr. Appelt GmbH & Co. KG	Germany
Bay. Landesamt für Gesundheit und Lebensmittelsicherheit	Germany
LAVES - IFF Cuxhaven	Germany
Landeslabor Berlin-Brandenburg	Germany
Kreis Mettmann Amt für Verbraucherschutz	Germany
Chemisches und Veterinäruntersuchungsamt Sigmaringen	Germany
Landesuntersuchungsanstalt für das Gesundheits- und Veterinärwesen	Germany
LAVES - Veterinary Institute Hannover	Germany
CVUA Karlsruhe	Germany
Sachsen-Anhalt	Germany
General Chemical State Laboratory, Chemical Div of Thessaloniki	Greece
General Chemical State Laboratory, Division of Ioannina	Greece
Centre for Food Safety	Hong Kong
Veszprém County Central Agriculture Office	Hungary
Fejér County Agricultural Office Foodchain Safety and Animal Directorate	Hungary
WESSLING Hungary Ltd.	Hungary
Marine Institute	Ireland
Health Service Executive	Ireland
National Centre of Veterinary Diagnostics	Moldovia, Rep. of

ORGANISATION	COUNTRY
National Scientific and Applied Centre for Preventive medicine	Moldovia, Rep. of
SGS Nederland BV	Netherlands
AsureQuality Auckland Laboratory	New Zealand
Trondheim kommune	Norway
NIFES- National Institute of Nutrition and Seafood research	Norway
SGS Philippines, Inc.	Philippines
Wojewodzki Inspektorat Weterynarii Zaklad Higieny Weterynaryjnej	Poland
Epidemiology Station	Poland
Univ. Católica Portuguesa - Esc. Sup. Biotecnologia	Portugal
DSVSA Calarasi	Romania
Danube Delta National Research Institute	Romania
Agri-Food and Veterinary Authority of Singapore	Singapore
Zavod za zdravstveno varstvo Maribor	Slovenia
Gobierno Vasco	Spain
ANFACO-CECOPESCA	Spain
Dirección de Área de Salud de Gran Canaria	Spain
CENTRO DE SALUD PÚBLICA DE ALICANTE	Spain
ALS Scandinavia AB	Sweden
Eurofins Environment Sweden	Sweden
Service de la consommation et des affaires vétérinaires	Switzerland
MSM Food Control Laboratory Inc	Turkey
Eurofins Laboratories Limited	United Kingdom
Michelson Laboratories, Inc.	United States

Abbreviations

AMC	Analytical Methods Committee of the Royal Society of Chemistry
APLAC	Asia Pacific Laboratory Accreditation Cooperation
CITAC	Co-operation for International Traceability in Analytical Chemistry
CRM	Certified Reference Material
EA	European Co-operation for Accreditation
EN	European Standard
EU	European Union
EURACHEM	A focus for Analytical Chemistry in Europe
EU-RL-HM	European Union Reference Laboratory for Heavy Metals in Feed and Food
HG-AAS	Hydride generation-atomic absorption spectrometry
HPLC-ICP-MS	High-performance liquid chromatography - inductively coupled plasma - mass spectrometry
HR-ICP-MS	High resolution - inductively coupled plasma - mass spectrometry
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
JRC	Joint Research Centre
NRC	National Research Council of Canada
NRL	National Reference Laboratory
PT	Proficiency Test
UKAS	United Kingdom Accreditation Service

References

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[6] Commission Regulation (EC) No 333/2007, Commission Regulation (EC) No 333/2007 of 28 March 2007 laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs (2007), issued by European Commission, Official Journal of the European Union, L 88/29.

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Annexes

Annex 1 : Invitation to EA to nominate laboratories

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements

IMEP®

Geel, 19 April 2010
JRC.DDG.D6/IBa/ive/ARES(2010)/200449

Mr Paul Greenwood
United Kingdom Accreditation Service
21-47 High Street
Feltham
Middlesex
TW13 4UN
UNITED KINGDOM

Dear Paul,

Intercomparison for trace elements and methylmercury in seafood

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-30, an interlaboratory comparison for the **"Determination of total arsenic, cadmium, lead, and mercury, and methylmercury in seafood"**.

In the frame of the EA-IRMM collaboration agreement, IRMM kindly invites EA to nominate laboratories for free participation. They should hold (or be in the process of obtaining) an accreditation for this type of measurement.

I suggest that you forward this invitation to the national EA accreditation bodies for their consideration. There is a limited number of samples at your disposal and the number of nominees should not exceed 2 laboratories per country.

Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing. Please inform the nominees of this disclosure.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 715. Fax: (32-14) 571 865.

E-mail: jrc-irmm-imep@ec.europa.eu

Registration of EA participants is open until 14 May 2010. Distribution of the samples is foreseen for mid-June 2010. Deadline for submission of results is 16 July 2010. In order to register, laboratories must:

1. **Enter** their details online:

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=419

2. **Print** the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by the European Cooperation for Accreditation to take part in this exercise **otherwise your laboratory will be invoiced for participation** normally applied for non-appointed laboratories.

3. **Send** the printout to both the IMEP-30 and the EA-IMEP-30 coordinators:

IMEP-30 coordinator	**EA-IMEP-30 coordinator**
Ms Ines Baer	Mr Paul Greenwood
Fax +32 14 571 865	Fax +44 208 917 8500
E-mail: jrc-irmm-imep@ec.europa.eu	E.Mail: pg@UKAS.com

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Ines Baer
IMEP-30 Coordinator

2

Annex 2 : Invitation to APLAC to nominate laboratories

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements

IMEP®

Geel, 19 April 2010
JRC.DDG.D6/IBa/ive/ARES(2010)/200406

Mr Daniel Tholen
Chairman, APLAC PT Committee

Dear Daniel,

Intercomparison for trace elements and methylmercury in seafood

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-30, an interlaboratory comparison for the **"Determination of total arsenic, cadmium, lead, and mercury, and methylmercury in seafood"**.

IRMM kindly invites APLAC to nominate 10 laboratories for free participation. However, they should hold (or be in the process of obtaining) an accreditation for this type of measurement. I suggest that you forward this invitation to a selection of specialised laboratories in this area.

Confidentiality of the participants and their results towards third parties is guaranteed.

Registration of APLAC participants is open until 14 May 2010. Distribution of the samples is foreseen for mid-June 2010. Deadline for submission of results is 16 July 2010.

In order to register, laboratories must:

1. **Enter** their details online:

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=419

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 715. Fax: (32-14) 571 865.
E-mail: jrc-irmm-imep@ec.europa.eu

2. **Print** the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by APLAC to take part in this exercise **otherwise your laboratory will be invoiced for participation** normally applied for non-appointed laboratories.

3. **Send** the printout to both the IMEP-30 and the APLAC coordinators:

IMEP-30 coordinator Ms Ines Baer Fax +32 14 571 865 E-mail: jrc-irmm-imep@ec.europa.eu	**APLAC coordinator** Mr Daniel Tholen Fax +1 231 941 9713 E.Mail: aplac.pt@gmail.com

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Ines Baer
IMEP-30 Coordinator

2

Annex 3 : Invitation sent to NRLs

IMEP-30 Trace elements in seafood - Message (Rich Text)

File Edit View Insert Format Tools Actions Help

Reply | Reply to All | Forward | Bcc Field | Arial | 10

This message was sent with High importance.

From: BAER Ines (JRC-GEEL)

Sent: Mon 17/05/2010 17:27

To: 'Adina STRIZU '; 'Albert GAMBIN '; 'Alena Šimáková'; 'Ana Isabel Blanch Cortés'; 'Anca Raluca OLARU'; 'Andrea LUGASI'; 'Ann RUTTENS'; 'Argiro KOUFOGIANNAKI/Ioannis GARDIKIS'; 'Arne Büchert'; 'Bernard MEDINA'; 'Bo SUNDQVIST'; 'Carolin STACHEL'; 'Daniela MARCHIS'; DE LA CALLE GUNTINAS Maria Beatriz (JRC-GEEL); 'Detlef BOHM'; 'Doris GAMBIN'; 'Dusan CHUDY'; 'Eija-Riitta VENALAINEN'; 'Eleni IOANNOU-KAKOURI'; 'Elzbieta Brulinska-Ostrowska '; 'Esko Niemi'; 'Eugenia CIRUGEDA '; 'Éva SUGAR'; 'Fabien BOLLE'; 'Fernando TOVAR '; 'François LACROIX'; 'Fred DAVIDSON'; 'Gabor DOMÁNY'; 'Gabrijela TAVCAR KALCHER '; 'Gerhard BURDICEK'; 'Guntis CEPURNIEKS '; 'Heli REINET'; 'Ignacia MARTIN DE LA HINOJOSA'; 'iispv RO NRL'; 'Inga JARMALAITE '; 'Ivo BREYL'; 'Jacques GAYES '; 'Jan ZMUDZKI'; 'Janne NIEMINEN'; 'Jean-Christophe PIZZOLON'; 'Jens J. SLOTH'; 'Jirí ZBÍRAL '; 'Joakim ENGMAN'; 'Johan PEETERS';

Cc: JRC IRMM IMEP

Subject: IMEP-30 Trace elements in seafood

Dear all,

IMEP is currently organising a proficiency test for the determination of total arsenic, cadmium, lead, and mercury, as well as methylmercury and inorganic As in seafood (the latter was added only recently), which is running in parallel with the IMEP-109 exercise for which you have been invited to register recently.
As you probably know, IMEP-30 is open to all laboratories interested in taking part (a **registration fee of 500 €** is to be paid for participation, though) while the participation in IMEP-109 is restricted to appointed National Reference Laboratories only, and no registration fee is to be paid. For the CRL-HM the interest of having the mentioned two exercises running in parallel is that it allows comparing the two populations, NRLs and the other laboratories.

If you know of laboratories interested in taking part in the IMEP-30 exercise, please forward this message to them. They can register via the following link :
https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=419

Please take note that **only 20 registrations** are available due to a limited number of test items.

Registration of participants is open until 06 June 2009. Distribution of the samples is foreseen for mid-June 2010 and reporting deadline for the 16 July 2010.
The measurands are: total As, Cd, Pb, and Hg, as well as MeHg and inorganic As.

For NRLs planning to pay for the laboratories in their country, please inform those laboratories that their identity will be diclosed to you.

Thank you for your interest
Kind regards
Ines Baer
IMEP-30 Coordinator

Ines Baer
EC-JRC-IRMM
☎ +32 (0)14 57 16 82
🖷 +32 (0)14 57 18 65
✉ jrc-irmm-imep@ec.europa.eu
http://irmm.jrc.ec.europa.eu/50

1960-2010
IRMM
50
Institute for Reference Materials and Measurements

Disclaimer: The views expressed are purely those of the writer and may not in any circumstances be regarded as stating an official position of the European Commission.

Annex 4 : Announcement on IRMM - IMEP website

EUROPA - JRC - Institute for Reference Materials and Measurements - Windows Internet Explorer

http://irmm.jrc.ec.europa.eu/html/interlaboratory_comparisons/imep/imep-30/index.htm

European Commission
Joint Research Centre
Institute for Reference Materials and Measurements

EUROPA > European Commission > JRC > IRMM > Interlaboratory comparisons > Imep > Imep-30

IMEP-30 Total As, Cd, Pb, and Hg, as well as MeHg and inorganic As in seafood

The IMEP-30 exercise focuses on the analysis of total arsenic, cadmium, lead, and mercury as well as methylmercury and inorganic arsenic. This interlaboratory comparison runs in parallel to IMEP-109 where only appointed National Reference Laboratories can take part in.

The IMEP-30 exercise is open to all laboratories, but only the first 60 registrations can be admitted.

The cost of this interlaboratory comparison is EUR 500 per registration.

Test materials and analytes

The test material to be analysed is seafood tissue contained in a glass bottle protected by a sealed aluminium bag.
Each participant will receive one bottle. The measurands are total As, Cd, Pb, and Hg, as well as CH3Hg and inorganic As.

General outline of the exercise

Participants are requested to perform 1 - 3 independent analyses using the method of their choice, and to report the mean and its expanded uncertainty. Detailed instructions will be sent together with the sample.

Schedule

Registration	Sample dispatch	Reporting of results	Report to participants
deadline 06/06/2010, prematurely closed due to limited number of test items	Mid June 2010	deadline 16/07/2010	October 2010

Last Update 26/05/2010

Annex 5 : Sample accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for reference materials and measurements
Food Safety & Quality

IMEP

Geel, 31 May 2010
JRC.DG.D6/IBa/ive/ARES(2010)/281654

«TITLE» «FIRSTNAME» «SURNAME»
«ORGANISATION»
«DEPARTMENT»
«ADDRESS»
«ADDRESS2»
«ADDRESS3»
«ADDRESS4»
«ZIP» «TOWN»
«COUNTRY»

Participation in IMEP-30, a proficiency test exercise for the determination of total arsenic, cadmium, lead, and mercury, as well as methylmercury and inorganic arsenic in seafood

Dear «TITLE» «SURNAME»,

Thank you for participating in the IMEP-30 intercomparison for the determination of total As, Cd, Pb, and Hg, as well as MeHg and inorganic As in seafood. **Please keep this letter**, you need it for reporting your results and your laboratory identification in the final report.

This parcel contains:
a) One bottle containing 20 g of the test material
b) A "Confirmation of Receipt" form
c) This accompanying letter

Please check whether the bottle containing the test material remained undamaged during transport. Then, please send the "Confirmation of receipt" form back (fax: +32-14-571865, e-mail: jrc-irmm-imep@ec.europa.eu). You should store the samples in a dark and cold place (not more than 18 ºC) until analysis.

The measurands are: **total As, Cd, Pb,** and **Hg**, as well as **MeHg** and **inorganic As**.
We would like to take this opportunity to continue the study on inorganic As determination that was initiated with IMEP-107 (Total and inorganic As in rice) and to extend it to a new type of food matrix, in this case seafood, which is known to be one of the main contributors of As to the human diet. For this reason, I would appreciate if those of you with measurement capabilities for inorganic As (certainly those that reported values for inorganic

«Part_key»

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 682. Fax: (32-14) 571 865.
E-mail: jrc-irmm-imep@ec.europa.eu

1/4

As in IMEP-107) make again an effort in helping us to elucidate whether the content of inorganic As found in food commodities is method dependent or not.

The procedure used for the analyses should resemble as closely as possible the one that you use in routine sample analysis.

The results are to be reported referring to dry mass and thus **corrected for humidity**. To calculate the water content in the test material, please apply the following procedure:

1. *Weigh accurately 1 g of test material in a glass container of 5-7 cm diameter, preferably with a lid.*
2. *Place it in an oven for 10 ± 1 min at 80 ± 2 ºC.*
3. *Place the glass container covered with a lid in a desiccator and wait 30 min before weighing the test material again.*

Note 1: *perform the measurements of the water content in triplicate.*
Note 2: ***do not use for the measurands' determination the aliquots of test material that you have used for the water content determination!***
Note 3: ***it is crucial that you respect the procedure described above to determine the water content. If you warm up the test material longer than 10 min or at temperatures higher than 80 ºC, losses of volatile compounds other than water will occur.***

Please perform two or three independent measurements per measurand. Correct the measurement results for recovery, and **report the corrected mean** and associated expanded **uncertainty**, the **coverage factor** and the **technique** you used on the reporting website. The results should be reported in the same form (e.g., number of significant figures) as those normally reported to the customer. Mean and uncertainty are to be reported in the same unit.

You can find the reporting website at https://irmm.jrc.ec.europa.eu/ilc/ilcReporting.do
To access this webpage you need a personal password key, which is: «Part_key». The system will guide you through the reporting procedure.

After entering all results, please also complete the relating questionnaire. Do not forget to save and submit when required. **For final submission please press "Confirm results and questionnaire"**. Check your results carefully for any errors before submission, since this is your definitive confirmation. You will then be prompted to print the completed report form. Please do so, sign the paper version and return it to IRMM by fax or by e-mail.

The deadline for submission of results is 16/07/2010.

Please keep in mind that collusion is contrary to professional scientific conduct and serves only to nullify the benefits of proficiency tests to customers, accreditation bodies and analysts alike.

2/4 «Part_key»

Your participation in this project is greatly appreciated. If you have any remaining questions, please contact me by e-mail: jrc-irmm-imep@ec.europa.eu

With kind regards

Dr. Ines Baer
IMEP-30 Co-ordinator

Enclosures: 1) one bottle containing the test material; 2) confirmation of receipt form; 3) Accompanying letter.

Cc: F. Ulberth

3/4 «Part_key»

Annex 6 : 'Confirmation of receipt' form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Food Safety & Quality

Annex to JRC.DDG.D6/IBa/ive/ARES(2010)/281654

«TITLE» «FIRSTNAME» «SURNAME»
«ORGANISATION»
«DEPARTMENT»
«ADDRESS»
«ADDRESS2»
«ADDRESS3»
«Address4»
«ZIP» «TOWN»
«COUNTRY»

IMEP-30

total As, Cd, Pb, and Hg, as well as MeHg and inorganic As in seafood

Confirmation of receipt of the samples

Please return this form at your earliest convenience.
This confirms that the sample package arrived.
In case the package is damaged,
please state this on the form and contact us immediately.

ANY REMARKS ....
....

Date of package arrival ....

Signature ....

Please return this form to:
Dr Ines Baer

IMEP-30 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

Fax : +32-14-571865
e-mail : jrc-irmm-imep@ec.europa.eu

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 682. Fax: (32-14) 571 865.

E-mail: jrc-irmm-imep@ec.europa.eu

Annex 7 : Questionnaire

Submission Form

Recovery factor (R, in %)

What are the recovery factors you applied to correct your measurement results? Please complete below table.

Questions/Response table	As	Cd	Pb	Hg	MeHg	Inorganic As
R (%)						

1. How did you determine the recovery factor (R)? By:

- [ ] a) adding a known amount of the same analyte to be measured (spiking)
- [ ] b) using a certified reference material
- [ ] c) other

1.1. If other, please specify:

____

2. What is the level of confidence reflected by the coverage factor k given with your results? (in %)

____

3. What is the basis of your uncertainty estimate? (multiple answers possible)

- [ ] a) uncertainty budget according to ISO-GUM
- [ ] b) known uncertainty of the standard method
- [ ] c) uncertainty of the method as determined during in-house validation
- [ ] d) measurement of replicates (i.e. precision)
- [ ] e) estimation based on judgement
- [ ] f) use of intercomparison data
- [ ] g) other

3.1. If other, please specify

____

4. Do you usually provide an uncertainty statement to your customer for this type of analysis?

- ○ No
- ○ Yes

5. Did you correct for the water content of the sample?

- ○ No
- ○ Yes

5.1. If yes, what is the water content (in % of the sample mass)?

____

5.2. If no, what was the reason not to do this?

____

6. Did you determine MeHg according to an official method?

- ○ No
- ○ Yes

6.1. If yes, which one?

____

6.2. If no, please describe in max 150 characters your:

6.2.1. sample pre-treatment

____

6.2.2. digestion step

____

6.2.3. extraction / separation step

____

6.2.4. derivatization

____

6.2.5. instrument calibration step

____

7. Did you determine inorganic As according to an official method?

- ○ No
- ○ Yes

7.1. If yes, which one?

7.2. If no, please describe in max 150 characters your:

7.2.1. sample pre-treatment

7.2.2. digestion step

7.2.3. extraction / separation step

7.2.4. instrument calibration step

8. Did you determine total As, Cd, Pb and Hg according to an official method?

- ○ No
- ○ Yes

8.1. If yes, which one?

8.2. If no, please describe in max 150 characters your:

8.2.1. sample pre-treatment

8.2.2. digestion step

8.2.3. extraction / separation step

8.2.4. instrument calibration step

9. Does your laboratory carry out MeHg analysis on a routine basis?

- ○ No
- ○ Yes

9.1. If yes, please estimate the number of samples :

- ○ a) 0-50 samples per year
- ○ b) 50-250 samples per year
- ○ c) 250-1000 samples per year
- ○ d) more than 1000 samples per year

10. Does your laboratory carry out inorganic As analysis on a routine basis?

- ○ No
- ○ Yes

10.1. If yes, please estimate the number of samples:

- ○ a) 0-50 samples per year
- ○ b) 50-250 samples per year
- ○ c) 250-1000 samples per year
- ○ d) more than 1000 samples per year

11. Does your laboratory carry out this type of analysis (As, Cd, Pb, Hg, matrix and method) on a routine basis?

- ○ No
- ○ Yes

11.1. If yes, please estimate the number of samples :

- ○ a) 0-50 samples per year
- ○ b) 50-250 samples per year
- ○ c) 250-1000 samples per year
- ○ d) more than 1000 samples per year

12. **Does your laboratory have a quality system in place?**

- ○ No
- ○ Yes

12.1. If yes, which:

- ☐ ISO 17025
- ☐ ISO 9000 series
- ☐ Other

12.1.1. If other, please specify:

[ ]

13. **Is your laboratory accredited for this type of analysis? (multiple answers possible)**

- ☐ MeHg
- ☐ inorganic As
- ☐ total As
- ☐ total Cd
- ☐ total Hg
- ☐ total Pb

13.1. By which Accreditation Body have you been accredited?

[ ]

14. **Does your laboratory take part in an interlaboratory comparison on a regular basis for the analysis of (multiple answers possible):**

- ☐ MeHg
- ☐ inorganic As
- ☐ total As
- ☐ total Cd
- ☐ total Hg
- ☐ total Pb

14.1. Which ILC scheme(s)?

[ ]

15. **Does your laboratory use a reference material for this type of analysis?**

- ○ No
- ○ Yes

15.1. If yes, which one?

[ ]

15.2. Is the material used for the validation of procedures?

- ○ No
- ○ Yes

15.3. Is the material used for calibration of instruments?

- ○ No
- ○ Yes

16. **Do you have any comments? Please let us know:**

[ ]

Annex 8 : DOLT-4 Certificate

Certified Reference Material

National Research Council Canada
Conseil national de recherches Canada

DOLT-4

Dogfish Liver Certified Reference Material for Trace Metals

This reference material is primarily intended for use in the calibration of procedures and the development of methods for the analysis of marine fauna and materials with a similar matrix.

Elements for which certified values have been established for this dogfish (*Squalus acanthias*) liver CRM, along with their expanded uncertainty ($U_{CRM} = ku_c$, where u_c is the combined standard uncertainty calculated according to the ISO Guide [1] and k=2 is the coverage factor) are listed in Table 1. It is intended that U_{CRM} encompasses every aspect that reasonably contributes to the uncertainty of the certified mass fraction [2]. Values are based on dry mass.

Table 1. Certified Values for DOLT-4

Element	Mass Fraction (mg/kg)		
Arsenic (d,e,h)	9.66	±	0.62
Cadmium (d,e,i,p)	24.3	±	0.8
Copper (d,e,i,p)	31.2	±	1.1
Iron (d,i)	1833	±	75
Lead (d,e,p)	0.16	±	0.04
Mercury (c,d,p)	2.58	±	0.22
Nickel (d,e,i,p)	0.97	±	0.11
Selenium (e,h)	8.3	±	1.3
Silver (d,e,p)	0.93	±	0.07
Zinc (d,i,p)	116	±	6
CH_3Hg (as Hg)(g,s,t)	1.33	±	0.12

Coding

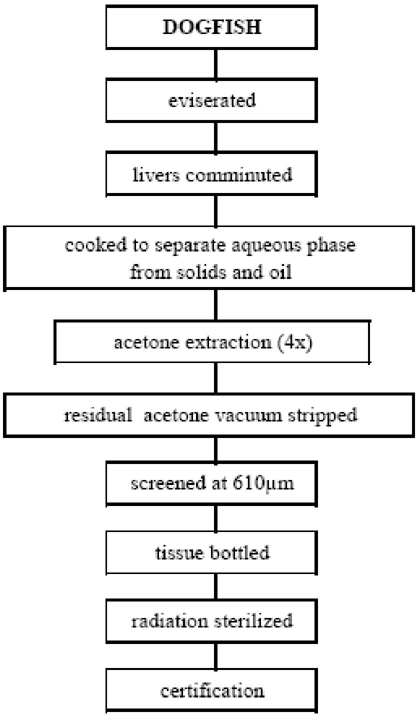
The coding refers only to the instrumental method of determination of the measurand.

c - Cold vapour atomic absorption spectrometry.
d - Inductively coupled plasma mass spectrometry.
e - Electrothermal vaporization atomic absorption spectrometry (ETAAS).
g - Solid phase microextraction (SPME) isotope dilution gas chromatography mass spectrometry.
h - Hydride generation atomic absorption spectrometry.
i - Inductively coupled plasma atomic emission spectrometry.
p - Isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS).
s - SPME isotope dilution gas chromatography ICPMS.
t - Ethylation cold vapor atomic fluorescence spectrometry.

NRC · CNRC

Preparation of DOLT-4

This reference material was processed at the Guelph Food Technology Center, Guelph Ontario. The preparation sequence is illustrated below.



The material was sterilized by gamma irradiation (miminimum dose of 25 kGy) at the Canadian Irradiation Centre, Laval, Québec

Sampling

A sample mass of 250 mg of material (dry mass basis) is the minimum sample intake for which the established uncertainty is valid.

Instructions for Drying

Moisture content should be determined using a separate sub-sample. DOLT-4 can be dried to contant mass by:
(1) drying at reduced pressure (e.g., 50 mm Hg) at room temperature in a vacuum desiccator over magnesium perchlorate for 24 hours;

(2) vacuum drying (about 0.5 mm Hg) at room temperature for 24 hours.

Information Values

Table 2 presents information values for elements which could not be certified because of insufficient information to accurately assess uncertainties.

Table 2. Information Values for DOLT-4

Element	Mass Fraction, (mg/kg)
Na	6800
Mg	1500
Al	200
K	9800
Ca	680
V	0.6
Cr	1.4
Co	0.25
Sr	5.5
Mo	1
Sn	0.17

Storage and Handling

This material should be kept in the original bottle tightly closed and stored in a cool location, away from any significant radiation sources such as ultraviolet lamps and sunlight. The contents should be well mixed by rotation and shaking prior to use, and the bottle tightly closed immediately after sampling.

- 2 -

Calculation of Certified Values

DOLT-4 was provided as an unknown sample to a group of laboratories participating in an annual intercomparison for trace metals in marine samples coordinated by NRCC [3]. Data generated by NRCC were also included in the pool of intercomparison results.

Laboratories were requested to provide triplicate results using an analytical method of choice based on total digestion of the sample. DOLT-3 was provided as a quality control sample.

Data were returned to NRCC for evaluation. Results from a select sub-group of participants were used for the certification of DOLT-4. Such laboratories were selected based on their performance history in previous intercomparisons.

The certified values were calculated from the unweighted means of the results. Data were first examined for outliers using the Dixon and Grubb's Tests. Testing of variances was conducted using the Cochran and Bartletts Tests.

Included in the overall uncertainty estimate are uncertainties in the batch characterisation (u_{char}) and uncertainties related to possible between-bottle variation (u_{hom}). Expressed as standard uncertainties these components can be combined as:

$$u^2_{c(CRM)} = u^2_{char} + u^2_{hom}$$

Based on NRC's experience with similar materials, uncertainty components for long and short term stability were considered negligible and are thus not included in the uncertainty budget.

Results for the various uncertainty components used to calculate the certified values are summarized in Table 3.

Table 3. Statistical Data for DOLT-4

Element	data sets	u_{char}, (mg/kg)	u_{hom}, (mg/kg)
As	10	0.22	0.21
Cd	12	0.25	0.31
Cu	10	0.31	0.46
Fe	10	22	30
Pb	8	0.016	0.013
Hg	8	0.014	0.11
Ni	9	0.024	0.049
Se	9	0.18	0.63
Ag	8	0.017	0.028
Zn	11	2	2
CH_3Hg	3	0.016	0.057

Expiration of Certificate

A predecessor CRM, DOLT-2, has been periodically analyzed for more than nine years and found to be both physically and chemically stable over this time interval. We expect similar characteristics from DOLT-4. The stability of this CRM will continue to be monitored and any significant irregularity will be posted on our web site.

The certified values for DOLT-4 are considered valid until April 2014, provided the CRM is handled and stored in accordance with instructions herein.

References

[1] Guide to the Expression of Uncertainty in Measurement, ISBN 92-67-10188-9, 1st ed. ISO, Geneva, Switzerland (1993).

[2] ISO Guide 35:2006, Reference materials — General and statistical principles for certification Geneva, Switzerland (2006)

[3] S. Willie, Twentieth Intercomparison for Trace Elements in Marine Sediments and Biological Tissues, NRC No. 50099, October 2007.

Acknowledgements

The following staff members of the Institute for National Measurement Standards, National Research Council Canada, participated in the certification: P. Maxwell, C. Scriver, L. Yang and S. Willie.

The cooperation of I. Britt and A. Mannen of the Guelph Food Technology Centre, Guelph, ON, Canada in the preparation of this material is gratefully acknowledged.

The following laboratories participated in the certification of DOLT-4:

ALS Environmental
Vancouver, B.C. V5L 1K5

Australian Institute of Marine Sciences
Queensland, 4810, Australia

Australian Nuclear Science and Technology Organizastion, Environmental Science Program
Menai, N.S.W., Australia

Battelle Pacific Northwest
Sequim Bay Road, Sequim, WA 98382

Massachusetts Water Resources Authority
Central Laboratory, Winthrop, MA 02152

NOAA, National Ocean Service,
Hollings Marine Laboratory, Charleston, SC 29412

San Francisco Public Utilities Commission
Southeast Laboratory, Sn Francisco, CA,

Texas A. & M.
College of Veterinary Medicine
Trace Element Research Laboratory
College Station, TX 77843-4458

Texas Parks and Wildlife
Environmental Contaminants Laboratory
San Marcos, TX 78666

U.S. Customs Laboratory
Savannah, GA 31408

USGS-WRD
3039 Amwiler Road, Atlanta, GA 30360-2824

Canada

Updates

Users of this material should ensure that the certificate in their possession is current. Please consult our web site at http://inms-ienm.nrc-cnrc.gc.ca/calserv/chemical_metrology_e.html for any new information.

As additional data become available, the certified values may be updated and reliable values assigned to additional measureands.

Certificate issued May 2008.

The results presented in this certificate are traceable to the SI through gravimetrically prepared standards of established purity and international measurement intercomparisons. As such, they serve as suitable reference materials for laboratory quality assurance programs, as outlined in ISO/IEC 17025. NRCC CRM's are registered at the Bureau International des Poids et Mesures (BIPM) in Appendix C of the Comité International des Poids et Mesures database listing Calibration and Measurement Capabilities accepted by signatories to the Mutual Recognition Arrangement of the Metre Convention.

Comments, information and inquiries should be addressed to:

Dr. R.E. Sturgeon
National Research Council Canada
Institute for National Measurement Standards
M-12, 1500 Montreal Road
Ottawa, Ontario, Canada K1A 0R6

Telephone (613) 993-2359
Facsimile (613) 993-2451
E-mail crm.inms@nrc.ca

Également disponible en français sur demande.

Annex 9 : Results for Total Arsenic

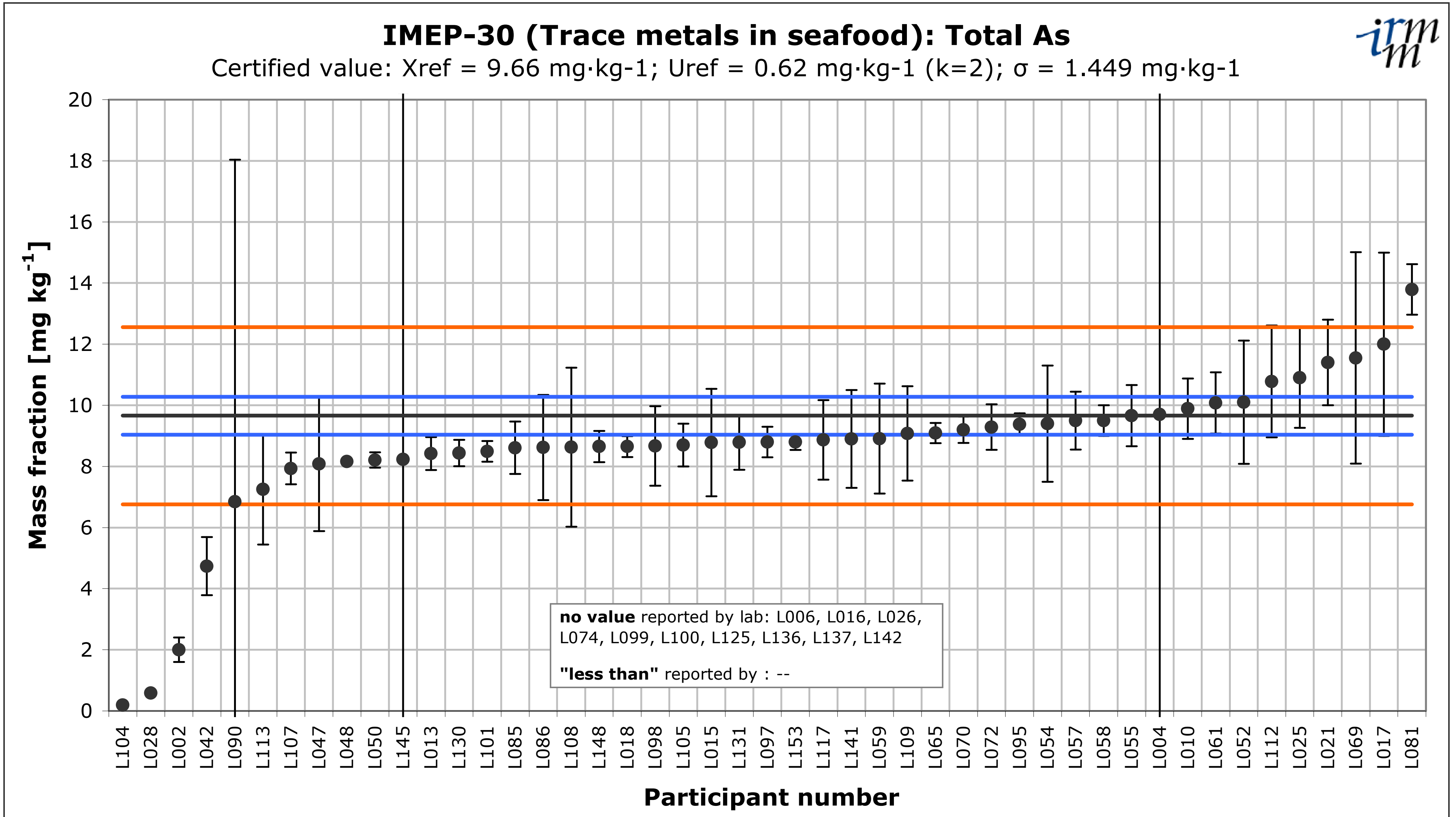
X_{ref} = 9.66 and U_{ref} = 0.62; all values are given in (mg kg^{-1})

Part Nr	Mean (x_{lab})	U_{lab}	k[a]	u_{lab}	Technique	z[b]	ζ [b]	Unc[c]
L002	2.0	0.4	2	0.2	colorimetria	-5.3	-20.8	b
L004	9.7	20	2	10	ICP-MS	0.0	0.0	c
L010	9.891	0.989	2	0.495	ICP-MS	0.2	0.4	a
L013	8.42	0.54	2	0.27	ICP-MS	-0.9	-3.0	b
L015	8.78	1.76	2.776	0.63	HG-AAS	-0.6	-1.2	a
L017	12	3	2	2	HG-AAS	1.6	1.5	c
L018	8.65	0.34	2	0.17	ICP-MS	-0.7	-2.9	b
L021	11.4	1.4	0.55	2.5	ICP-MS	1.2	0.7	c
L025	10.9	1.64	2	0.82	ICP-MS	0.9	1.4	a
L028	0.582	0.052	2	0.026	HG-ICP-OES	-6.3	-29.2	b
L042	4.738	0.948	0.95	0.998	HG-AAS	-3.4	-4.7	a
L047	8.08	2.20	2	1.10	HR-ICP-MS	-1.1	-1.4	a
L048	8.16	0	√3	0	HG-AAS	-1.0	-4.8	b
L050	8.21	0.25	2	0.13	AFS	-1.0	-4.3	b
L052	10.1	2.02	2	1.01	ICP-MS	0.3	0.4	a
L054	9.4	1.9	√3	1.1	ICP-MS	-0.2	-0.2	a
L055	9.66	1.0	3	0.3	ICP-MS	0.0	0.0	a
L057	9.50	0.95	2	0.48	ICP-OES	-0.1	-0.3	a
L058	9.5	0.5	3	0.2	HR-ICP-MS	-0.1	-0.5	b
L059	8.91	1.80	3	0.60	ICP-MS	-0.5	-1.1	a
L061	10.08	1.00	2	0.50	ICP-MS	0.3	0.7	a
L065	9.09	0.33	0.994	0.33	ICP-OES	-0.4	-1.3	a
L069	11.55	3.46	2	1.73	HG-AAS	1.3	1.1	c
L070	9.20	0.429	√3	0.248	ICP-MS	-0.3	-1.2	b
L072	9.2871	0.743	0.99	0.751	ICP-MS	-0.3	-0.5	a
L081	13.79	0.83	2	0.42	ICP-OES	2.9	8.0	a
L085	8.61	0.86	1	0.86	ICP-MS	-0.7	-1.1	a
L086	8.62	1.72	2	0.86	ICP-MS	-0.7	-1.1	a
L090	6.84	11.2	2	5.6	ETAAS	-1.9	-0.5	c
L095	9.38	0.36	2	0.18	ICP-MS	-0.2	-0.8	b
L097	8.8	0.50	2	0.25	ETAAS	-0.6	-2.2	b
L098	8.67	1.30	2	0.65	ICP-MS	-0.7	-1.4	a
L101	8.49	0.3373	2	0.1687	ICP-MS	-0.8	-3.3	b
L104	0.193	0.008	2	0.004	HG-AAS	-6.5	-30.5	b
L105	8.7	0.7	2	0.4	ICP-MS	-0.7	-2.1	a
L107	7.93	0.52	2	0.26	ETAAS	-1.2	-4.3	b
L108	8.63	2.6	2	1.3	ICP-OES	-0.7	-0.8	a
L109	9.08	1.54	2	0.77	HG-AAS	-0.4	-0.7	a
L112	10.78	1.83	1.048	1.75	ICP-MS	0.8	0.6	c
L113	7.25	1.81	2	0.91	FAAS	-1.7	-2.5	a
L117	8.87	1.30	2	0.65	CV-AAS	-0.5	-1.1	a
L130	8.44	0.43	√3	0.25	ICP-MS	-0.8	-3.1	b
L131	8.79	0.9	√3	0.5	ICP-MS	-0.6	-1.4	a
L141	8.9	1.6	2	0.8	ETAAS	-0.5	-0.9	a
L145	8.23	12	2	6	ICP-MS	-1.0	-0.2	c
L148	8.65	0.51	2	0.26	ICP-MS	-0.7	-2.5	b
L153	8.80	0.26	2	0.13	ICP-MS	-0.6	-2.6	b

[a] √3 is set by the ILC coordinator when no expansion factor k is reported. The reported uncertainty was assumed to have a rectangular distribution with k=√3. For explanation see Ch 9.3

[b] **Satisfactory**, **Questionable**, **Unsatisfactory**

[c] Where: **a** = $u_{min} \leq u_{lab} \leq u_{max}$, **b** : $u_{lab} < u_{min}$, and **c** : $u_{lab} > u_{max}$



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to X_{ref}, the blue lines mark the boundary of the reference interval ($X_{ref} \pm 2u_{ref}$), and the orange lines that of the target interval ($X_{ref} \pm 2\sigma$).

Annex 10 : Results for Total Cadmium

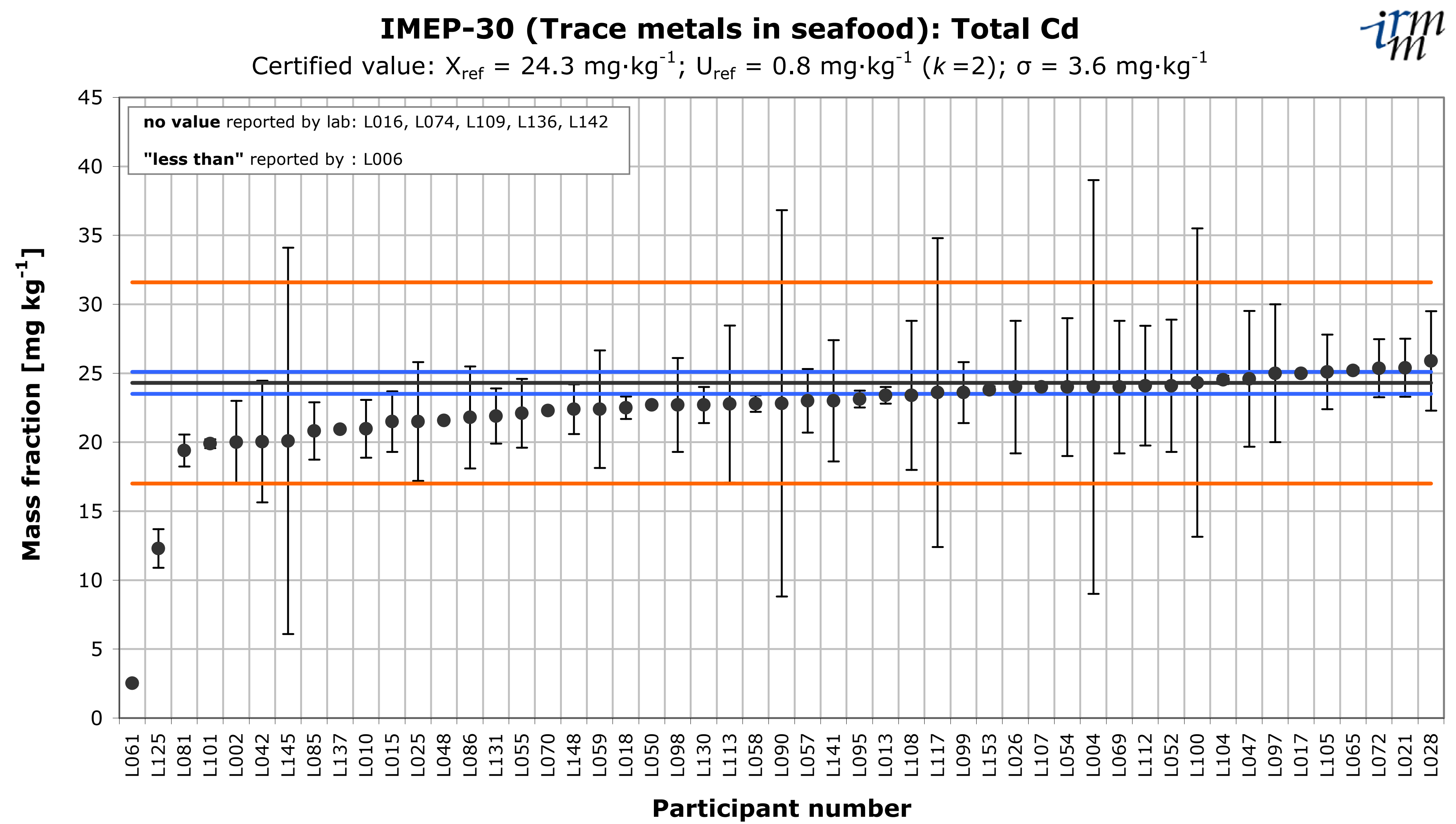
X_{ref} = 24.3 and U_{ref} = 0.8; all values are given in (mg kg^{-1})

Part Nr	Mean (x_{lab})	U_{lab}	k[a]	u_{lab}	Technique	z[b]	ζ[b]	Unc[c]
L002	20.0	3.0	2	1.5	FAAS	-1.2	-2.8	a
L004	24	15	2	8	ICP-MS	-0.1	0.0	c
L006	<5.000				ETAAS			
L010	20.971	2.097	2	1.049	ICP-MS	-0.9	-3.0	a
L013	23.4	0.6	2	0.3	ICP-MS	-0.2	-1.8	b
L015	21.5	2.2	2.776	0.8	ETAAS	-0.8	-3.2	a
L017	25	0	2	0	GF-AAS	0.2	1.8	b
L018	22.5	0.82	2	0.41	ICP-MS	-0.5	-3.1	a
L021	25.4	2.1	0.85	2.5	ICP-MS	0.3	0.4	a
L025	21.5	4.3	2	2.2	ICP-MS	-0.8	-1.3	a
L026	24.0	4.80	2	2.40	ETAAS	-0.1	-0.1	a
L028	25.9	3.6	2	1.8	ETAAS	0.4	0.9	a
L042	20.046	4.410	1.2	3.675	GFAAS	-1.2	-1.2	c
L047	24.6	4.92	2	2.46	HR-ICP-MS	0.1	0.1	a
L048	21.58	0	√3	0	FAAS	-0.7	-6.8	b
L050	22.7	0.12	2	0.06	FAAS	-0.4	-4.0	b
L052	24.1	4.8	2	2.4	ICP-MS	-0.1	-0.1	a
L054	24	5	√3	3	ICP-MS	-0.1	-0.1	a
L055	22.1	2.5	3	0.8	ETAAS	-0.6	-2.4	a
L057	23.0	2.30	2	1.15	ICP-OES	-0.4	-1.1	a
L058	22.8	0.6	3	0.2	ICP-MS	-0.4	-3.4	b
L059	22.4	4.26	3	1.42	ICP-MS	-0.5	-1.3	a
L061	2.53	0.17	2	0.09	ICP-MS	-6.0	-53.2	b
L065	25.2	0.22	1.062	0.21	ICP-OES	0.2	2.0	b
L069	24.0	4.8	2	2.4	FAAS	-0.1	-0.1	a
L070	22.30	0.014	√3	0.008	ICP-MS	-0.5	-5.0	b
L072	25.3636	2.1	0.99	2.1	ICP-MS	0.3	0.5	a
L081	19.40	1.16	2	0.58	ICP-OES	-1.3	-7.0	a
L085	20.82	2.08	1	2.08	ICP-MS	-1.0	-1.6	a
L086	21.8	3.7	2	1.9	ICP-MS	-0.7	-1.3	a
L090	22.82	14	2	7	ETAAS	-0.4	-0.2	c
L095	23.13	0.61	2	0.31	ICP-MS	-0.3	-2.3	b
L097	25	5.0	2	2.5	ETAAS	0.2	0.3	a
L098	22.7	3.4	2	1.7	ICP-MS	-0.4	-0.9	a
L099	23.6	2.2	2	1.1	ETAAS	-0.2	-0.6	a
L100	24.32	11.18	1.15	9.72	FAAS	0.0	0.0	c
L101	19.9	0.3204	2	0.1602	ICP-MS	-1.2	-10.2	b
L104	24.52	0.30	2	0.15	ICP-OES	0.1	0.5	b
L105	25.1	2.7	2	1.4	ICP-MS	0.2	0.6	a
L107	24.0	0.06	2	0.03	FAAS	-0.1	-0.7	b
L108	23.4	5.4	2	2.7	ICP-OES	-0.2	-0.3	a
L112	24.1	4.34	0.992	4.38	ICP-MS	-0.1	0.0	c
L113	22.77	5.69	2	2.85	FAAS	-0.4	-0.5	a
L117	23.6	11.2	2	5.6	AAS-ETA	-0.2	-0.1	c
L125	12.3	1.4	1.64	0.9	ETAAS	-3.3	-12.7	a
L130	22.7	1.31	√3	0.76	ICP-MS	-0.4	-1.9	a
L131	21.9	2.0	√3	1.2	ICP-MS	-0.7	-2.0	a
L137	20.94	0	√3	0	FAAS	-0.9	-8.4	b
L141	23	4.4	2	2.2	ETAAS	-0.4	-0.6	a
L145	20.1	14	2	7	ICP-MS	-1.2	-0.6	c
L148	22.4	1.8	2	0.9	ICP-MS	-0.5	-1.9	a
L153	23.8	0.26	2	0.13	ICP-MS	-0.1	-1.2	b

[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

[b] **Satisfactory**, **Questionable**, **Unsatisfactory**

[c] Where: **a** = $u_{min} \leq u_{lab} \leq u_{max}$, **b** : $u_{lab} < u_{min}$, and **c** : $u_{lab} > u_{max}$



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to $\mathbf{X_{ref}}$, the blue lines mark the boundary of the reference interval ($\mathbf{X_{ref} \pm 2u_{ref}}$), and the orange lines that of the target interval ($\mathbf{X_{ref} \pm 2\sigma}$).

Annex 11 : Results for Total Lead

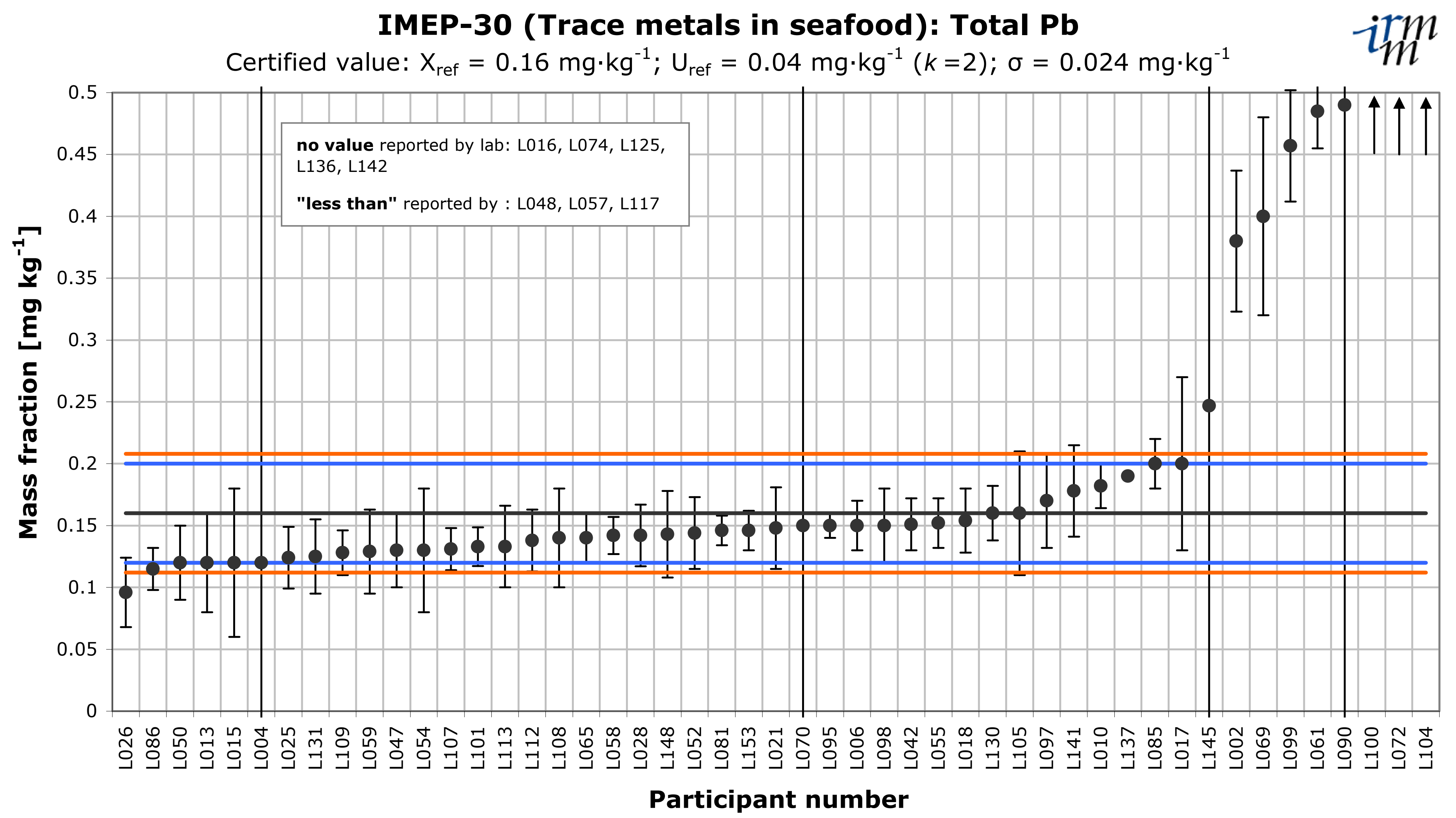
X_{ref} = 0.16 and U_{ref} = 0.04; all values are given in (mg kg^{-1})

Part Nr	Mean (x_{lab})	U_{lab}	k^a	u_{lab}	Technique	z^b	ζ^b	Unc^c
L002	0.38	0.057	2	0.029	FAAS	9.2	6.3	c
L004	0.12	30	2	15	ICP-MS	-1.7	0.0	c
L006	0.15	0.02	2	0.01	ETAAS	-0.4	-0.4	b
L010	0.182	0.018	2	0.009	ICP-MS	0.9	1.0	b
L013	0.12	0.04	2	0.02	HR-ICP-MS	-1.7	-1.4	a
L015	0.12	0.06	2.776	0.02	ETAAS	-1.7	-1.4	a
L017	0.20	0.07	2	0.04	GF-AAS	1.7	1.0	c
L018	0.154	0.026	2	0.013	ICP-MS	-0.3	-0.3	b
L021	0.148	0.033	0.013	2.538	ICP-MS	-0.5	0.0	c
L025	0.124	0.025	2	0.013	ICP-MS	-1.5	-1.5	b
L026	0.096	0.028	2	0.014	ETAAS	-2.7	-2.6	b
L028	0.142	0.025	2	0.013	ETAAS	-0.8	-0.8	b
L042	0.151	0.021	1.1	0.019	GFAAS	-0.4	-0.3	b
L047	0.130	0.030	2	0.015	HR-ICP-MS	-1.3	-1.2	b
L048	<0.02				ETAAS			
L050	0.12	0.030	2	0.015	ETAAS	-1.7	-1.6	b
L052	0.144	0.029	2	0.015	ICP-MS	-0.7	-0.6	b
L054	0.13	0.05	√3	0.03	ICP-MS	-1.3	-0.9	c
L055	0.152	0.02	3	0.01	ICP-MS	-0.3	-0.4	b
L057	<0.20				ICP-OES			
L058	0.142	0.015	3	0.005	ICP-MS	-0.8	-0.9	b
L059	0.129	0.034	3	0.011	ICP-MS	-1.3	-1.3	b
L061	0.485	0.030	2	0.015	ICP-MS	13.5	13.0	b
L065	0.14	0.02	0.993	0.02	Graphite tube AAS with Zeeman background correction	-0.8	-0.7	a
L069	0.4	0.08	2	0.04	FAAS	10.0	5.4	c
L070	0.15	1.180	√3	0.681	ICP-MS	-0.4	0.0	c
L072	2.6866	0.257	0.99	0.260	ICP-MS	105.3	9.7	c
L081	0.146	0.012	2	0.006	ICP-OES	-0.6	-0.7	b
L085	0.20	0.02	1	0.02	ICP-MS	1.7	1.4	a
L086	0.115	0.017	2	0.009	ICP-MS	-1.9	-2.1	b
L090	0.49	10.5	2	5.3	ETAAS	13.8	0.1	c
L095	0.150	0.010	2	0.005	ICP-MS	-0.4	-0.5	b
L097	0.17	0.038	2	0.019	ETAAS	0.4	0.4	b
L098	0.15	0.03	2	0.02	ICP-MS	-0.4	-0.4	b
L099	0.457	0.045	2	0.023	ETAAS	12.4	9.9	a
L100	2.68	1.02	1.17	0.87	ETAAS	105.0	2.9	c
L101	0.133	0.0157	2	0.0079	ICP-MS	-1.1	-1.3	b
L104	5.30	0.06	2	0.03	ICP-OES	214.2	142.6	c
L105	0.16	0.05	2	0.03	ICP-MS	0.0	0.0	c
L107	0.131	0.017	2	0.009	ETAAS	-1.2	-1.3	b
L108	0.14	0.04	2	0.02	ICP-OES	-0.8	-0.7	a
L109	0.128	0.018	2	0.009	HR-ICP-MS	-1.3	-1.5	b
L112	0.138	0.025	0.87	0.029	ICP-MS	-0.9	-0.6	c
L113	0.133	0.033	2	0.0165	FAAS	-1.1	-1.0	b
L117	<0.25				AAS-ETA			
L130	0.16	0.022	√3	0.013	ICP-OES	0.0	0.0	b
L131	0.125	0.03	√3	0.02	ICP-MS	-1.5	-1.3	b
L137	0.19	0	√3	0	FAAS	1.3	1.5	b
L141	0.178	0.037	2	0.019	ETAAS	0.7	0.7	b
L145	0.247	15	2	8	ICP-MS	3.6	0.0	c
L148	0.143	0.035	2	0.018	ICP-MS	-0.7	-0.6	b
L153	0.146	0.016	2	0.008	ICP-MS	-0.6	-0.6	b

[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

[b] **Satisfactory**, **Questionable**, **Unsatisfactory**

[c] Where: **a** = $u_{min} \leq u_{lab} \leq u_{max}$, **b** : $u_{lab} < u_{min}$, and **c** : $u_{lab} > u_{max}$



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to $\mathbf{X_{ref}}$, the blue lines mark the boundary of the reference interval ($\mathbf{X_{ref} \pm 2u_{ref}}$), and the orange lines that of the target interval ($\mathbf{X_{ref} \pm 2\sigma}$).

Annex 12 : Results for Total Mercury

X_{ref} = 2.58 and U_{ref} = 0.22; all values are given in (mg kg^{-1})

Part Nr	Mean (x_{lab})	U_{lab}	k[a]	u_{lab}	Technique	z[b]	ζ [b]	Unc[c]
L004	2.5	20	2	10	ICP-MS	-0.2	0.0	c
L006	1.44	0.41	2	0.21	HG-AAS	-2.9	-4.9	a
L010	2.587	0.259	2	0.130	ICP-MS	0.0	0.0	a
L015	2.45	0.50	2.776	0.18	CV-AFS	-0.3	-0.6	a
L016	2.6	0.3	√3	0.2	AMA 254	0.1	0.1	a
L017	1.8	0.3	2	0.2	CV-AAS	-2.0	-4.2	a
L018	3.08	0.18	2	0.09	CV-AAS	1.3	3.5	b
L021	2.71	0.26	0.11	2.36	ICP-MS	0.3	0.1	c
L025	2.04	0.51	2	0.26	CV-AAS	-1.4	-1.9	a
L026	2.67	0.53	2	0.27	CV-AAS	0.2	0.3	a
L028	2.62	0.52	2	0.26	HG-ICP-OES	0.1	0.1	a
L042	3.085	0.524	1.02	0.514	AAS	1.3	1.0	c
L047	2.22	0.741	2	0.371	HR-ICP-MS	-0.9	-0.9	a
L048	2.58	0	√3	0	CV-AAS	0.0	0.0	b
L050	2.57	0.082	2	0.041	AFS	0.0	-0.1	b
L052	2.14	0.28	2	0.14	CV-AAS	-1.1	-2.5	a
L054	2.6	0.8	√3	0.5	ICP-MS	0.1	0.0	c
L055	2.53	0.3	3	0.1	CV-AAS	-0.1	-0.3	b
L057	2.10	0.21	2	0.11	CV-AAS	-1.2	-3.2	b
L058	2.73	0.1	3	0.0	CV-AAS	0.4	1.3	b
L059	2.17	0.30	3	0.10	HG-AAS	-1.1	-2.8	b
L061	0.259	0.026	2	0.013	ICP-MS	-6.0	-21.0	b
L065	2.57	0.038	1.009	0.038	AFS	0.0	-0.1	b
L069	2.6	0.52	2	0.26	CV-AAS	0.1	0.1	a
L070	2.40	0.002	√3	0.001	CV-AAS	-0.5	-1.6	b
L072	2.5491	0.562	0.99	0.568	CV-AAS	-0.1	-0.1	c
L081	1.65	0.12	2	0.06	ICP-OES	-2.4	-7.4	b
L085	2.43	0.24	1	0.24	CV-AAS	-0.4	-0.6	a
L086	2.46	0.44	2	0.22	CV-AAS	-0.3	-0.5	a
L090	2.87	10	2	5	CV-AAS	0.7	0.1	c
L095	2.631	0.073	2	0.037	ICP-MS	0.1	0.4	b
L097	2.6	0.39	2	0.20	FIAS-AAS	0.1	0.1	a
L098	2.67	0.40	2	0.20	ICP-MS	0.2	0.4	a
L099	2.43	0.14	2	0.07	CV-AAS	-0.4	-1.2	b
L100	2.55	0.88	1.38	0.64	CV-AAS	-0.1	0.0	c
L101	2.59	0.1023	2	0.0512	CV-AFS	0.0	0.1	b
L104	1.15	0.05	2	0.03	HG-AAS	-3.7	-12.7	b
L105	2.1	0.4	2	0.2	ICP-MS	-1.2	-2.1	a
L107	2.62	0.05	2	0.03	CV-AAS	0.1	0.4	b
L108	2.53	0.76	2	0.38	ICP-OES	-0.1	-0.1	a
L109	2.55	0.38	2	0.19	CV-AAS	-0.1	-0.1	a
L112	2.58	0.46	1.004	0.46	ICP-MS	0.0	0.0	c
L113	2.58	0.39	2	0.20	CV-AAS	0.0	0.0	a
L117	3.48	1.22	2	0.61	CV-AAS	2.3	1.5	c
L125	2.08	0.233	1.64	0.142	CV-AFS	-1.3	-2.8	a
L130	2.74	0.12	√3	0.07	ICP-MS	0.4	1.2	b
L131	2.55	0.3	√3	0.2	CV-AAS	-0.1	-0.1	a
L141	2.5	0.5	2	0.3	CV-AAS	-0.2	-0.3	a
L142	1.92	0.31	2	0.16	CV-AFS	-1.7	-3.5	a
L145	2.90	17	2	9	CV-AAS	0.8	0.0	c
L148	2.68	0.10	2	0.05	CV-AAS	0.3	0.8	b
L153	2.69	0.04	2	0.02	ICP-MS	0.3	1.0	b

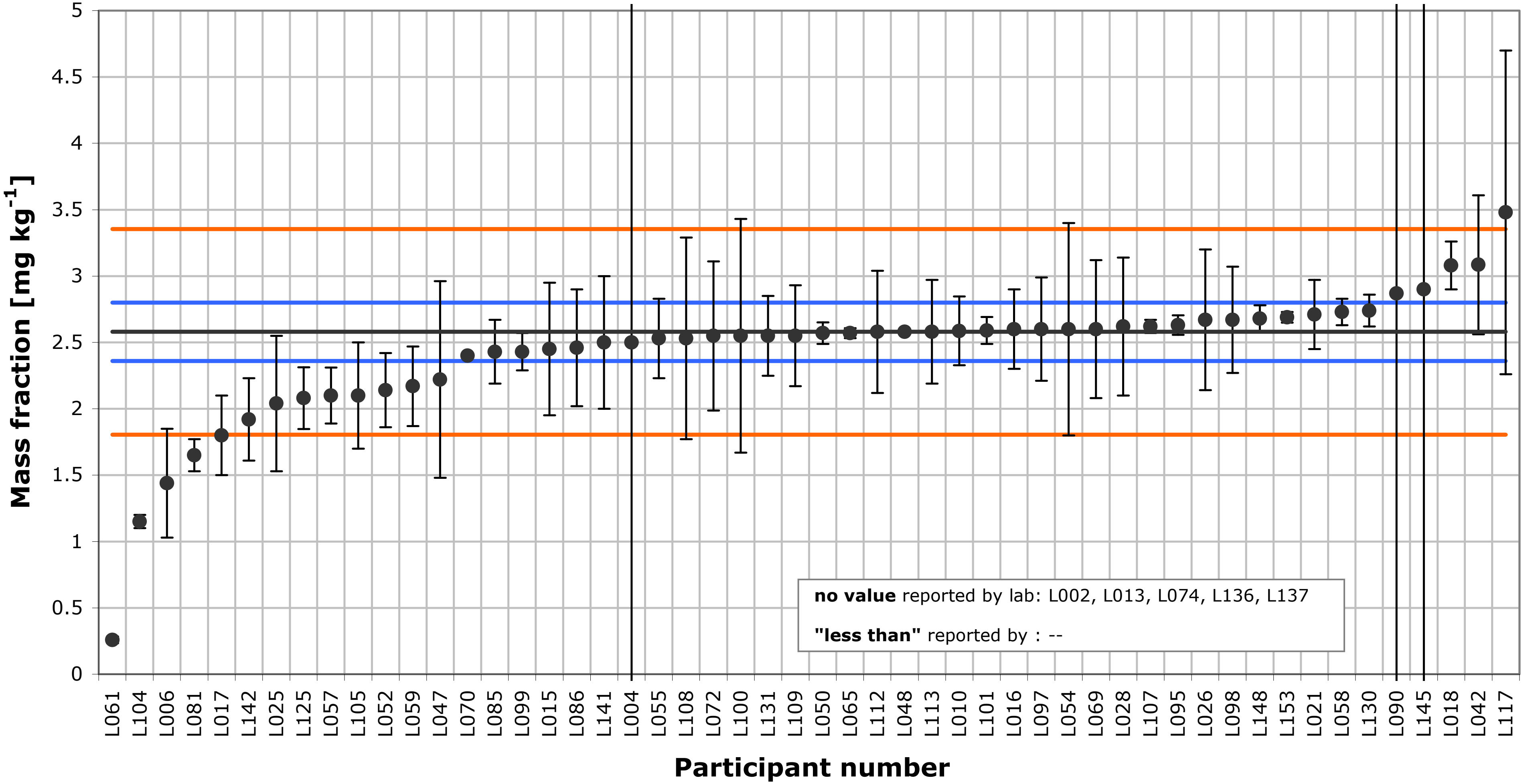
[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

[b] **Satisfactory**, **Questionable**, **Unsatisfactory**

[c] Where: **a** = $u_{min} \leq u_{lab} \leq u_{max}$, **b** : $u_{lab} < u_{min}$, and **c** : $u_{lab} > u_{max}$

IMEP-30 (Trace metals in seafood): Total Hg

Certified value: X_{ref} = 2.58 mg·kg^{-1}; U_{ref} = 0.22 mg·kg^{-1} (k =2); σ = 0.39 mg·kg^{-1}

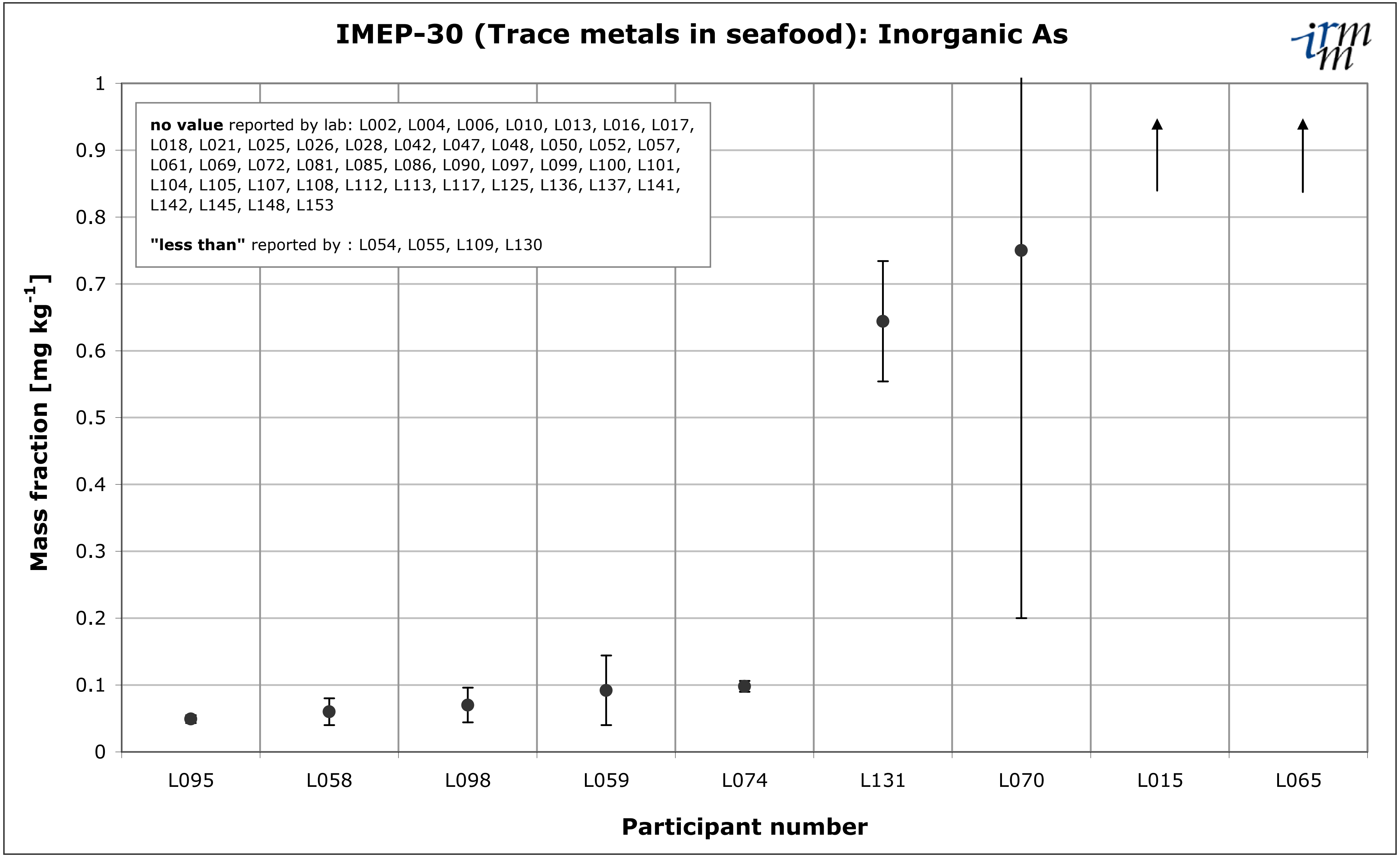


This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to $\mathbf{X_{ref}}$, the blue lines mark the boundary of the reference interval ($\mathbf{X_{ref} \pm 2u_{ref}}$), and the orange lines that of the target interval ($\mathbf{X_{ref} \pm 2\sigma}$).

Annex 13 : Results for Inorganic Arsenic

All values are given in (mg kg^{-1})

Part Nr	Mean (x_{lab})	U_{lab}	k^a	u_{lab}	Technique
L015	3.23	0.60	2.776	0.22	EN 15517:2008
L054	<0.010				HPLC-ICP-MS
L055	<0.1				HG-AAS
L058	0.06	0.02	3	0.01	ICP-MS
L059	0.092	0.052	3	0.017	HG-AAS
L065	5.29	0.065	0.910	0.071	ICP-MS
L070	0.75	0.550	1.732	0.318	ETAAS
L074	0.098	0.008	2	0.004	HG-ICP-MS
L095	0.049	0.006	2	0.003	HG-AAS
L098	0.070	0.026	2	0.013	HG-AAS
L109	<0.100				LC-ICPMS
L130	<0.040				HPLC- ICPMS
L131	0.644	0.09	1.732	0.05	HG-AAS


IMEP-30 (Trace metals in seafood): Inorganic As
no value reported by lab: L002, L004, L006, L010, L013, L016, L017, L018, L021, L025, L026, L028, L042, L047, L048, L050, L052, L057, L061, L069, L072, L081, L085, L086, L090, L097, L099, L100, L101, L104, L105, L107, L108, L112, L113, L117, L125, L136, L137, L141, L142, L145, L148, L153
"less than" reported by : L054, L055, L109, L130
Mass fraction [mg kg-1]
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
L095
L058
L098
L059
L074
L131
L070
L015
L065
Participant number

Annex 14 : Results for Methylmercury

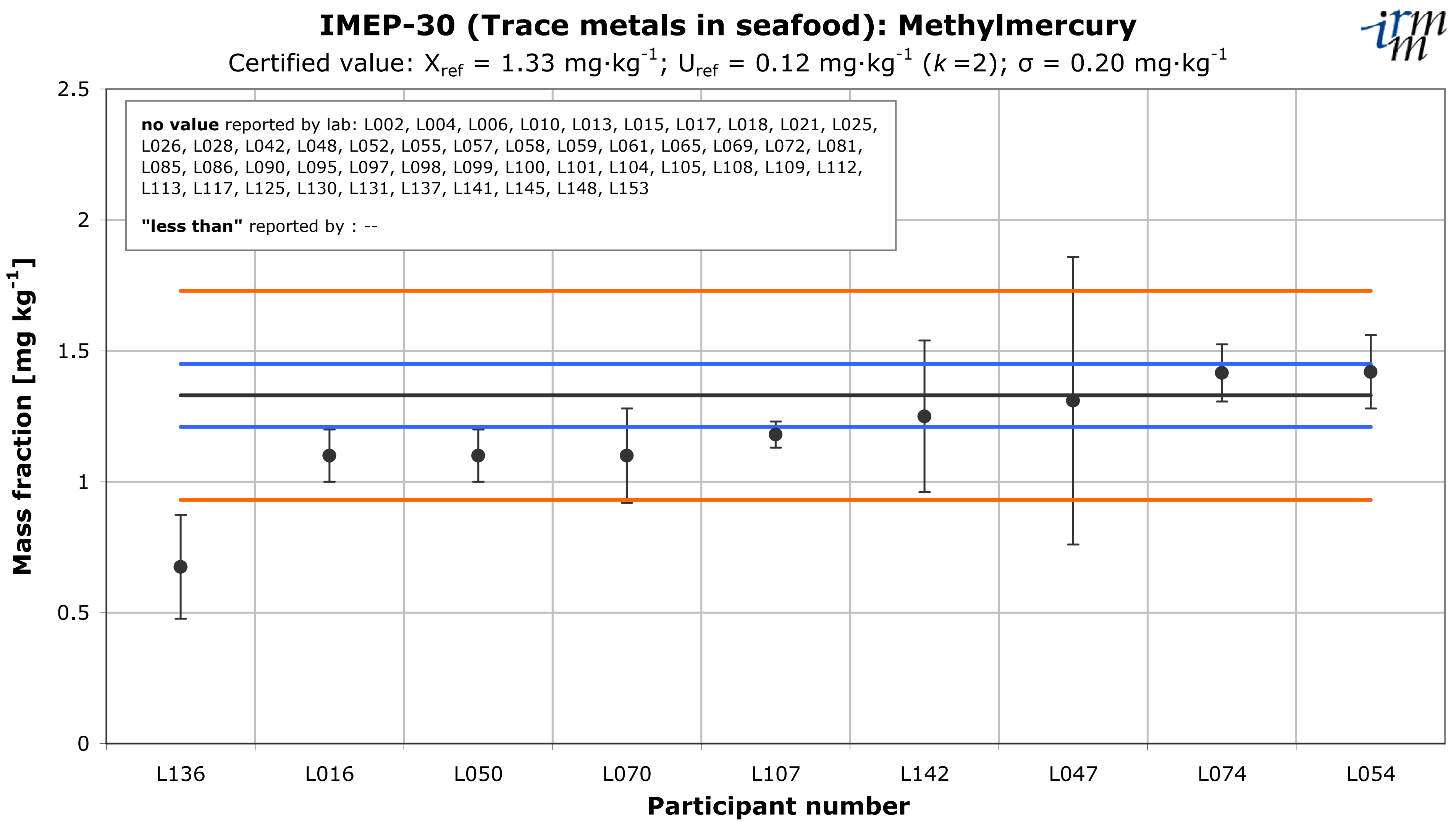
X_{ref} = 1.33 and U_{ref} = 0.11; all values are given in (mg kg^{-1})

Part Nr	Mean (x_{lab})	U_{lab}	k[a]	u_{lab}	Technique	z[b]	ζ[b]	Unc[c]
L016	1.1	0.1	√3	0.1	GC AFS Specification System	-1.2	-2.8	**b**
L047	1.31	0.549	2	0.275	GC-MS	-0.1	-0.1	**c**
L050	1.1	0.10	2	0.05	HPLC-ICP-MS	-1.2	-2.9	**b**
L054	1.42	0.14	√3	0.081	GC-ICP-MS quant by isotopic dilution	0.5	0.9	**a**
L070	1.10	0.180	√3	0.104	LC-ICP-MS	-1.2	-1.9	**a**
L074	1.416	0.109	2	0.055	GC-ICP/MS	0.4	1.1	**b**
L107	1.18	0.05	2	0.03	GC-AED	-0.8	-2.3	**b**
L136	0.675	0.198	2	0.099	GC ECD	-3.3	-5.7	**a**
L142	1.25	0.29	2	0.15	CV-AFS	-0.4	-0.5	**a**

[a] √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

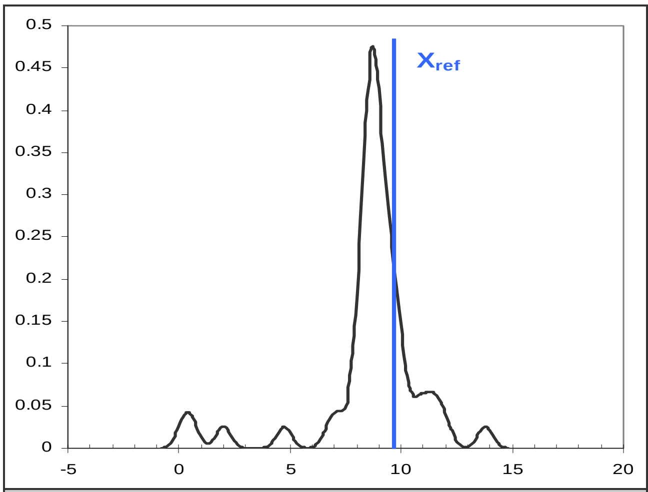
[b] **Satisfactory**, **Questionable**, **Unsatisfactory**

[c] Where: **a** = $u_{min} \leq u_{lab} \leq u_{max}$, **b** : $u_{lab} < u_{min}$, and **c** : $u_{lab} > u_{max}$

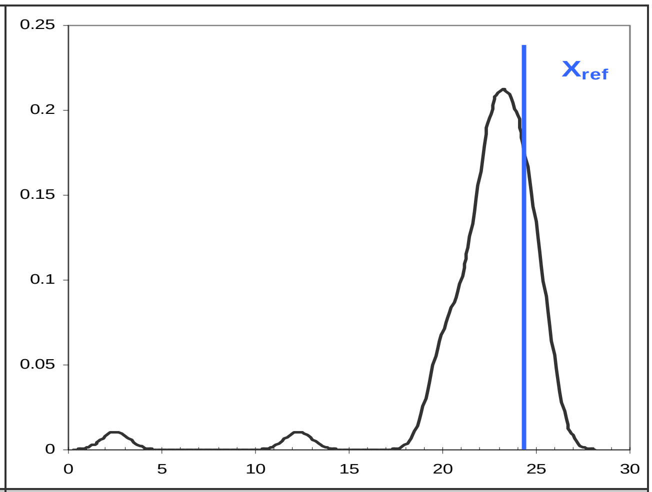


This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to X_{ref}, the blue lines mark the boundary of the reference interval ($X_{ref} \pm 2u_{ref}$), and the orange lines that of the target interval ($X_{ref} \pm 2\sigma$).

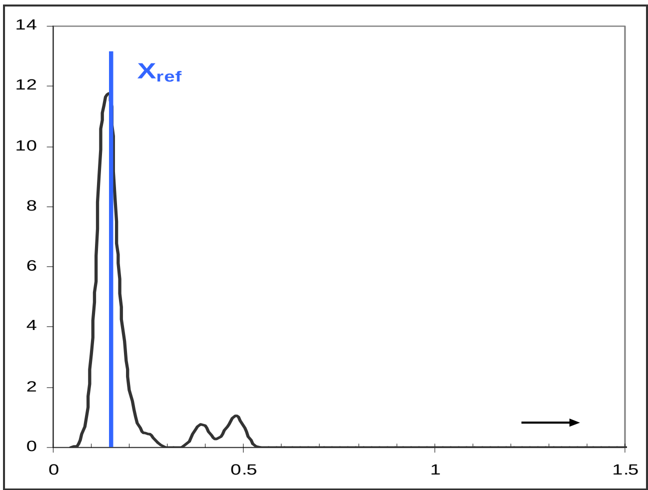
Annex 15 : Kernel densities [mg kg^{-1}]



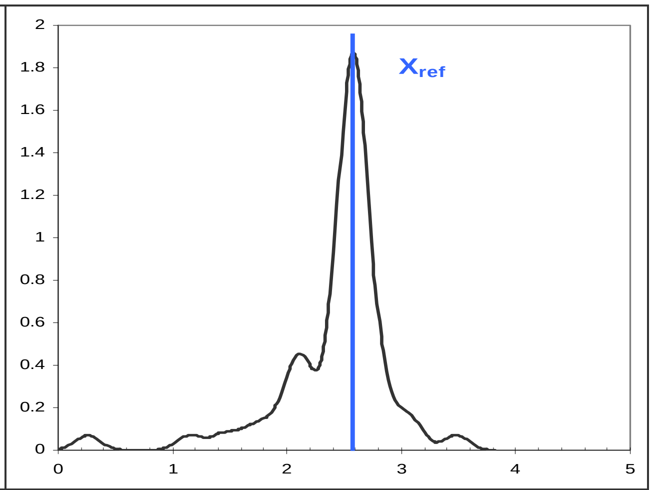
Total Arsenic



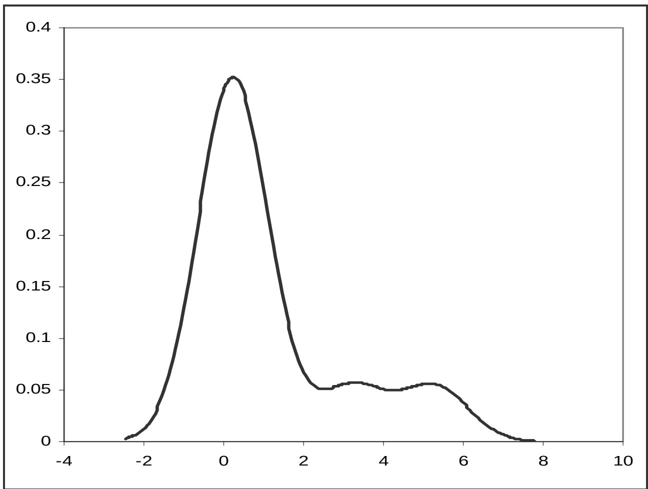
Total Cadmium



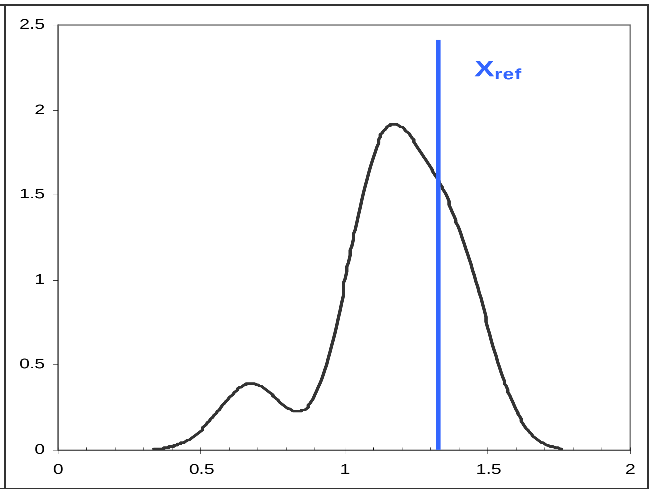
Total Lead



Total Mercury



Inorganic Arsenic



Methylmercury

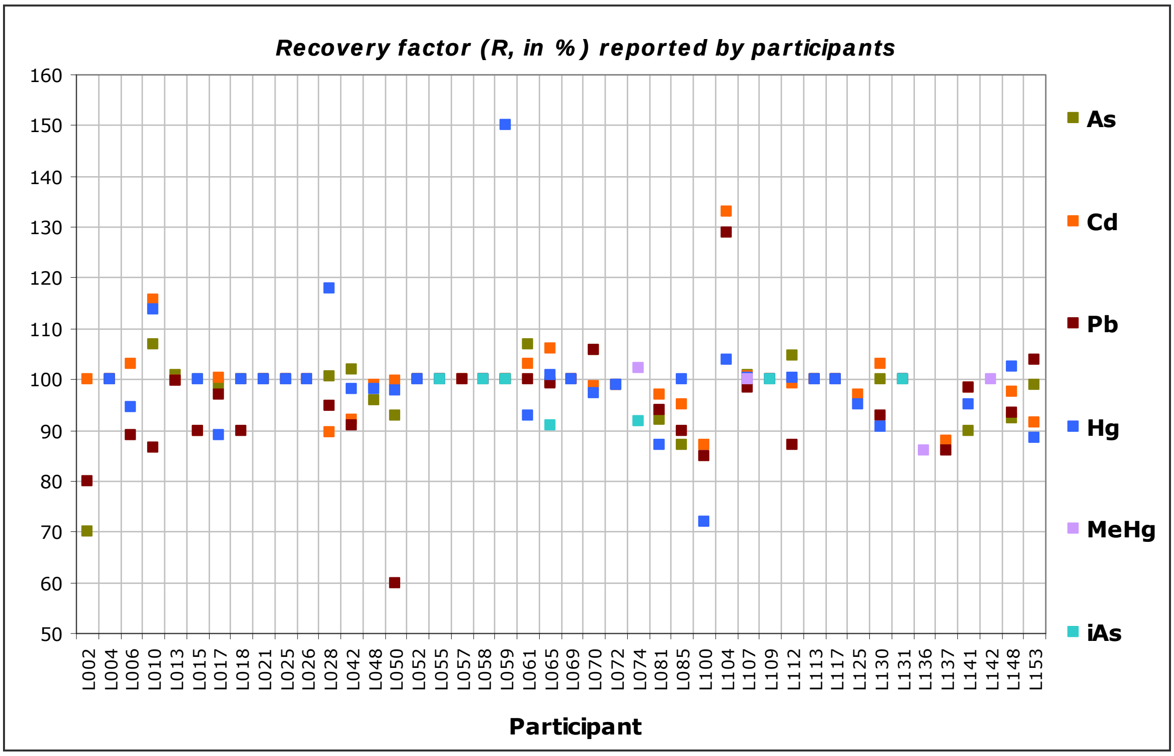
Annex 16 : Summary of scorings

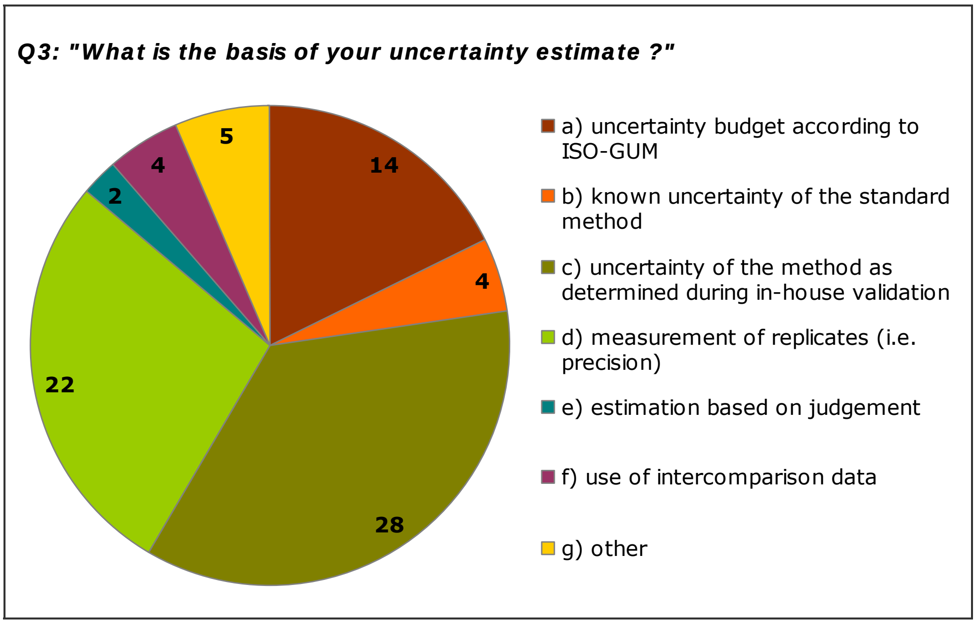
Part Nr	Total As			Total Cd			Total Pb			Total Hg			Methylmercury		
	z†	ζ †	Unc*	z†	ζ †	Unc*	z†	ζ †	Unc*	z†	ζ †	Unc*	z†	ζ †	Unc*
L002	-5.3	-20.8	b	-1.2	-2.8	a	9.2	6.3	c						
L004	0.0	0.0	c	-0.1	0.0	c	-1.7	0.0	c	-0.2	0.0	c			
L006							-0.4	-0.4	b	-2.9	-4.9	a			
L010	0.2	0.4	a	-0.9	-3.0	a	0.9	1.0	b	0.0	0.0	a			
L013	-0.9	-3.0	b	-0.2	-1.8	b	-1.7	-1.4	a						
L015	-0.6	-1.2	a	-0.8	-3.2	a	-1.7	-1.4	a	-0.3	-0.6	a			
L016										0.1	0.1	a	-1.2	-2.8	b
L017	1.6	1.5	c	0.2	1.8	b	1.7	1.0	c	-2.0	-4.2	a			
L018	-0.7	-2.9	b	-0.5	-3.1	a	-0.3	-0.3	b	1.3	3.5	b			
L021	1.2	0.7	c	0.3	0.4	a	-0.5	0.0	c	0.3	0.1	c			
L025	0.9	1.4	a	-0.8	-1.3	a	-1.5	-1.5	b	-1.4	-1.9	a			
L026				-0.1	-0.1	a	-2.7	-2.6	b	0.2	0.3	a			
L028	-6.3	-29.2	b	0.4	0.9	a	-0.8	-0.8	b	0.1	0.1	a			
L042	-3.4	-4.7	a	-1.2	-1.2	c	-0.4	-0.3	b	1.3	1.0	c			
L047	-1.1	-1.4	a	0.1	0.1	a	-1.3	-1.2	b	-0.9	-0.9	a	-0.1	-0.1	c
L048	-1.0	-4.8	b	-0.7	-6.8	b				0.0	0.0	b			
L050	-1.0	-4.3	b	-0.4	-4.0	b	-1.7	-1.6	b	0.0	-0.1	b	-1.2	-2.9	b
L052	0.3	0.4	a	-0.1	-0.1	a	-0.7	-0.6	b	-1.1	-2.5	a			
L054	-0.2	-0.2	a	-0.1	-0.1	a	-1.3	-0.9	c	0.1	0.0	c	0.5	0.9	a
L055	0.0	0.0	a	-0.6	-2.4	a	-0.3	-0.4	b	-0.1	-0.3	b			
L057	-0.1	-0.3	a	-0.4	-1.1	a				-1.2	-3.2	b			
L058	-0.1	-0.5	b	-0.4	-3.4	b	-0.8	-0.9	b	0.4	1.3	b			
L059	-0.5	-1.1	a	-0.5	-1.3	a	-1.3	-1.3	b	-1.1	-2.8	b			
L061	0.3	0.7	a	-6.0	-53.2	b	13.5	13.0	b	-6.0	-21.0	b			
L065	-0.4	-1.3	a	0.2	2.0	b	-0.8	-0.7	a	0.0	-0.1	b			
L069	1.3	1.1	c	-0.1	-0.1	a	10.0	5.4	c	0.1	0.1	a			
L070	-0.3	-1.2	b	-0.5	-5.0	b	-0.4	0.0	c	-0.5	-1.6	b	-1.2	-1.9	a
L072	-0.3	-0.5	a	0.3	0.5	a	105.3	9.7	c	-0.1	-0.1	c			
L074													0.4	1.1	b
L081	2.9	8.0	a	-1.3	-7.0	a	-0.6	-0.7	b	-2.4	-7.4	b			
L085	-0.7	-1.1	a	-1.0	-1.6	a	1.7	1.4	a	-0.4	-0.6	a			
L086	-0.7	-1.1	a	-0.7	-1.3	a	-1.9	-2.1	b	-0.3	-0.5	a			
L090	-1.9	-0.5	c	-0.4	-0.2	c	13.8	0.1	c	0.7	0.1	c			
L095	-0.2	-0.8	b	-0.3	-2.3	b	-0.4	-0.5	b	0.1	0.4	b			
L097	-0.6	-2.2	b	0.2	0.3	a	0.4	0.4	b	0.1	0.1	a			
L098	-0.7	-1.4	a	-0.4	-0.9	a	-0.4	-0.4	b	0.2	0.4	a			
L099				-0.2	-0.6	a	12.4	9.9	a	-0.4	-1.2	b			
L100				0.0	0.0	c	105.0	2.9	c	-0.1	0.0	c			
L101	-0.8	-3.3	b	-1.2	-10.2	b	-1.1	-1.3	b	0.0	0.1	b			
L104	-6.5	-30.5	b	0.1	0.5	b	214.2	142.6	c	-3.7	-12.7	b			
L105	-0.7	-2.1	a	0.2	0.6	a	0.0	0.0	c	-1.2	-2.1	a			
L107	-1.2	-4.3	b	-0.1	-0.7	b	-1.2	-1.3	b	0.1	0.4	b	-0.8	-2.3	b
L108	-0.7	-0.8	a	-0.2	-0.3	a	-0.8	-0.7	a	-0.1	-0.1	a			
L109	-0.4	-0.7	a				-1.3	-1.5	b	-0.1	-0.1	a			
L112	0.8	0.6	c	-0.1	0.0	c	-0.9	-0.6	c	0.0	0.0	c			
L113	-1.7	-2.5	a	-0.4	-0.5	a	-1.1	-1.0	b	0.0	0.0	a			
L117	-0.5	-1.1	a	-0.2	-0.1	c				2.3	1.5	c			
L125				-3.3	-12.7	a				-1.3	-2.8	a			
L130	-0.8	-3.1	b	-0.4	-1.9	a	0.0	0.0	b	0.4	1.2	b			
L131	-0.6	-1.4	a	-0.7	-2.0	a	-1.5	-1.3	b	-0.1	-0.1	a			
L136													-3.3	-5.7	a
L137				-0.9	-8.4	b	1.3	1.5	b	-0.2	-0.3	a			
L141	-0.5	-0.9	a	-0.4	-0.6	a	0.7	0.7	b	-1.7	-3.5	a			
L142													-0.4	-0.5	a
L145	-1.0	-0.2	c	-1.2	-0.6	c	3.6	0.0	c	0.8	0.0	c			
L148	-0.7	-2.5	b	-0.5	-1.9	a	-0.7	-0.6	b	0.3	0.8	b			
L153	-0.6	-2.6	b	-0.1	-1.2	b	-0.6	-0.6	b	0.3	1.0	b			

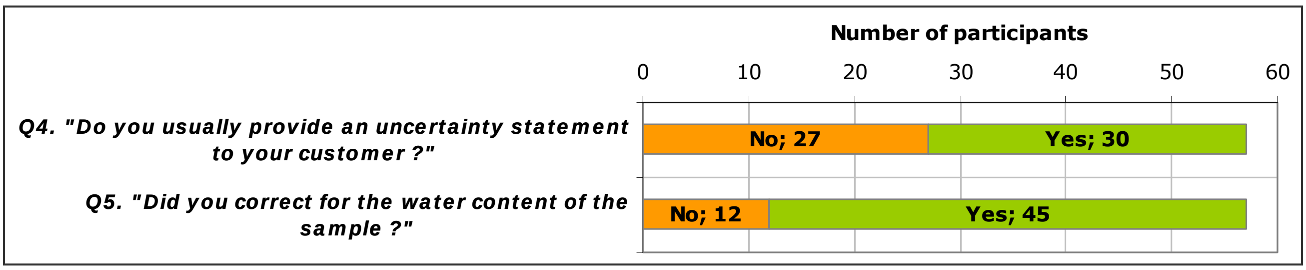
† **Satisfactory**, **Questionable**, **Unsatisfactory**

* Where: **a** = $u_{min} \leq u_{lab} \leq u_{max}$, **b** : $u_{lab} < u_{min}$, and **c** : $u_{lab} > u_{max}$

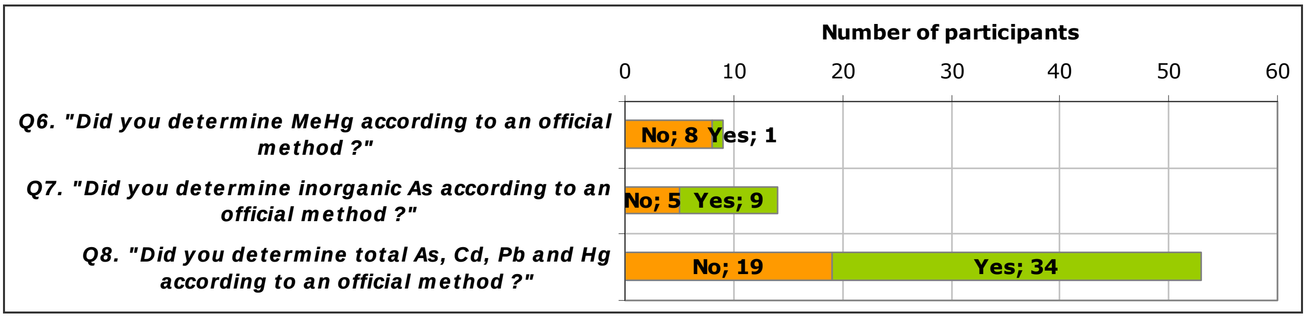
Annex 17 : Evaluation of questionnaire

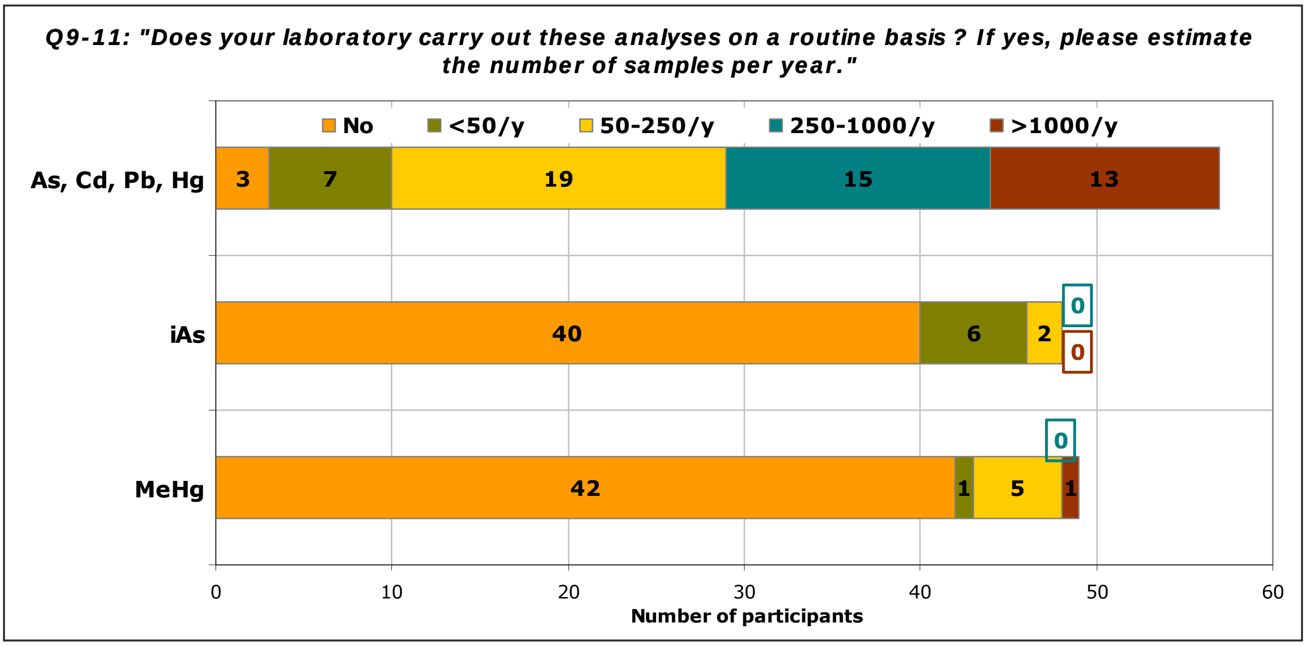


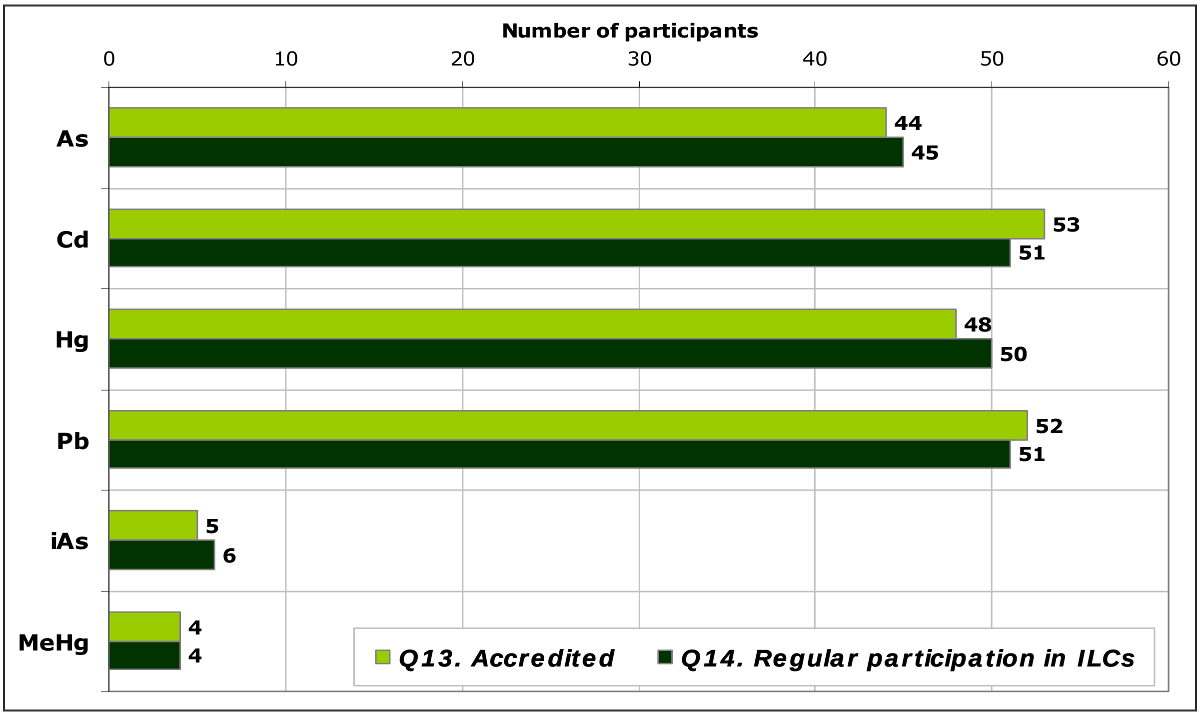


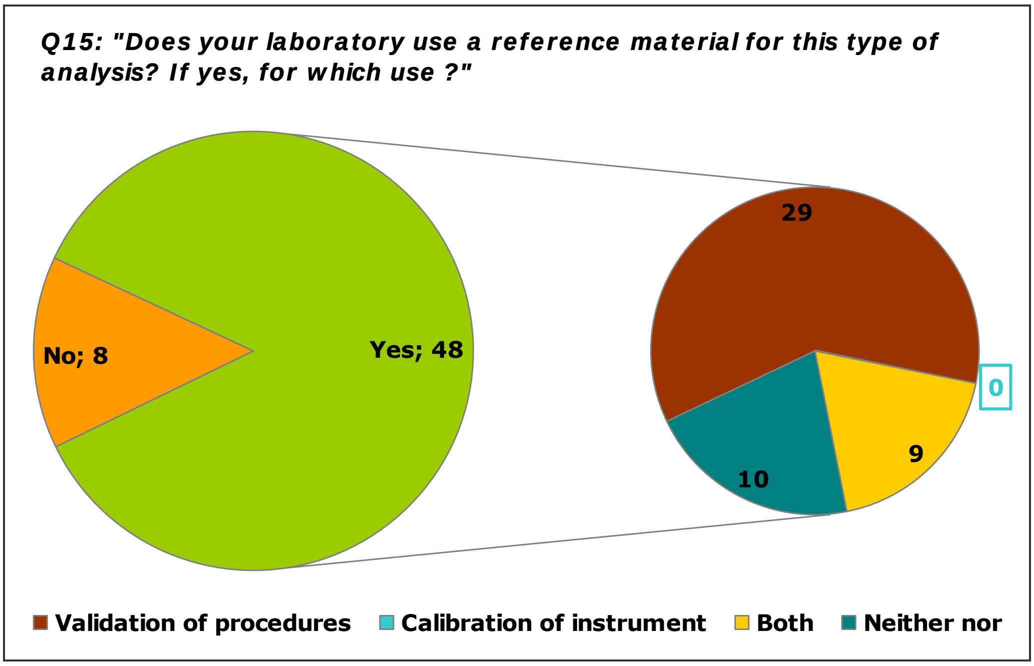



Q5.1: Water content as given by participants in the questionnaire
Water content [%]
4
3.5
3
2.5
2
1.5
1
0.5
0
L010 L018 L105 L117 L055 L112 L052 L057 L050 L081 L048 L142 L004 L141 L101 L058 L013 L136 L015 L097 L047 L026 L099 L085 L002 L042 L104 L090 L072 L137 L109 L061 L069 L148 L028 L021 L074 L016 L070 L065 L059 L130 L025 L095 L107 L098
Participant number


Number of participants
0
10
20
30
40
50
60
Q6. "Did you determine MeHg according to an official method ?"
No; 8
Yes; 1
Q7. "Did you determine inorganic As according to an official method ?"
No; 5
Yes; 9
Q8. "Did you determine total As, Cd, Pb and Hg according to an official method ?"
No; 19
Yes; 34


Q9-11: "Does your laboratory carry out these analyses on a routine basis ? If yes, please estimate the number of samples per year."
No
<50/y
50-250/y
250-1000/y
>1000/y
As, Cd, Pb, Hg
3
7
19
15
13
iAs
40
6
2
0
0
MeHg
42
1
5
0
1
0
10
20
30
40
50
60
Number of participants


Number of participants
0
10
20
30
40
50
60
As
44
45
Cd
53
51
Hg
48
50
Pb
52
51
iAs
5
6
MeHg
4
4
Q13. Accredited
Q14. Regular participation in ILCs


Q15: "Does your laboratory use a reference material for this type of analysis? If yes, for which use ?"
No; 8
Yes; 48
29
0
9
10
Validation of procedures
Calibration of instrument
Both
Neither nor

Annex 18 : Experimental details (Q6-8, Annex 7)

Q6 - Methylmercury

Part Nr	Official Method?	If yes, which:	If no - sample pre-treatment ?	If no - digestion step ?	If no - extraction / separation ?	If no - derivatization ?	If no - instrument calibration ?
L016	No		acid-base and organic extraction with DCM				
L047	No		Weight-in, spiking with Me198Hg	methanol, MQ (50:50) in UV-bath.	Filtration, dilution (1:500)	Add. of STEB in order to form MeHg-Et and EtHg-Et	Two different manufacturers of MeHg (one for Q-control).
L050	Yes	DB/T895-2009 Detn. of methylmercury and ethylmercury in environmental samples by HPLC-ICP-MS					
L054	No		Sample solved in TMAH		Extraction by hexane	NaBEt4	
L070	No		Add in extraction solution 1%w/v L-cysteine HCL.H2O		place in water bath at 60 C and shake for 10-15min. Centrifuge, take supernatant and filter.		calibration standards are prepared in 15ml PP centrifuge tubes and diluted by mass using 1%L-cysteine.HCL.H2O
L074	No		Homogenization	Enzymatic and acid digestion	solvent-solvent extraction	derivatize by tetraphenyl borate	internal standard
L107	No		weighing	methanolic KOH	n-Hexan	sodium tetra-ethyl-borate	external calibration 5-step-calibration
L136	Yes	983.2					
L142	No		Homogenization by Ultra-Turrax	Digestion with Tetramethyl ammonium hydroxide	Stripping extraction with Nitrogene	with Sodium tetraethyl borate	

Q7 – inorganic Arsenic

Part Nr	Official Method ?	If yes, which:	If no - sample pre-treatment ?	If no - digestion step ?	If no - extraction / separation ?	If no - instrument calibration ?
L015	Yes	MSZ EN 15517:2008				
L054	No		Heating in base			ICP-MS tuning against arsenic standard
L055	Yes	L25.06-1				
L058	Yes	Extraction by DIN EN 15571 (0.07m HCL 2 h, 37°C)				Calibration with As3+ and As5+, no interference from As-betaine (column AS7)
L059	Yes	§ 64 LFGB L25.06-1				
L065	Yes	§64 LFBG L 25.06 mod.				
L070	No		Add 10ml 9.2N HCl and 10ml 50% KI	Distilled at 110C		Calibration standards are prepared by reducing As standard using 50%KI and 50% urea
L074	No		Homogenization	HCl digestion followed by reduction	chloroform extraction	external calibration
L095	Yes	ASU § 64 LFGB 25.06-1				
L098	Yes	Amtliche Sammlung von Untersuchungsverfahren nach §64 LFGB: 25.06-1 (2008)				
L109	No				TMAOH	External Calibration plus post-column reference standard
L130	No		0.07M HCl / 10% H202		microwave	HPLC-ICPMS
L131	Yes	§64 LFGB L00.00-19/6				

Q8 – Total arsenic, cadmium, lead and mercury

Part Nr	Official Method ?	If yes, which:	If no - sample pre-treatment ?	If no - digestion step ?	If no - extraction / separation ?	If no - instrument calibration ?
L002	Yes	GOST 30178-96 (Pb, Cd), GOST 26930-86 (standards used in Russia and other former Soviet Union Republiks)				
L004	Yes	NEN-EN 13805 NEN-EN 15763				
L006	No		Homogenisation	Microwave, 1.5 g sample	Dilute up to 50 ML	Linear regression including 5 points: 0, 0.5, 1, 2, 5 ug/L
L010	No		homogenize sample by shaking the container	acid digestion using concentrated nitric acid	dilution in deionised water	stability check, tuning and calibration of the method
L013	No		microwave digestion	using three microwave warming steps		Pb were determined by ICP-MS after constant volume 10 mL. Cd and As were determined by ICP-MS after dilution 10 times.
L015	Yes	Cd, Pb: MSZ EN 14084:2003				
L016		For total Hg the sample is directly processed				
L017	No			acid digestion		daily calibration
L018	No		Homogenising	Microwave with HNO3/H2O2	no extraction	external calibration
L021	No					
L025	Yes	NMKL 161				
L026	Yes	NS EN 1483 (Hg), NS EN ISO 15586 (Pb, Cd),				
L028	Yes	digestion for all: AOAC 999.10 / determination: Cd & Pb: AOAC 999.10; Hg: NMKL 170; As: EN 14627				
L042	Yes	As, Cd, Pb, Hg				
L047	Yes	EN 13805 and EPA methods (mod) 200.8 (ICP-SFMS)				
L048	Yes	As: MSZ EN 14546:2005, Pb and Cd: MSZ EN 14084:2003, Hg: MSZ EN 13806:2002				
L050	Yes	Total Arsenic:GB/T5009.11-2003;Cadmium,Lead :GB17378.6-2007;Mercury:GB/T5009.17-2003				

Part Nr	Official Method ?	If yes, which:	If no - sample pre-treatment ?	If no - digestion step ?	If no - extraction / separation ?	If no - instrument calibration ?
L052	No		homogenization	As, Cd and Pb microwave digestion with nitric acid. Hg wet digestion with nitric and sulfuric acids	no one	As, Cd and Pb with external calibration using different internal standards. Hg with standard addition
L054	Yes	NMKL metode nr 186, 2007				
L055	Yes	L00.00-19/3; L00.00-19/6; L00.00-19/4; L00.00-19				
L057	Yes	based on EPA 6010B		Nitric acid and Hydrogen Peroxide	90min on a 90C hot block	Yes
L058	Yes	DIN EN 13805		closed vessel, nitric acid, > 200°C		External calibration, As75 in High resolution
L059	Yes	DIN EN ISO 11885				
L061	No		Digestion in a microwave oven with 6,5 ml HNO3 and 0,5 ml HCl	5 min- 180 C; 5 min - 180 C;5 min-200 C; 15 min - 200 C		external calibration with internal standard
L065	Yes	As, Cd: DIN EN ISO 11885 // Pb: §64 LFGB L 00.00-19/3 incl. DIN EN 14083 // Hg: §64 LFGB L 00.00-19/4				
L069	Yes	PZH Warszawa 1996, PN-EN 14546:2005,				
L070	No		Add HNO3 and H2O2/ Add HNO3 and H2SO4 (for Hg)	Microwave/ Digest using heating mantle (for Hg)		Standards are prepared using 2% HNO3/ Standards are prepared using 20% H2SO4
L072	Yes	US EPA 3051:1994				
L081	No		no pre-treatment	nitric acid + hydrogen peroxide; bomb digestion	no	yes
L085	No			Acid digestion with microwave (HNO3, H2O2, H2O)		ICP-MS for As, Cd, Pb and cold vapour-atomic absorption spectrometry for Hg
L086	Yes	EN 15763				
L090	No		For As, Cd, Pb sample pre-treatment with conc. HNO3 and H2O2 in waterbath at 85 C, for Hg with conc. HNO3 in waterbath at 65 C			calibration with Atomic Spectroscopy Standard Solutions, Fluka
L095	Yes	ASU § 64 LFGB L-00.00 19/1; DIN EN Iso 17294 Part 1 and 2 (E36, E29)				
L097	No		no	microwave digestion with nitric acid and hydrogen peroxide	no	calibration curve

Part Nr	Official Method ?	If yes, which:	If no - sample pre-treatment ?	If no - digestion step ?	If no - extraction / separation ?	If no - instrument calibration ?
L098	Yes	Amtliche Sammlung von Untersuchungs-verfahren nach § 64 LFGB: L 00.00-19/E und 1 (2003)				
L099	Yes	EN 14082:2003				
L100	Yes	SR EN ISO 14082/2003, SR EN ISO 14084/200SR EN ISO 13804/2003, SR EN ISO 13806/2003				
L101	Yes	DIN EN 13805 and ISO 17 294-2:2005 and ISO 17 852:2006				
L104	Yes	all				
L105	No		none	microwave	none	multi point calibration
L107	Yes	ASU L00-00-19				
L108	Yes	ISO 15510:2007				
L109	No			Microwave Digestion for Pb, & Hg Microwave Digestion & ashing for As	None	External Calibration
L112	No		crushing of 100g sample	soft digestion at 95°C in concentrated HNO3	no	external calibration with internal standards, by ICP-MS
L113	No		no pre-treatment	mineralisation (HNO3 / 65%) - microwave	no extraction or separation	linear regression (5 points including blank)
L117	No		none	microwave digestion with nitric acid & hydrogen peroxide for Cd and Pb; microwave digestion with nitric acid only for Hg; for As, digest with nitric acid and hydrogen peroxide then secondary digest with 4% potassium persulfate	for As, digest is combined with K iodide/ascorbic acid in 25% HCl; for Hg, digest is reacted with KMnO4, hydroxylamine sulphate and K2Cr2O7 then reduced with Tin(II) Chloride	external standards run with batch
L125	Yes	§64 LFGB		microwave oven, quarz tube	HNO3 / H2O2	ext. standards
L130	Yes	FM073				
L131	Yes	As, Cd, Pb: EN ISO 17294-2 (E29), Hg: DIN EN 1483 (E12-4)				
L137	Yes	flame atomic absorbtion spectrometer for the GOST 30178-96				
L141	No		none	microwave digestion in HNO3/H2O2	none	normal calibration with aqueous standards
L142						
L145	Yes	EVS EN ISO 17294-2:2004; EVS EN 1483	microwave digestion	3		5
L148	Yes	§ 64 of the German Food and Feed Code (LFGB)				
L153	Yes	EPA 6020A				

European Commission

EUR 24604 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: IMEP-30: Total arsenic, cadmium, lead and mercury, as well as methylmercury and inorganic arsenic in seafood
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Abstract
The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme® IMEP. It organises interlaboratory comparisons (ILC's) in support to EU policies. This report presents the results of an ILC which focussed on the determination of total As, Cd, Pb, and Hg, as well as methylmercury and inorganic arsenic in seafood.

The test material used in this exercise was the Certified Reference Material (CRM) DOLT-4, dogfish liver of the National Research Council of Canada (NRC). The material was relabelled and was dispatched end of May 2010. Each participant received one bottle containing approximately 20 g of test material. Fifty-seven laboratories from 29 countries registered to the exercise and all of them reported results.

The assigned values and their associated uncertainties for total As, Cd, Pb, Hg and methylmercury are the certified values taken from the DOLT-4 certificate. An attempt was made to establish an assigned value for inorganic As (iAs) using the results provided by a group of five laboratories expert in the field, following a similar approach to that used in IMEP-107 [1], a ILC on total and inorganic arsenic in rice. Unfortunately, contrary to what was observed in IMEP-107, the results obtained by the expert laboratories for iAs showed a large spread reason and no assigned value could be established.

Participants were invited to report the uncertainty of their measurements. This was done by the majority of the laboratories taking part in this exercise. Laboratory results were rated with z- and ζ-scores (zeta-scores) in accordance with ISO 13528 [2]. No scoring was provided to laboratories for submitted results of iAs. The standard deviation for proficiency assessment (also called target standard deviation) was fixed to 15 % by the advisory board of this ILC, on the basis of the outcome of previous ILCs organised by IMEP and on the state-of-the-art in this field of analysis.

The outcome of the exercise was in general positive, the share of satisfactory z-scores ranging between 80 and 96 %. Results for total As, and to a lesser extent for total Cd, showed a tendency for underestimation. As for iAs, the same spread of result than for the certifiers could be observed with the participants' results. No method influence could be detected, but the matrix seems to have a major impact.

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