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EURL-HM-25 Proficiency Test Report

Determination of the mass fraction of the total As, Cd, Pb, Hg, inorganic As and other trace elements in complete feed for fish

F. Cordeiro, J. Snell, P. Dehouck,
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European Union Reference Laboratory
Heavy Metals in Feed and Food

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268-PT Accredited by the
Belgian Accreditation Body (BELAC)

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Executive summary

The European Union Reference Laboratory for Heavy Metals in Feed and Food (EURL-HM) organised a proficiency test (EURL-HM-25) for the determination of the mass fractions of total As, Cd, Pb, Hg and inorganic As (iAs) in complete feed for fish, to support the Directive 2002/32/EC on undesirable substances in animal feed. This proficiency test was open to National Reference Laboratories (NRLs) and official feed control laboratories (OCLs).

A complete feed for fish was provided by the Italian NRL. It was further processed and spiked with As, Hg and Pb at the JRC premises in Geel. The homogeneity and stability of the test item were evaluated and the assigned values were derived from the results reported by the selected expert laboratories.

Forty NRLs from thirty two countries, representing Iceland, Norway, Serbia, and all the EU Member States (except Finland), and six OCLs (from Croatia, France, Iran and The Former Yugoslav Republic of Macedonia) registered to the exercise and reported results.

Laboratory results were rated using z (or z') and zeta (ζ) scores in accordance with ISO 13528:2015. The following relative standard deviations for proficiency assessment (σ_{pt}) were set according to the modified Horwitz equation: 13 % for total As; 18 % for Cd; 14 % for Pb and 22 % for Hg and iAs (where each percentage refers to the respective assigned value).

More than 91 % of the participating laboratories reported satisfactory results (according to the z score) for total Cd, Pb and Hg (78 % for total As). These results confirm the ability of most NRLs in monitoring maximum levels set by the EU Directive 2002/32/EC in this type of animal feed. However, only 9 laboratories reported satisfactorily for iAs.

The majority of the participating laboratories provided realistic estimates of their measurement uncertainties.

List of abbreviations

AAS	Atomic Absorption Spectrometry
CV-AAS	Cold Vapour Atomic Absorption Spectrometry
CV-AFS	Cold Vapour Atomic Fluorescence Spectrometry
DG SANTE	Directorate General for Health and Food Safety
DMA	Direct Mercury Analyzer (also called Elemental Mercury Analyzer, EMA)
ET-AAS	Electro Thermal – Atomic Absorption Spectrometry (also called Graphite Furnace Atomic Absorption Spectroscopy, GF-AAS)
FAAS	Flame Atomic Absorption Spectrometry
GUM	Guide for the Expression of Uncertainty in Measurement
HG-AAS	Hydride Generation – Atomic Absorption Spectrometry
HPLC	High Performance Liquid Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
JRC	Joint Research Centre
LC	Liquid Chromatography
LOD	Limit of Detection
NRL	National Reference Laboratory
OCL	Official Control Laboratory
PT	Proficiency Test

1. Introduction

The European Union Reference Laboratory for Heavy Metals in Feed and Food (EURL-HM), hosted by the Joint Research Centre in Geel (JRC-Geel), organised the proficiency test (PT) EURL-HM-25 for the determination of the mass fraction of total As, Cd, Pb, Hg and inorganic arsenic (iAs) in a complete feed for fish. The total mass fraction of six additional trace elements (Cu, Co, Fe, Mn, Se and Zn) could also be reported on a voluntary basis.

This PT was agreed with the Directorate General for Health and Food Safety (DG SANTE) as part of the EURL-HM annual work programme 2017. The PT was open to National Reference Laboratories (NRLs) and to feed Official Control Laboratories (OCLs) willing to participate.

This report summarises the outcome of the PT.

2. Scope

As stated in Regulation (EC) No 882/2004 [1] one of the core duties of EURLs is to organise interlaboratory comparisons for the benefit of NRLs.

The present PT aims to assess the performance of NRLs and OCLs in the determination of the mass fractions of total arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg) and inorganic arsenic (iAs) in a complete feed for fish. Participants were also asked to evaluate the conformity of the investigated feed according to the maximum levels (MLs) set in Directive 2002/32/EC on undesirable substances in animal feed [2].

In addition, participants were offered the possibility to report - on a voluntary basis - the total mass fractions of copper (Cu), cobalt (Co), iron (Fe), manganese (Mn), selenium (Se) and zinc (Zn), in support of Regulation (EC) No 1334/2003 amending the conditions for authorisation of a number of additives in feedingstuffs belonging to the group of trace elements [3].

The reported results were assessed following the administrative and logistic procedures of the JRC Unit in charge of the EURL-HM, which is accredited for the organisation of PTs according to ISO 17043:2010 [4].

This PT is identified as EURL-HM-25.

3. Set up of the exercise

3.1 Time frame

The organisation of the EUR-HM-25 exercise was agreed upon by the NRL network at the 11th EURL-HM Workshop held in Geel on October 5, 2016. The exercise was announced on the JRC webpage (Annex 1) and an invitation letter was sent (via e-mail) to all NRLs of the network on March 8, 2017 (Annex 2). The registration deadline was set to April 30, 2017. Samples were sent to participants on May 11-12, 2017. The dispatch was monitored by the PT coordinator using the messenger's parcel tracking system on the internet. The deadline for reporting of results was set to June 30, 2017.

3.2 Confidentiality

The procedures used for the organisation of PTs are accredited according to ISO 17043:2010 [4] and guarantee that the identity of the participants and the information provided by them is treated as confidential. However, the lab codes of the NRLs that

have been appointed in line with Regulation (EC) No 882/2004 may be disclosed to DG SANTE upon request for the purpose of an assessment of their (long-term) performance.

3.3 Distribution

Each participant received:

- One bottle of the test item (containing approx. 5 g of material);
- The "Test item accompanying letter" (Annex 3); and
- A "Confirmation of receipt form" to be sent back to JRC-Geel after receipt of the test item (Annex 4).

3.4 Instructions to participants

Detailed instructions were given to participants in the "Test item accompanying letter" mentioned above. Measurands were defined as "the mass fractions of total As, Cd, Pb, Hg and iAs (mandatory) and Co, Cu, Fe, Mn, Se and Zn (optional) in a complete feed for fish".

Participants were asked to perform two or three independent measurements, to report their calculated mean (x_i) and the associated expanded measurement uncertainty ($U(x_i)$) together with the coverage factor (k) and the analytical technique used for analysis.

Results were to be reported relative to a feed with a moisture content of 12 % in line with Directive 2002/32/EC.

Upon specific request from DG SANTE, no instructions were provided by the EURL-HM to laboratories on how to perform the moisture corrections necessary for reporting, since official control laboratories are supposed to know the proper procedure.

Participants received an individual code to access the on-line reporting interface, to report their measurement results and to complete the related questionnaire. A dedicated questionnaire was used to gather additional information related to measurements and laboratories (Annex 5).

Participants were informed that the procedure used for the analysis should resemble as closely as possible their routine procedures for this type of matrix/analytes and mass fraction levels.

The laboratory codes were given randomly and communicated to the participants by e-mail.

4. Test item

4.1 Preparation

A complete feed for fish in granulated form (25 kg) was prepared by the Italian NRL (CReAA) and kindly provided to the EURL-HM for the preparation of the test item. It consists of: fishmeal (50 m/m %), soybean protein concentrate (10 %), soybean extraction flour (15 %), corn gluten (10 %), cod liver oil, vitamins and minerals.

Upon arrival at the JRC-Geel the test material was dried and milled. The material was cryogenically milled using a Palla VM-KT vibrating mill from Humboldt-Wedag (Köln, Germany). After milling, the material was sieved over a 250 µm stainless steel sieve. About 8.5 kg of the fine fraction was collected and stored at 4 °C.

The performed panoramic analysis (screening) showed that the levels of the mandatory analytes were far below the maximum levels (MLs) set by Directive 2002/32/EC [2], except for cadmium. It was therefore decided to spike the test material with lead,

mercury and arsenic (using arsenobetaine, an organic arsenic compound naturally present in fish).

About 4.9 kg was mixed in a Dynamix CM-200 (WAB, Basel, Switzerland) for one hour and then placed in a 60 L plastic drum to which 10 L of MilliQ water was added to make a homogeneous suspension. The material was then spiked with 1 L of a solution containing Pb, Hg, and As (as arsenobetaine), and the slurry was stirred for 30 min. The resulting material was freeze dried in a Martin Christ model Epsilon 2-100D freeze dryer (Osterode, Germany). The final powder material was mixed in a Dynamix CM-200 for one hour.

Portions of 5 g were manually filled into 50 ml amber glass acid-washed bottles using acid washed plastic spoons under an extraction point. The bottles were closed with acid washed inserts and screw caps.

The final test item was analysed once again and the mass fractions obtained were below the MLs set by Directive 2002/32 EC [2]. Therefore, this material is to be considered as "compliant".

Each vial was identified with a unique number and the name of the PT exercise.

4.2 Homogeneity and stability

Measurements for the homogeneity and stability studies were performed by ALS Scandinavia AB (Luleå, Sweden) - for the mandatory analytes only (As, Cd, Hg and Pb). It was assumed that the homogeneity and stability of As and iAs are similar. No homogeneity nor stability analyses were performed for the "optional" trace elements.

Inductively coupled plasma mass spectrometry (ICP-MS) was used after microwave digestion (0.3 - 0.5 g of sample in a mixture of HNO_3/H_2O_2) to determine the mass fractions of total As, Cd, Pb and Hg.

The statistical treatment of data was performed by the EURL-HM.

Homogeneity was evaluated according to ISO 13528:2015 [5]. The test item proved to be adequately homogeneous for the investigated analytes.

The stability study confirmed that the material was stable and the uncertainty contribution due to stability was set to zero (u_{st} = 0) for all analytes.

The contribution from homogeneity (u_{hom}) to the standard uncertainty of the assigned value ($u(x_{pt})$) was calculated using SoftCRM [6]. The analytical results reported by the expert laboratories and the statistical evaluation of the homogeneity and stability studies are presented in Annex 6 and Table 1a.

5. Assigned values and corresponding uncertainties

5.1 Assigned values

The assigned values (x_{pt}) of several "mandatory" measurands (mass fractions of total As, Hg and iAs in the complete feed for fish relative to a moisture content of 12 %), were derived from the results reported by several expert laboratories, all selected on the basis of their demonstrated measurement capabilities.

The assigned values for Cd and Pb were obtained by one laboratory with demonstrated measurement capabilities applying ID-ICP-MS (JRC-Geel).

For the "optional" trace elements (Co, Cu, Mn, Fe, Se and Zn), the assigned values were derived as consensus values from results reported by the participants for each of these elements applying Algorithm A (ISO 13528:2015 – Annex C, [5]).

The following six expert laboratories analysed one or more measurands:

- ALS Scandinavia AB (Luleå, Sweden);
- CSPA - Centro de Salud Pública de Alicante (Alicante, Spain);
- SCK-CEN - Studiecentrum voor Kernenergie (Mol, Belgium);
- UBA - Umweltbundesamt GmbH (Wien, Austria);
- Institute for Chemistry, University of Graz (Graz, Austria)
- JRC-Geel, Directorate F - Health, Consumers and Reference Materials (Belgium)

The expert laboratories were asked to use the method of analysis of their choice and no further requirements were imposed regarding methodology. They were also requested to report their results together with the associated expanded measurement uncertainty and with a clear and detailed description on how their measurement uncertainty was calculated. Results were to be reported in dry mass. The EURL-HM converted afterwards these results to a feed with moisture content of 12 % as required by Directive 2002/32/EC.

- ALS Scandinavia used inductively coupled plasma mass spectrometry (ICP-MS) after closed microwave digestion using nitric acid (HNO_3), hydrogen peroxide (H_2O_2) and hydrofluoric acid (HF) in sealed Teflon containers for the determination of the total content of As and Hg. For the arsenic speciation ion chromatography was used with post-column hydride generation and detection by ICP-MS.

- CSPA used ICP-MS after microwave digestion of the sample (approx. 0.25 g in quartz digestion vessels) using HNO_3 and H_2O_2 for measuring total As. The measurement of Hg was performed by Direct Mercury Analyser (DMA). For inorganic As high performance liquid chromatography coupled with an ICP-MS was used after extraction with a microwave digestion.

- SCK-CEN applied instrumental neutron activation analysis (k_0-NAA) for the determination of total As and Hg mass fractions. Three samples of (approx. 320 mg) were transferred in standard high-density polyethylene vials and weighed. Samples were irradiated for seven hours in channel Y4 of the BR1 reactor together with several IRMM-530 (Al-0.1 % Au alloy) neutron flux monitors and three reference materials (SMELLS II, SMELS III and BCR 278) used for validation.

- UBA used ICP-MS according to ISO 17294-2 for the determination of As. The measurement of Hg was done by Cold Vapour Atomic Absorption Spectrometry (CV-AAS) according to ISO 12846, while iAs was determined using HPLC-ICP-MS according to ISO 17294-2.

- The University of Graz determined total As in about 250 mg of the sample after microwave-assisted digestion with HNO_3 by ICP-MS. For iAs, samples of about 500 mg were analysed by anion exchange HPLC-ICP-MS.

- JRC-Geel analysed total Cd, Pb and Hg by direct ID-ICP-MS applying the following experimental protocols:

  Samples (0.25 to 0.5 g) were blended with isotopically enriched certified reference materials (CRMs), as pure solutions of elements. The CRMs IRMM-622 (^{111}Cd enriched), an Inorganic Ventures isotopic standard (^{206}Pb enriched) or ERM AE640 (^{202}Hg enriched) was used.

Sample-spike blends were digested in a Milestone Ultraclave micro-wave digestion apparatus with 5 mL concentrated HNO_3 and 0.5 mL of concentrated (HF). Digests for Hg measurement were mixed with 1 mL of a 6 % potassium permanganate solution and a 20 % hydroxylamine solution was added until the solutions were colourless. For measurement, digests were further diluted in 2 % HNO_3 solution, and for Pb measurement, about 1 µg L^{-1} Tl (IRMM-649 isotopic CRM) was added.

All elements were measured on an Agilent 7500ce inductively coupled plasma mass spectrometer. For Hg, a CETAC cold-vapour generation system was used for sample introduction together with a conventional nebuliser and spray chamber to introduce a dilute IRMM 649 solution.

To correct for instrumental mass discrimination, digests of an unspiked sample were measured in sequence with samples for Cd, while for Hg and Pb the $^{203}Tl/^{205}Tl$ ratio of IRMM 649 was measured at the same time as samples. Cd and Hg were assumed to have natural isotopic composition as tabulated by IUPAC, and the isotopic composition of Pb was measured in an unspiked sample using the IRMM-649 (Tl) as reference.

5.2 Associated uncertainties

The associated standard uncertainties of the assigned values ($u(x_{pt})$) were calculated following the law of uncertainty propagation, combining the standard measurement uncertainty of the characterization (u_{char}) with the standard uncertainty contributions from homogeneity (u_{hom}) and stability (u_{st}), in compliance with ISO Guide 35 [7]:

$$u(x_{pt}) = \sqrt{u_{char}^2 + u_{hom}^2 + u_{st}^2} \qquad \text{Eq. 1}$$

The uncertainty u_{char} is estimated according to the recommendations of ISO Guide 35:

$$u_{char} = \frac{s}{\sqrt{p}} \qquad \text{Eq. 2}$$

Where "s" refers to the standard deviation of the mean values obtained by the expert laboratories and "p" refers to the number of expert laboratories.

For the "optional" trace elements, robust statistics (cf. Algorithm-A, ISO 13528:2015, [5]) was used to derive the uncertainty associated with the assigned value $u(x_{pt})$ from the results reported by the participants as follows:

$$u(x_{pt}) = 1.25 \frac{s^*}{\sqrt{n}} \qquad \text{Eq. 3}$$

Where "s^*" is the robust standard deviation, and n is the number of reporting participants.

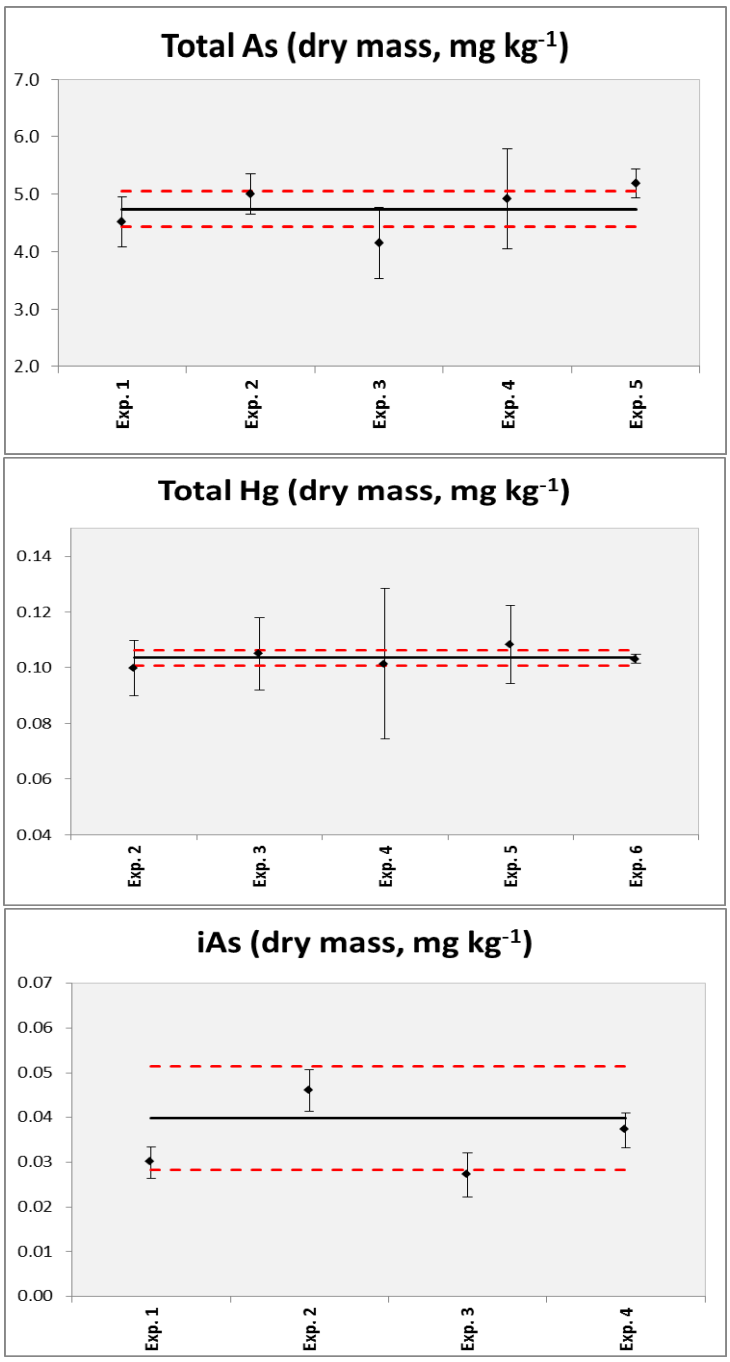

Figure 1: Assigned values for EURL-HM-25. Circles and error bars represent reported values by the retained expert laboratories ($x_i \pm 2u_i$). The solid line represents the assigned value (x_{pt}) while the dashed lines represent the assigned range ($x_{pt} \pm 2\ u(x_{pt})$)

Table 1a: Results and associated expanded measurement uncertainties for the "mandatory" contaminants; the assigned values (x_{pt}, $u(x_{pt})$ and $U(x_{pt}, k=2)$); the standard uncertainties (u_{char}, u_{hom} and u_{st});and the standard deviation for PT assessment σ_{pt}. Values are expressed in mg kg^{-1} relative to feed with a moisture content of 12 %.

	As	iAs	Cd	Pb	Hg
Expert 1	3.98 ± 0.38	0.0263 ± 0.0031			
Expert 2	4.40 ± 0.31	0.041 ± 0.0041			0.0879 ± 0.0088
Expert 3	3.65 ± 0.55	0.0239 ± 0.0044			0.0924 ± 0.0114
Expert 4	4.33 ± 0.77	0.0327 ± 0.0034			0.0892 ± 0.0238
Expert 5	4.57 ± 0.22				0.0953 ± 0.0123
Expert 6			0.4549 ± 0.0067	2.603 ± 0.026	0.0908 ± 0.0014
x_{pt}	**4.19**	**0.0309**	**0.4549**	**2.603**	**0.0911**
u_{char}	0.17	0.0037	0.0033	0.013	0.0013
u_{hom}	0.03	0.0002	0.0023	0.042	0.0017
u_{st}	0	0	0	0	0
$u(x_{pt})$	**0.17**	**0.0037**	**0.0040**	**0.044**	**0.0022**
$U(x_{pt})$	0.34	0.0074	0.0081	0.087	0.0044
σ_{pt}	**0.54**	**0.0068**	**0.0819**	**0.364**	**0.0200**
σ_{pt} (% x_{pt})	13%	22%	18%	14%	22%
$u(x_{pt})/\sigma_{pt}$	**0.3**	**0.5**	**0.1**	**0.1**	**0.1**

Table 1b: The assigned values and corresponding expanded uncertainties (x_{pt}, $U(x_{pt}, k=2)$ for the *"optional"* trace elements; and the corresponding standard deviation for PT assessment (σ_{pt}). Values are expressed in mg kg^{-1} relative to a feed with a moisture content of 12 %.

	Co	Cu	Fe	Mn	Se	Zn
x_{pt}	**0.339**	**15.3**	**289**	**37.2**	**0.952**	**93.5**
$s^* = \sigma_{pt}$	0.046	2.8	27	4.1	0.163	10.3
n	15	21	20	15	16	21
$u(x_{pt})$	**0.014**	**0.7**	**7.2**	**1.3**	**0.047**	**2.9**
$U(x_{pt})$	0.028	1.5	14	2.6	0.094	5.7
σ_{pt} (% x_{pt})	14%	18%	9%	11%	17%	11%
$u(x_{pt})/\sigma_{pt}$	**0.3**	**0.3**	**0.3**	**0.3**	**0.3**	**0.3**

5.3 Standard deviation for proficiency assessment, σ_{pt}

The relative standard deviations for PT assessment (σ_{pt}, in mg kg^{-1} and %) for the "mandatory" elements (Table 1a) were calculated using the Horwitz equation modified by Thompson [8]. For the "optional" elements (Table 1b) σ_{pt} was set equal to the robust standard deviation (s^*) according to ISO 13528 [5].

6. Evaluation of results

6.1 Scores and evaluation criteria

The individual laboratory performance was expressed in terms of z and ζ scores according to ISO 13528:2015 [5]:

$$z = \frac{x_i - x_{pt}}{\sigma_{pt}} \qquad \text{Eq. 4}$$

$$\zeta = \frac{x_i - x_{pt}}{\sqrt{u^2(x_i) + u^2(x_{pt})}} \qquad \text{Eq. 5}$$

Where: x_i is the measurement result reported by a participant;

$u(x_i)$ is the standard measurement uncertainty reported by a participant;

x_{pt} is the assigned value;

$u(x_{pt})$ is the standard measurement uncertainty of the assigned value;

σ_{pt} is the standard deviation for proficiency test assessment.

According to ISO 13528:2015 [5], when $u(x_{pt}) > 0.3\sigma_{pt}$ (as for iAs, see Table 1a) the uncertainty of the assigned value ($u(x_{pt})$) can be taken into account by expanding the denominator of the z score and calculating the z' score, as follows:

$$z'_i = \frac{x_i - x_{pt}}{\sqrt{\sigma_{pt}^2 + u^2(x_{pt})}} \qquad \text{Eq. 6}$$

The interpretation of the z (or z') and ζ performance scores is done according ISO 13528:2015 [5]:

|score| ≤ 2	satisfactory performance	(green in Annexes 7 - 18)
2 < |score| < 3	questionable performance	(yellow in Annexes 7 - 18)
|score| ≥ 3	unsatisfactory performance	(red in Annexes 7 - 18)

The z scores compare the participant's deviation from the assigned value with the standard deviation for proficiency test assessment (σ_{pt}) used as common quality criterion.

The ζ scores state whether the laboratory's result agrees with the assigned value within the respective uncertainty. The denominator is the combined uncertainty of the assigned value $u(x_{pt})$ and the measurement uncertainty as stated by the laboratory $u(x_i)$. The ζ score includes all parts of a measurement result, namely the expected value (assigned value), its measurement uncertainty in the unit of the result 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 measurement uncertainty, or both.

The standard measurement uncertainty of the laboratory $u(x_i)$ was obtained by dividing the reported expanded measurement uncertainty by the reported coverage factor, k. When no uncertainty was reported, it was set to zero ($u(x_i) = 0$). When k was not specified, the reported expanded measurement uncertainty was considered as the half-width of a rectangular distribution; $u(x_i)$ was then calculated by dividing this half-width by $\sqrt{3}$, as recommended by Eurachem [9].

Uncertainty estimation is not trivial, therefore an additional assessment was provided to each laboratory reporting measurement uncertainty, indicating how reasonable their measurement uncertainty estimation was.

The standard measurement uncertainty from the laboratory $u(x_i)$ is most likely to fall in a range between a minimum and a maximum allowed uncertainty (case a": $u_{min} \leq u_i \leq u_{max}$). u_{min} is set to the standard uncertainties of the assigned values $u(x_{pt})$. It is unlikely that a laboratory carrying out the analysis on a routine basis would determine the measurand with a smaller measurement uncertainty than the expert laboratories chosen to establish the assigned value. u_{max} is set to the standard deviation accepted for the PT assessment (σ_{pt}). Consequently, case "a" becomes: $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$.

If $u(x_i)$ is smaller than $u(x_{pt})$ (case "b") the laboratory may have underestimated its measurement uncertainty. Such a statement has to be taken with care as each laboratory reported only measurement uncertainty, whereas the measurement uncertainty associated with the assigned value also includes contributions for homogeneity and stability of the test item. If those are large, measurement uncertainties smaller than $u(x_{pt})$ are possible and plausible.

If $u(x_i)$ is larger than σ_{pt} (case "c") the laboratory may have overestimated its measurement uncertainty. An evaluation of this statement can be made when looking at the difference between the reported value and the assigned value: if the difference is smaller than the expanded uncertainty $U(x_{pt})$ then overestimation is likely. If the difference is larger but x_i agrees with x_{pt} within their respective expanded measurement uncertainties, then the measurement uncertainty is properly assessed resulting in a satisfactory performance expressed as a ζ score, though the corresponding performance, expressed as a z score, may be questionable or unsatisfactory.

It should be pointed out that "u_{max}" is a normative criterion when set by legislation.

6.2 General observations

Forty NRLs from thirty two countries registered to the exercise, representing Iceland, Norway, Serbia, and all EU Member States (except Finland). Two NRLs (L25 and L35) did not report their results due to technical problems. Six additional OCLs (from Croatia, France, Iran and The Former Yugoslav Republic of Macedonia) registered and reported their results.

For the "optional" trace elements from 15 (cf. Co, Mn) to 21 (Cu and Zn) laboratories reported results (Table 1b).

***Table 2**: Overview of the number of reported results per measurand (out of 44)*

Element	Reported Results	Comments
As	37 (84 %)	
iAs	16 (36 %)	Of which 3 "*less than*" values
Cd	43 (98 %)	No results from L44: 1 "*less than*" value
Pb	43 (98 %)	No results from L44
Hg	43 (98 %)	No results from L24

6.3 Laboratory results and scorings

6.3.1 Performances

Annexes 7 to 17 present the reported results as tables and graphs for each measurand (NRLs are presented in filled marks, while OCLs are in empty ones).

The corresponding Kernel density plots included are obtained using the software available from the Statistical Subcommittee of the Analytical Methods Committee of the UK Royal Society of Chemistry [10].

The laboratory performance for the determination of total As, Cd, Pb, Hg, Co, Cu, Fe, Mn, Se and Zn in the complete feed for fish was assessed using the z and ζ scores. However, the ISO 13528:2015 recommendation was applied for iAs (for which $u(x_{pt}) > 0.3\sigma_{pt}$, cf. Table 1b) and the z' was used as performance score instead of the z score.

Total As, Cd, Pb, Hg and iAs

Figure 2 present the laboratory performances for the five "mandatory" mass fractions investigated assessed by the z (z' for iAs) and ζ scores. Most of the participants having reported results performed satisfactorily for these measurands: 78 % and above for the z score and 74 % and above for the ζ scores. Twenty three laboratories (out of 34) performed satisfactorily for the determination of the four measurands (total As, Cd, Pb and Hg). Only 8 participants reported satisfactorily for iAs.

More than 92 % of the laboratories using ICP-MS reported results for As, Cd and Pb with satisfactory performance (expressed as z score) while only 58 % to 83 % of the results obtained by atomic absorption spectrometry (AAS) were satisfactory (see Annex 7 - 9).

For Hg the direct mercury analyser (DMA, also called elemental mercury analyser, EMA) was the most reliable technique with 100 % of satisfactory performance, followed by ICP-MS (92 %) and cold vapour-AAS (CV-AAS) (70 %).

Total Cu, Co, Fe, Mn, Se, Zn

Figure 3 presents the laboratory performances for the six "optional" mass fractions investigated assessed by the z and ζ scores. Most of the laboratories having reported results (on a voluntary basis) performed satisfactorily: 80 % and above for the z score and 72 % and above for the ζ scores.

The assigned values for these analytes were obtained as a consensus value from participant results. These values were further confirmed by the experimental results reported by the JRC-Geel and CReAA or SCK CEN applying ICP-OES, ICP-MS and k_0-NAA,

respectively (see Annexes 12-17). This enables a graphical assessment on how the assigned value compares with an independent reference value.

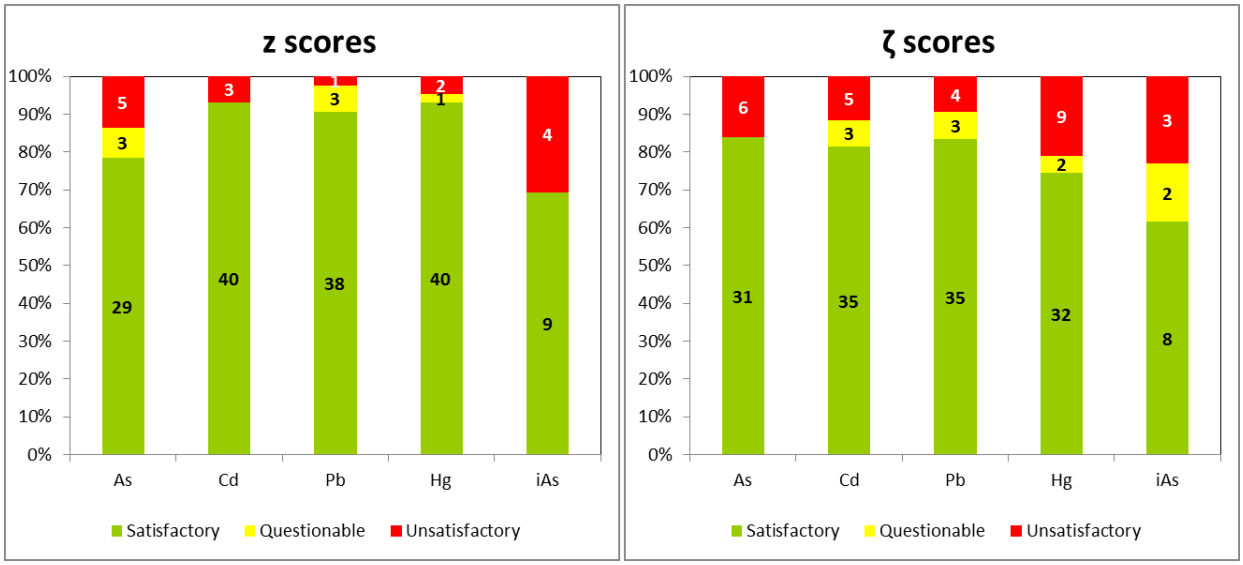

Figure 2: Overview of laboratory performance per measurand according to *z* and *ζ* scores, for As, Cd, Pb, Hg and iAs. Corresponding number of laboratories included in the graph. Satisfactory, questionable and unsatisfactory performances indicated in green, yellow and red, respectively.

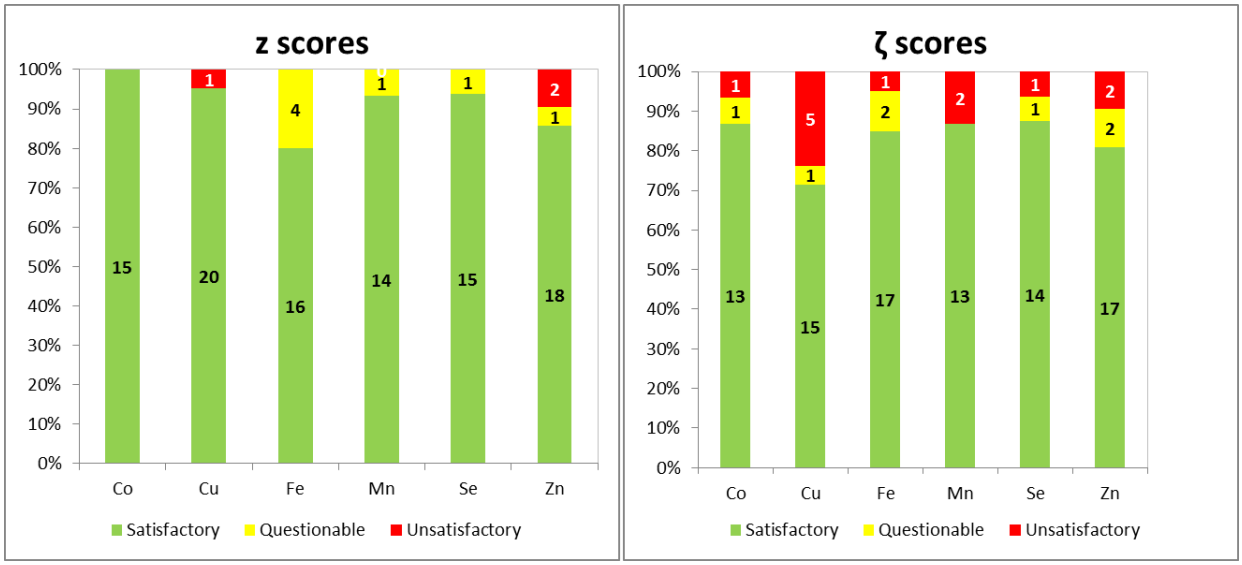

Figure 3: Overview of laboratory performance per measurand according to *z* and *ζ* scores, for Co, Cu, Fe, Mn, Se and Zn. Corresponding number of laboratories included in the graph. Satisfactory, questionable and unsatisfactory performances indicated in green, yellow and red, respectively.

6.3.2 Truncated values

Four "*less than X*" values were reported, one for Pb and three for iAs. Such values usually correspond to the limits of quantification (LOQ) or limits of detection (LOD) of the applied methods. Those reporting "*less than X*" values were not included in the data evaluation. However, reported "*less than X*" values were compared with the

corresponding x_{pt} – $U(x_{pt})$. If the reported limit value "X" is lower than the corresponding x_{pt} – $U(x_{pt})$, this statement is considered incorrect, since the laboratory should have detected the respective analyte. All the four "*less than X*" reported values in this PT exercise were correct statements.

6.3.3 Measurement uncertainties

Figure 4 presents the measurement uncertainty assessment per measurand. Most of the participants (above 79 %) reported realistic measurement uncertainty estimates for Cd, Hg, and Pb (case "a": $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$). A lower number of realistic (case "a") was obtained for total As and iAs (54 % and 46 %).

Five participants who may have underestimated their measurement uncertainties (case "b": $u_i < u(x_{pt})$) for total As, reported standard measurement uncertainties ranging from 0.125 to 0.150 mg kg^{-1} - to be compared to $u(x_{pt})$ = 0.167 mg kg^{-1}. One laboratory did not report any measurement uncertainty statement.

Similarly for iAs, three laboratories reported a standard measurement uncertainty ranging from 0.0030 to 0.0035 mg kg^{-1} – to be compared to 0.004 mg kg^{-1}.

The extremely high measurement uncertainties reported by L45 may be due to the wrong unit used (% instead of mg kg^{-1}).

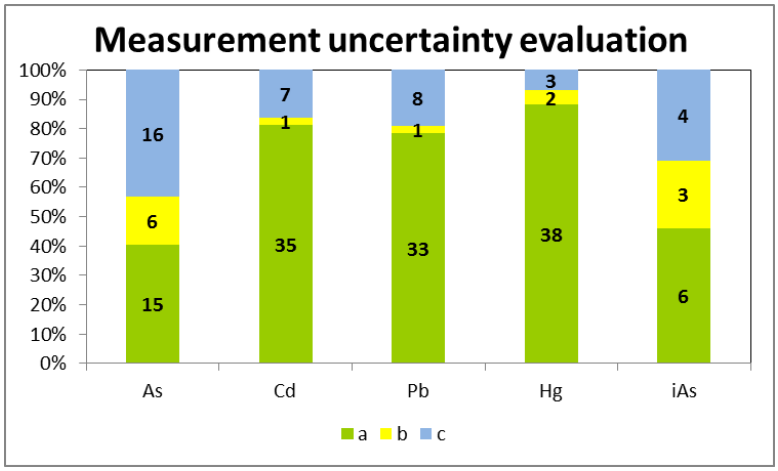

Figure 4: Review of uncertainties reported per measurand. Corresponding number of laboratories indicated in the graph. Case "a" (green): $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$; Case "b" (yellow): $u(x_i) < u(x_{pt})$; Case "c" (blue): $u(x_i) > \sigma_{pt}$

6.3.4 Compliance assessment

Directive 2002/32/EC on undesirable substances in animal feed set maximum levels (MLs) for As, Cd, Pb and Hg in complete feed for fish relative to a feed with a moisture content of 12 %. Since all the assigned expanded ranges of interest are below the MLs (Table 3), this test item is considered compliant according to this Directive.

Table 3: Maximum limits (MLs), assigned values and their associated expanded uncertainties. All values expressed in mg kg^{-1}, relative to a feed with a moisture content of 12 %.

Elements	$x_{pt} \pm U(x_{pt})$	MLs
As	4.19 ± 0.34	10
Cd	0.4549 ± 0.0081	1
Pb	2.603 ± 0.086	5
Hg	0.0911 ± 0.0044	0.2

Participants were requested to assess the compliance of the test item, and to provide proper justification supporting their statement. In order to assess the consistency of the laboratory compliance statement, the following three components have to be considered:

- the laboratory compliance statement (compliant or non-compliant);
- the laboratory measurement results:
  - reported (or not) for the relevant analyte;
  - to be compared to the relevant ML: x_i - U_i > ML? (selecting the correct feed matrix (product intendent for animal feed));
- the laboratory justification (correct or incorrect).

Thirty eight laboratories (out of 41 participants having made a compliance assessment), assessed correctly the test item to be compliant according to Directive 2002/32/EC. Only two laboratories (L06 and L18) correctly stated that the selenium content in the feed was above the ML set in Regulation 1831/2003/EC and considered the test item as non-compliant.

L08 and L26 did not compare their accurate results to the proper ML, but selected instead MLs set for "complete feed (other than fish)" or "complementary feed".

Finally, L09 erroneously assessed the test item as non-compliant, while the results reported for As and Hg were below their respective MLs.

6.3.5 Additional information extracted from the questionnaire

The questionnaire was answered by all except one participants giving valuable information on the laboratories, their way of working and their analytical methods.

Several approaches were used to estimate measurement uncertainties (Table 4). Most of the laboratories derived their uncertainty estimates from their single-laboratory validation study. The majority of the NRLs (31 out of 40) routinely report uncertainties for this type of analysis to their customers.

Table 4: Overview of the approaches used to estimate measurement uncertainties (multiple selections were possible).

Approach	N° of labs
According to ISO-GUM	9
From known uncertainty of a standard method	3
Derived from a single-laboratory validation study	23
Determined as standard deviation of replicate measurements	8
Estimation based on judgment	3
Derived from interlaboratory comparison data	6

The recovery factor was mostly determined by using a (certified) reference material (57 %) or by spiking (36 %) a known amount of the same analyte.

The majority of the participants stated that they have an ISO/IEC 17025 accreditation and confirmed that they are accredited for one or more of the investigated measurands in feed.

It appears that the experience in this type of analysis (evaluated as number of analyses per year) does not support the observed performances: the majority of the participants with unsatisfactory performance claim to analyse 50 to 249 similar samples per year.

Annex 18 summarises the experimental details, the technique used and the limits of detection (LOD) for the determination of total As, Cd, Pb, Hg and iAs. Large discrepancies in reported LODs are observed even among laboratories using the same technique.

7. Conclusion

The EURL-HM-25 PT was organised in 2017 to assess the analytical capabilities of the EU NRLs and OCLs on the determination of the mass fractions of total As, Cd, Pb, Hg and iAs in a complete feed for fish. Participants were allowed to report on a voluntary basis results for six additional trace elements (Co, Cu, Fe, Mn, Se and Zn).

The overall performance of the participants in the determination of total As, Cd, Pb and Hg was satisfactory. This confirms the analytical capabilities of the NRLs to enforce the European Directive 2002/32/EC setting levels for these particular undesirable substances in feed. However, only 8 laboratories reported satisfactory results for iAs.

Most of the participants (93 %) correctly assessed the test item to be compliant according to Directive 2002/32/EC. The remaining three laboratories based their conclusion on wrongly selected MLs.

The reasonable measurement uncertainty estimates reported by the NRLs demonstrate the effectiveness of the various PTs and training courses organised by the EURL-HM in the past 10 years. However, improvements are expected from the participating OCLs.

Acknowledgements

The EURL-HM wishes to thank the Italian NRL (CReAA) for providing the complete feed for fish granulates later processed and used as test item for this proficiency test.

The authors wish to thank colleagues from the JRC-Geel site for their valuable contributions during the preparation of the proficiency test item.

The forty six laboratories listed hereafter are kindly acknowledged for their participation in the PT.

Organisation	Country
AGES GmbH	AUSTRIA
CODA-CERVA	BELGIUM
Central Laboratory for Chemical Testing and Control (CLCTC)	BULGARIA
Central Laboratory of Veterinary Control and Ecology	BULGARIA
EUROINSPEKT CROATIAKONTROLA d.o.o.	CROATIA
Croatian Institute of Public Health	CROATIA
Croatian Veterinary Institute	CROATIA
Inspecto laboratorij d.o.o.	CROATIA
Analytical Laboratories Section	CYPRUS
Central Institute for Supervising and Testing in Agriculture (UKZUZ)	CZECH REPUBLIC
State Veterinary Institute Olomouc	CZECH REPUBLIC
Danish Veterinary and Food Administration	DENMARK
National Food Institute (DTU Food)	DENMARK
Agricultural Research Centre	ESTONIA
Laboratoire SCL de Bordeaux	FRANCE
Service Commun des Laboratoires DGDDI+DGCCRF	FRANCE
INOVALYS	FRANCE
LABOCEA	FRANCE
Federal Office of Consumer Protection and Food Safety	GERMANY
Regional Center of Plant Protection and Quality Control of Magnissia	GREECE
National Food Chain Safety Office	HUNGARY
National Food Chain Office Food and Feed Safety	HUNGARY
Matis	ICELAND
Office of Vice Chancellor for Food and Drugs, TUMS	IRAN
The State Laboratory	IRELAND
Istituto Zooprofilattico Sperimentale del Piemonte, Liguria e Valle D'Aosta	ITALY
Istituto Superiore Sanità	ITALY
Institute of Food Safety, Animal Health and Environment	LATVIA
National Food and Veterinary Risk Assessment Institute	LITHUANIA
Laboratoire National de Santé	LUXEMBOURG
Environmental Health Directorate	MALTA
RIKILT WUR	NETHERLANDS
ALcontrol Stjørdal	NORWAY
NIFES	NORWAY
National Veterinary Institute	POLAND
Instituto Nacional de Investigação Agrária e Veterinária	PORTUGAL
Portuguese Institute of Sea and Atmosphere (IPMA)	PORTUGAL
Hygiene and Vetyerinary Public Health Institute	ROMANIA
SP Laboratorija A.D.	SERBIA
Veterinary and Food Institute in Košice	SLOVAKIA
NLZOH	SLOVENIA
National Veterinary Institute	SLOVENIA
Laboratorio Arbitral Agroalimentario (MAPAMA)	SPAIN
National Food Agency	SWEDEN
Faculty of Veterinary Medicine-Skopje	The former Yugoslav Republic of Macedonia
Fera	UNITED KINGDOM

References

[1] Commission Regulation, (EC) No 882/2004 of the European Parliament and of the Council of 29 April 2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules, Off. J. Eur. Union. L165/1 (2004).

[2] European Commission, Directive 2002/32/EC of The European Parliament and of The Council of 7 May 2002 on undesirable substances in animal feed, Off. J. Eur. Communities. L 140 (2002).

[3] Commission Regulation (EC) No 1334/2003 amending the conditions for authorisation of a number of additives in feedingstuffs belonging to the group of trace elements, Off. J. Eur. Communities L187 (2003).

[4] ISO/IEC 17043 *"Conformity assessment – General requirements for proficiency testing"*, issued by ISO-Geneva (CH), International Organisation for Standardization, 2010.

[5] ISO 13528:2015 *"Statistical methods for use in proficiency testing by interlaboratory comparisons"*, issued by ISO-Geneva (CH), International Organisation for Standardization, 2015.

[6] SoftCRM, (n.d.). http://www.eie.gr/iopc/softcrm/index.html.

[7] ISO Guide 35 *"Reference materials - General and statistical principles for certification"*, issued by ISO-Geneva (CH), International Organisation for Standardization, 2006.

[8] M. Thompson, *"Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing"*, Analyst. 125 (2000) 385–386. doi:10.1039/B000282H.

[9] Eurachem/Citac, *"Quantifying Uncertainty in Analytical Measurement"*, 2012. http://www.eurachem.org.

[10] Analytical Methods Committee, *"Representing data distributions with kernel density estimates"*, AMC Tech. Br. 4 (2006) 2. http://www.rsc.org/images/brief4_tcm18-25925.pdf.

Annex 1: JRC web announcement

EU SCIENCE HUB

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- **Training**

EURL-HM-25

Description:
Determination of the mass fractions of total As, Cd, Pb, Hg and iAs in complete feed for fish

Status:	Registration Open
Year:	2017
Type:	Proficiency Test
Participation:	Restricted
Contact:	JRC-EURL-HEAVY-METALS@ec.europa.eu
IL category:	IMEP

The EURL-HM-25 proficiency test (PT) focuses on the determination of the mass fractions of total arsenic, cadmium, lead, mercury and inorganic arsenic in complete feed for fish. This PT is organised in support to Directive 2002/32/EC on undesirable substances in animal feed.

The main objective of this exercise is to assess the analytical capabilities of nominated National Reference Laboratories (NRLs) in the determination of the specific trace elements in complete feed for fish.

Participation in EURL-HM-25 is open to NRLs and obligatory for those having mandate for this type of analysis. Participation in EURL-HM-25 is also open to appointed Official Control Laboratories (OCLs) in the field of feed compliance.

Participation is free of charge.

Test materials and analytes

The test material to be analysed is a complete feed for fish. Each participant will receive one test item. The measurands are the mass fractions of total As, Cd, Pb, Hg and iAs in complete feed for fish.

General outline of the exercise

Participants are requested to perform one to three independent analyses using the method of their choice, and to report the mean of their measurement results, the associated expanded measurement uncertainty and coverage factor *k*.

Detailed instructions will be sent together with the test item.

Registration URL:	https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?sel...
Registration deadline:	Sunday, 30 April, 2017
Sample dispatch:	May 2017
Reporting of results:	Deadline 30/06/2017
Report to participants:	November 2017
Keywords:	food/feed
Reference laboratories:	EURL for heavy metals in feed and food

Annex 2: Invitation letter

EUROPEAN COMMISSION
Joint Research Centre
Directorate F – Health, Consumers & Reference Materials
European Union Reference Laboratory for Heavy Metals

Geel, 31 January 2017
Ares(2017) xxxxxxx

(sent by e-mail)

Subject: Invitation to participate in EURL-HM-25

Dear National Reference Laboratory representative,

The EURL-HM would like to invite you to participate in the proficiency test EURL-HM-25 for the **"Determination of the mass fractions of total As, Cd, Pb, Hg and iAs in complete feed for fish"**.

According to Regulation (EC) No 882/2004 it is your duty as NRL to participate in PTs organised by the EURL-HM if you hold a mandate for this type of matrix.

Your participation is free of charge.

Please register using the following link:

https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparison=1701

Once you submitted your registration online, check carefully the generated registration form. In case of identified mistakes please contact the ILC coordinator as soon as possible before the registration deadline.

The deadline for registration is **March 31, 2017**.

Samples will be sent to participants during the **second half of April 2017**.

The deadline for submission of results is **June 30, 2017**.

Do not hesitate to contact us, in case of questions/doubts,

Yours sincerely

/signed electronically in Ares/

Dr. Fernando Cordeiro
EURL-HM-25 Coordinator

/signed electronically in Ares/

Dr. Piotr Robouch
Operating Manager EURL-HM

Cc: Hendrik Emons (Head of Unit, Food & Feed Compliance, F.5)

Retieseweg 111, B-2440 Geel - Belgium.
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 1980
jrc-eurl-heavy-metals@ec.europa.eu
https://ec.europa.eu/jrc/en/eurl/heavy-metals

Annex 3: Test item accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Directorate F – Health, Consumers and Reference Materials
European Union Reference Laboratory for Heavy Metals

Geel, 10 May 2017
Ares(2017)2273549

«Title» «Firstname» «Surname»
«Organisation»
«Department»
«Address»
«Address2»
«Zip» «Town»
«Country»

Subject: Participation in EURL-HM-25

Dear «Title» «Surname»,

Thank you for participating in the EURL-HM-25 proficiency test**.** This PT is organised in support to DIR 2002/32/EC on undesirable substances in animal feed.

The parcel you received contains, in addition to this letter:

- one vial of the test item (approx. 5 g); and
- the "Confirmation of receipt" form.

Please keep this letter. You will need it to report your results.

Upon arrival of this parcel, please check whether the test item is undamaged after transport, and send us by fax or email the "Confirmation of receipt" form.

Store the samples until analysis in a dark place at +4°C (fridge).

The mandatory measurands are **the mass fraction of total As, Cd, Pb, Hg and iAs in complete feed for fish.**

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

Determine the moisture content and correct the measurement results for moisture content as prescribed in DIR 2002/32/EC.

Perform two or three independent measurements and report:

- the result for the **moisture content** determination (in % w/w),
- the **mean** of your two or three measurements results (in mg kg^{-1}),
- the associated expanded **uncertainty** (in mg kg^{-1}),
- the **coverage factor,** and
- the **analytical technique** used.

Retieseweg 111, B-2440 Geel - Belgium. Tel: +32 14 571 374. https://ec.europa.eu/jrc/en/eurl/heavy-metals.
E-mail: jrc-eurl-heavy-metals@ec.europa.eu

The results should be reported in the same form (e.g. number of significant figures) as you normally report to customers.

The reporting website is https://web.jrc.ec.europa.eu/ilcReportingWeb

To access the webpage you need the following personal password key: **«Part_key»**.

The system will guide you through the reporting procedure. Then complete the corresponding questionnaire. **Do not forget to submit and confirm when required.**

You may be interested to perform on a voluntary basis **additional analysis** to determine the **mass fraction of total Co, Cu, Fe, Mn, Se and Zn in complete feed for fish**. The corresponding assigned values will be derived as "consensus" value from results reported by participants.

Directly after submitting your results and the questionnaire information online, you will be requested to print the completed report form.

Please check carefully your report. In the case mistakes are detected contact the PT coordinator as soon as possible before the reporting deadline.

The deadline for submission of results is **30/06/2017**.

Remember 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.

Your participation in this project is greatly appreciated.

Do not hesitate to contact me for further information.

With kind regards,

/signed electronically in Ares/

Dr. Fernando Cordeiro
EURL-HM-25 Coordinator

Cc: H. Emons (Head of Unit, Food & Feed Compliance unit)
P. Robouch (Operating Manager EURL-HM)

Annex 4: Confirmation of receipt form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Directorate F – Health, Consumers and Reference Materials
European Union Reference Laboratory for Heavy Metals

Geel, 10 May 2017
Ares(2017)2273549

Attn.: «Title» «Firstname» «Surname»
«Organisation»
«Department»
«Country»

Subject: "Confirmation receipt" form
EURL-HM-25 – Heavy metals in complete feed for fish

Please return this form at your earliest convenience, to confirm that the package arrived well. If samples are damaged, mention it under "Remarks" and contact us as soon as possible.

Date of package arrival _____

Remarks _____

_____

Signature _____

Thank you for returning this form by email to:

Dr. F. Cordeiro
EURL-HM-25 Coordinator
e-mail : jrc-eurl-heavy-metals@ec.europa.eu

Retieseweg 111, B-2440 Geel – Belgium Tel.: +32 14 57 12 11. Direct line: +32 14 57 16 87.
https://ec.europa.eu/jrc/en/eurl/heavy-metals; E-mail: jrc-eurl-heavy-metals@ec.europa.eu

Annex 5: Questionnaire

Milc questionnaire

Comparison for EURL-HM-25

Please fill the questionnaire. These answers are used by the PT provider to identify the reasons for the differences in performance among the participants and to provide recommendations for improvement (ISO 17043 Ch. 4.8).

Submission Form

1. **Are you a National Reference Laboratory (NRL)?**

- ○ a) Yes
- ○ b) No

1.1. If "No" have you been nominated by your National Accreditation Body (NAB) or by your NRL?

- ○ a) Yes
- ○ b) No

1.1.1. If "Yes" please identify your NAB or NRL.

2. **Test item compliant with European legislation (Directive 2002/32/EC)?**

- ○ a) Test item compliant
- ○ b) Test item Not compliant

2.1. If not compliant specify why

3. **Are you accredited for this type of matrix/analyte?**

Questions/ Response table	As	Cd	Hg	Pb	iAs	Info
Accredited for:	☐	☐	☐	☐	☐	

4. **Did you follow a standard method of analysis? (if "Yes" specify)**

See table **Standard method** at bottom

5. **Provide the analytical recovery (in %) and the LoD**

See table **Recovery & LoD** at bottom

6. **How did you estimate the recovery?**

- ☐ a) Spiking
- ☐ b) Using a CRM
- ☐ c) Other

6.1. If "Other" please specify

7. **Did you use a CRM for method validation or for instrument calibration? Which one?**

See table **CRM** at bottom

8. **Does your laboratory carry out this type of analysis on a regular basis? (samples /year)**

Questions/ Response table	1) 0-50	2) 50-250	3) 250-1000	4) > 1000	Never	Info
As	○	○	○	○	○	

Questions/ Response table	1) 0-50	2) 50-250	3) 250-1000	4) > 1000	Never	Info
Cd	○	○	○	○	○	
iAs	○	○	○	○	○	
Pb	○	○	○	○	○	
Hg	○	○	○	○	○	

9. **Which type of digestion type, digestion mixture, time and temperature did you use?**

See table **Digestion type/mixture, time and temperature:** at bottom

10. **Did you correct for the moisture content of the test sample?**

- ○ a) Yes
- ○ b) No

10.1. If "Yes" what was the moisture content of the sample (in % of the sample mass)

10.2. If "No" what was the reason for not having done this correction?

11. **What was the basis of your measurement uncertainty evaluation?**

- ☐ a) Uncertainty budget (ISO GUM)
- ☐ b) Known uncertainty of standard method (ISO 21748)
- ☐ c) From in-house method validation
- ☐ d) Measurement of replicates (precision)
- ☐ e) Evaluation based on judgment
- ☐ f) From interlaboratory comparison

- ☐ g) Other

12. **Do you usually provide an uncertainty statement to your customers?**

- ○ a) Yes
- ○ b) No

13. **Does your laboratory have a quality management system?**

- ○ a) Yes
- ○ b) No

13.1. If "Yes" based on which standard?

- ☐ a) ISO 17025
- ☐ b) ISO 9001
- ☐ c) Other

13.2. If "No" please specify:

14. **Does your laboratory participate in interlaboratory comparisons for this type of analysis?**

- ○ a) Yes
- ○ b) No

15. **Do you have any comments? Let us know!**

CRM

Questions/Response table	*As*	*Cd*	*Pb*	*Hg*	*iAs*
Validation of measurement procedure					
Instrument calibration					

Digestion type/mixture, time and temperature:

Questions/Response table	*As*	*Cd*	*Pb*	*Hg*	*iAs*
Digestion type					
Digestion mixture					
Digestion time (min)					
Digestion temperature (C)					

Recovery & LoD

Questions/Response table	*As*	*Cd*	*Pb*	*Hg*	*iAs*
Recovery (%)					
LoD (mg/kg)					

Standard method

Questions/Response table	*Standard method (yes / No)*	*Standard method (identification)*
As		
Cd		
Pb		
Hg		
iAs		

Annex 6: Homogeneity and stability results

6.1 Homogeneity study (all values in mg kg^{-1})

	As		Cd		Pb		Hg	
Bottle ID	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2
1	4.86	4.80	0.523	0.529	2.79	2.78	0.0918	0.0945
2	4.59	4.54	0.525	0.527	2.75	2.69	0.0970	0.0938
3	4.93	4.51	0.534	0.530	2.74	2.91	0.0960	0.0954
4	4.57	5.02	0.532	0.537	2.77	3.02	0.0923	0.1080
5	4.87	4.90	0.539	0.524	2.80	2.99	0.0972	0.0956
6	4.70	4.55	0.537	0.534	2.86	2.84	0.0955	0.0937
7	4.72	4.86	0.527	0.525	2.69	2.83	0.0924	0.0948
8	4.99	4.86	0.543	0.529	2.70	2.82	0.0940	0.0934
9	4.86	4.85	0.525	0.523	2.70	2.76	0.0903	0.0912
10	4.70	4.84	0.532	0.531	2.74	2.82	0.0933	0.0950
Mean	4.776		0.530		2.80		0.0948	
$\boldsymbol{\sigma_{pt}}$	0.540		0.082		0.361		0.0200	
$0.3*\sigma_{pt}$	0.162		0.0246		0.1083		0.006	
s_x	0.113		0.004		0.064		0.002	
s_w	0.152		0.005		0.094		0.004	
$\boldsymbol{s_s}$	0.033		0.003		0		0	
$\boldsymbol{s_s \leq 0.3*\sigma_{pt}}$	passed		passed		passed		passed	

Where: σ_{pt} is the standard deviation for the PT assessment,
s_x is the standard deviation of the sample averages,
s_w is the within-sample standard deviation,
s_s is the between-sample standard deviation,

6.2 Stability study (at 18 °C, time in weeks (w), all values in mg kg^{-1})

Time	0 w	3 w	5 w	8 w	Slope significance [a]	Assessment
As	4.71	4.88	4.30	4.82	No	Stable
	4.65	4.70	4.65	4.82		
Cd	0.510	0.521	0.529	0.527	No	Stable
	0.517	0.524	0.514	0.525		
Pb	2.83	2.81	2.77	2.73	No	Stable
	2.82	2.87	2.85	2.81		
Hg	0.0943	0.0903	0.0932	0.0936	No	Stable
	0.0965	0.0970	0.0943	0.0951		

[a] Slope of the linear regression significantly different from "0" at a 95 % level

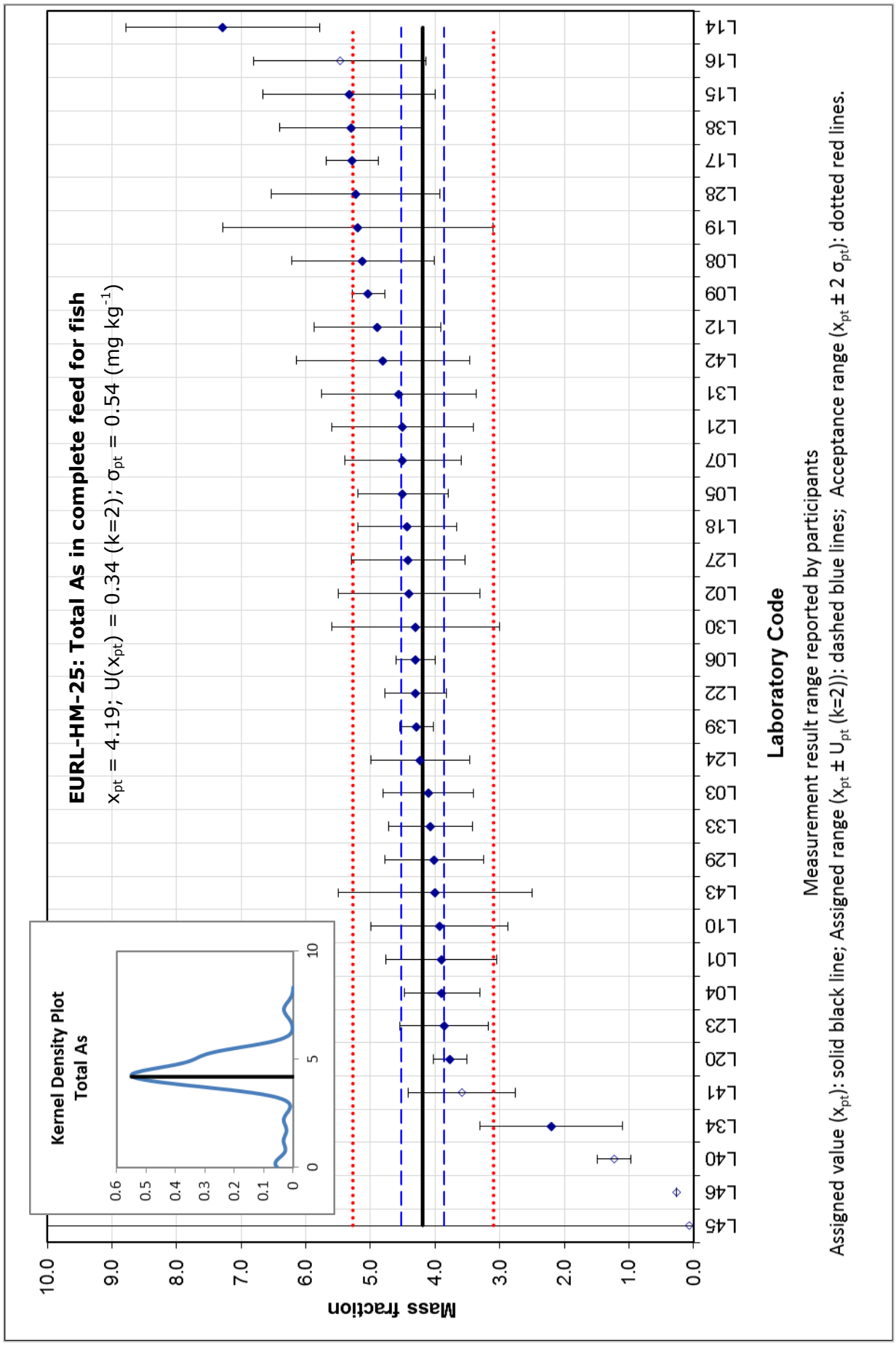
Annex 7: Results for arsenic (As)

Assigned range: x_{pt} = 4.19; $U(x_{pt})$ (k = 2.0) = 0.34; σ_{pt} = 0.54 (all values in mg kg^{-1})

Lab	x_i	U_i	k	u_i	Technique	z score [a]	ζ score [a]	Unc [b]
L01	3.9	0.86	2	0.43	AAS	-0.53	-0.63	a
L02	4.4	1.1	2	0.55	ICP-MS	0.39	0.37	c
L03	4.1	0.7	2	0.35	ICP-MS	-0.17	-0.23	a
L04	3.89	0.58	2	0.29	ICP-MS	-0.55	-0.90	a
L05	4.5	0.7	2	0.35	ICP-MS	0.57	0.80	a
L06	4.3	0.3	2	0.15	ICP-MS	0.20	0.49	b
L07	4.5	0.9	2	0.45	ICP-MS	0.57	0.65	a
L08	5.116	1.099	2	0.5495	ICP-MS	1.70	1.61	c
L09	5.03	0.25	2	0.125	ICP-MS	1.54	**4.03**	b
L10	3.93	1.06	2	0.53	ICP-MS	-0.48	-0.47	a
L12	4.89	0.979	2	0.4895	ICP-MS	1.29	1.35	a
L14	7.29	1.5	2	0.75	ICP-MS	**5.69**	**4.03**	c
L15	5.328	1.332	2	0.666	ICP-MS	**2.09**	1.66	c
L16	5.471	1.335	2	0.6675	AAS	**2.35**	1.86	c
L17	5.28	0.4	2	0.2	HG-GFAAS	2.00	**4.18**	a
L18	4.43	0.76	2	0.38	ICP-MS	0.44	0.58	a
L19	5.2	2.09	2	1.045	ICP-MS	1.85	0.95	c
L20	3.77	0.26	2	0.13	ICP-MS	-0.77	-1.98	b
L21	4.5	1.1	2	0.55	ICP-MS	0.57	0.54	c
L22	4.297	0.473	2	0.2365	ICP-MS	0.20	0.37	a
L23	3.86	0.69	2	0.345	AAS	-0.61	-0.86	a
L24	4.23	0.76	2	0.38	HG-AAS	0.07	0.10	a
L27	4.42	0.88	2	0.44	ICP-MS	0.42	0.49	a
L28	5.23	1.31	2	0.655	ICP-MS	1.91	1.54	c
L29	4.019	0.76361	2	0.38181	ICP-MS	-0.31	-0.41	a
L30	4.3	1.3	2	0.65	ICP-MS	0.20	0.16	c
L31	4.557	1.2	2	0.6	ICP-MS	0.67	0.59	c
L33	4.07	0.651	2	0.3255	ICP-MS	-0.22	-0.33	a
L34	2.2	1.1	2	0.55	ET-AAS	**-3.65**	**-3.46**	c
L38	5.3	1.1	2	0.55	ICP-MS	**2.04**	1.93	c
L39	4.284	0.26	2	0.13	ICP-MS	0.17	0.44	b
L40	1.23	0.262	2	0.131	ET-AAS	**-5.43**	**-13.95**	b
L41	3.587	0.825	1	0.825	HG-AAS	-1.11	-0.72	c
L42	4.805	1.338	2	0.669	HG-AAS	1.13	0.89	c
L43	4	1.5	2	0.75	HG-AAS	-0.35	-0.25	c
L45	0.069	**41**	2	20.5	HG-AAS	**-7.57**	-0.20	c
L46	0.2647			0	AAS	**-7.21**	**-23.50**	b

[a] performance: satisfactory, questionable, unsatisfactory,

[b] a : $u_{min}(u(x_{pt})) \leq u_i \leq u_{max}(\sigma_{pt})$; b : $u_i < u(x_{pt})$; and c : $u_i > \sigma_{pt}$


EURL-HM-25: Total As in complete feed for fish
x_{pt} = 4.19; U(x_{pt}) = 0.34 (k=2); σ_{pt} = 0.54 (mg kg^{-1})
Kernel Density Plot
Total As
Mass fraction
Laboratory Code
Measurement result range reported by participants
Assigned value (x_{pt}): solid black line; Assigned range ($x_{pt} \pm U_{pt}$ (k=2)): dashed blue lines; Acceptance range ($x_{pt} \pm 2\ \sigma_{pt}$): dotted red lines.

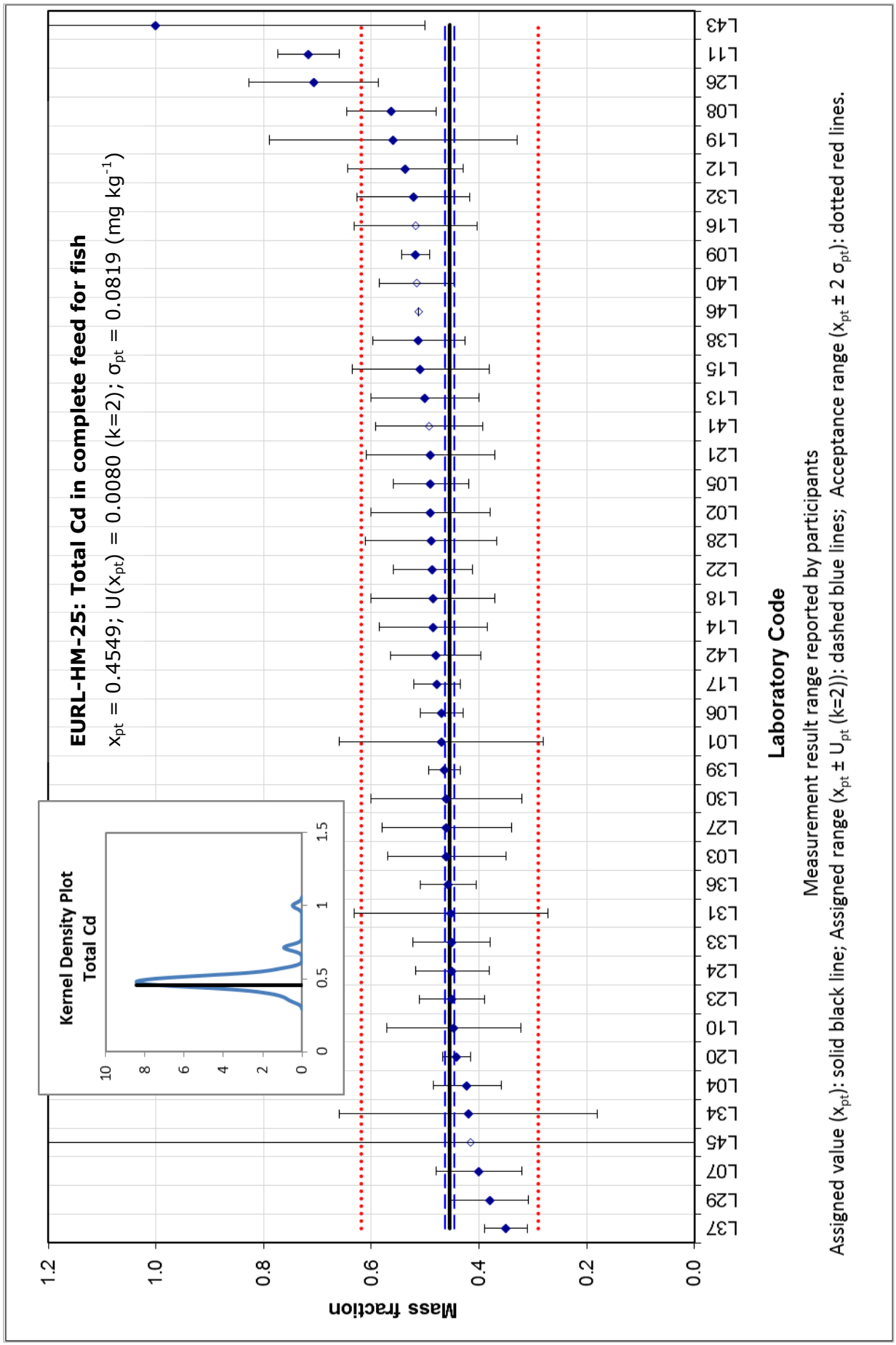
Annex 8: Results for cadmium (Cd)

Assigned range: x_{pt} = 0.4549; $U(x_{pt})$ (k = 2.0) = 0.0080; σ_{pt} = 0.0819 (all values in mg kg^{-1})

Lab	x_i	U_i	k	u_i	Technique	z score [a]	ζ score [a]	Unc [b]
L01	0.47	0.19	2	0.095	AAS	0.18	0.16	c
L02	0.49	0.11	2	0.055	ICP-MS	0.43	0.64	a
L03	0.46	0.11	2	0.055	ICP-MS	0.06	0.09	a
L04	0.422	0.063	2	0.0315	ICP-MS	-0.40	-1.04	a
L05	0.49	0.07	2	0.035	ICP-MS	0.43	1.00	a
L06	0.47	0.04	2	0.02	ICP-MS	0.18	0.74	a
L07	0.4	0.08	2	0.04	ICP-MS	-0.67	-1.37	a
L08	0.562	0.083	2	0.0415	ICP-MS	1.31	**2.57**	a
L09	0.518	0.026	2	0.013	ICP-MS	0.77	**4.64**	a
L10	0.447	0.125	2	0.0625	ICP-MS	-0.10	-0.13	a
L11	0.717	0.057	2	0.0285	ET-AAS	**3.20**	**9.11**	a
L12	0.537	0.107	2	0.0535	ICP-MS	1.00	1.53	a
L13	0.5	0.1	2	0.05	ET-AAS	0.55	0.90	a
L14	0.485	0.1	2	0.05	ICP-MS	0.37	0.60	a
L15	0.509	0.127	2	0.0635	ICP-MS	0.66	0.85	a
L16	0.518	0.114	2	0.057	AAS	0.77	1.10	a
L17	0.478	0.043	2	0.0215	ET-AAS	0.28	1.06	a
L18	0.485	0.115	2	0.0575	ICP-MS	0.37	0.52	a
L19	0.56	0.23	2	0.115	ICP-MS	1.28	0.91	c
L20	0.442	0.026	2	0.013	ICP-MS	-0.16	-0.95	a
L21	0.49	0.12	2	0.06	ICP-MS	0.43	0.58	a
L22	0.486	0.073	2	0.0365	ICP-MS	0.38	0.85	a
L23	0.45	0.061	2	0.0305	AAS	-0.06	-0.16	a
L24	0.45	0.068	2	0.034	AAS	-0.06	-0.14	a
L26	0.707	0.12	2	0.06	ET-AAS	**3.08**	**4.19**	a
L27	0.46	0.12	2	0.06	ICP-MS	0.06	0.08	a
L28	0.489	0.122	2	0.061	ICP-MS	0.42	0.56	a
L29	0.38	0.0722	2	0.0361	ICP-MS	-0.91	**-2.06**	a
L30	0.46	0.14	2	0.07	ICP-MS	0.06	0.07	a
L31	0.452	0.18	2	0.09	ICP-MS	-0.04	-0.03	c
L32	0.522	0.104	2	0.052	AAS	0.82	1.29	a
L33	0.451	0.072	2	0.036	ICP-MS	-0.05	-0.11	a
L34	0.42	0.24	2	0.12	ET-AAS	-0.43	-0.29	c
L36	0.457	0.052	2	0.026	AAS	0.03	0.08	a
L37	0.35	0.04	2	0.02	ET-AAS	-1.28	**-5.14**	a
L38	0.512	0.086	2	0.043	ICP-MS	0.70	1.32	a
L39	0.464	0.03	2	0.015	ICP-MS	0.11	0.59	a
L40	0.516	0.07	2	0.035	ET-AAS	0.75	1.73	a
L41	0.493	0.099	1	0.099	ET-AAS	0.47	0.38	c
L42	0.48	0.084	2	0.042	ET-AAS	0.31	0.59	a
L43	1	0.5	2	0.25	ET-AAS	**6.66**	**2.18**	c
L45	0.416	**60**	2	30	AAS	-0.48	0.00	c
L46	0.5123			0	AAS	0.70	**14.35**	b

[a] performance: satisfactory, questionable, unsatisfactory,

[b] a : $u_{min}(u(x_{pt})) \leq u_i \leq u_{max}(\sigma_{pt})$; b : $u_i < u(x_{pt})$; and c : $u_i > \sigma_{pt}$


EURL-HM-25: Total Cd in complete feed for fish
x_{pt} = 0.4549; U(x_{pt}) = 0.0080 (k=2); σ_{pt} = 0.0819 (mg kg^{-1})
Kernel Density Plot
Total Cd
Mass fraction
Laboratory Code
Measurement result range reported by participants
Assigned value (x_{pt}): solid black line; Assigned range ($x_{pt} \pm U_{pt}$ (k=2)): dashed blue lines; Acceptance range ($x_{pt} \pm 2\ \sigma_{pt}$): dotted red lines.

Annex 9: Results for lead (Pb)

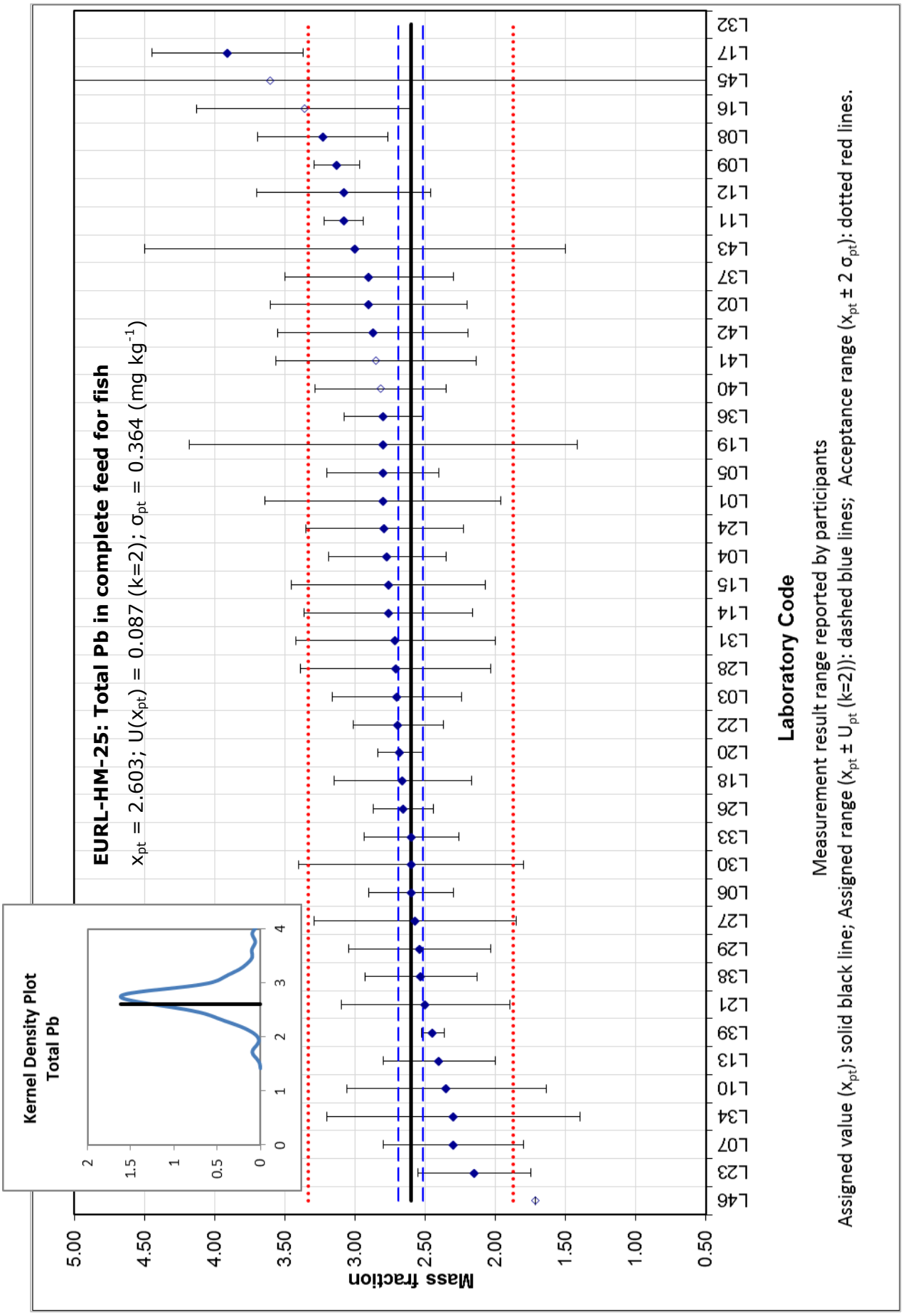
Assigned range: x_{pt} = 2.603; $U(x_{pt})$ ($k = 2.0$) = 0.087; σ_{pt} = 0.364 (all values in mg kg^{-1})

Lab	x_i	U_i	k [a]	u_i	Technique	z score [b]	ζ score [b]	Unc [c]
L01	2.8	0.84	2	0.42	AAS	0.54	0.47	c
L02	2.9	0.7	2	0.35	ICP-MS	0.81	0.84	a
L03	2.7	0.46	2	0.23	ICP-MS	0.27	0.41	a
L04	2.77	0.42	2	0.21	ICP-MS	0.46	0.78	a
L05	2.8	0.4	2	0.2	ICP-MS	0.54	0.96	a
L06	2.6	0.3	2	0.15	ICP-MS	-0.01	-0.02	a
L07	2.3	0.5	2	0.25	ICP-MS	-0.83	-1.19	a
L08	3.229	0.465	2	0.2325	ICP-MS	1.72	**2.65**	a
L09	3.13	0.16	2	0.08	ICP-MS	1.45	**5.80**	a
L10	2.35	0.71	2	0.355	ICP-MS	-0.69	-0.71	a
L11	3.08	0.14	2	0.07	ET-AAS	1.31	**5.81**	a
L12	3.08	0.617	2	0.3085	ICP-MS	1.31	1.53	a
L13	2.4	0.4	2	0.2	ET-AAS	-0.56	-0.99	a
L14	2.76	0.6	2	0.3	ICP-MS	0.43	0.52	a
L15	2.762	0.691	2	0.3455	ICP-MS	0.44	0.46	a
L16	3.36	0.769	2	0.3845	AAS	**2.08**	1.96	c
L17	3.909	0.539	2	0.2695	ET-AAS	**3.58**	**4.79**	a
L18	2.66	0.49	2	0.245	ICP-MS	0.16	0.23	a
L19	2.8	1.38	2	0.69	ICP-MS	0.54	0.28	c
L20	2.68	0.16	2	0.08	ICP-MS	0.21	0.85	a
L21	2.5	0.6	2	0.3	ICP-MS	-0.28	-0.34	a
L22	2.692	0.323	2	0.1615	ICP-MS	0.24	0.53	a
L23	2.15	0.4	2	0.2	AAS	-1.24	**-2.21**	a
L24	2.79	0.56	2	0.28	AAS	0.51	0.66	a
L26	2.655	0.212	2	0.106	ET-AAS	0.14	0.45	a
L27	2.57	0.72	2	0.36	ICP-MS	-0.09	-0.09	a
L28	2.71	0.68	2	0.34	ICP-MS	0.29	0.31	a
L29	2.539	0.5078	2	0.2539	ICP-MS	-0.18	-0.25	a
L30	2.6	0.8	2	0.4	ICP-MS	-0.01	-0.01	c
L31	2.713	0.71	2	0.355	ICP-MS	0.30	0.31	a
L32	<3.0				AAS			
L33	2.6	0.337	2	0.1685	ICP-MS	-0.01	-0.02	a
L34	2.3	0.9	2	0.45	ET-AAS	-0.83	-0.67	c
L36	2.8	0.28	2	0.14	AAS	0.54	1.35	a
L37	2.9	0.6	2	0.3	ET-AAS	0.81	0.98	a
L38	2.53	0.4	2	0.2	ICP-MS	-0.20	-0.36	a
L39	2.447	0.08	√3	0.0462	ICP-MS	-0.43	**-2.47**	a
L40	2.818	0.467	2	0.2335	ET-AAS	0.59	0.91	a
L41	2.852	0.713	1	0.713	ET-AAS	0.68	0.35	c
L42	2.873	0.679	2	0.3395	ET-AAS	0.74	0.79	a
L43	3	1.5	2	0.75	ET-AAS	1.09	0.53	c
L45	3.605	**60**	2	30	AAS	**2.75**	0.03	c
L46	1.7166			0	AAS	**-2.43**	**-20.61**	b

[a] √3 is set by the ILC coordinator when no coverage factor k is reported. The reported uncertainty was assumed to have a rectangular distribution with k = √3,

[b] performance: satisfactory, questionable, unsatisfactory,

[c] a : $u_{min}(u(x_{pt})) \leq u_i \leq u_{max}(\sigma_{pt})$; *b* : $u_i < u(x_{pt})$; *and c* : $u_i > \sigma_{pt}$


EURL-HM-25: Total Pb in complete feed for fish
x_{pt} = 2.603; U(x_{pt}) = 0.087 (k=2); σ_{pt} = 0.364 (mg kg^{-1})
Mass fraction
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
Laboratory Code
L46 L23 L07 L34 L10 L13 L39 L21 L38 L29 L27 L06 L30 L33 L26 L18 L20 L22 L03 L28 L31 L14 L15 L04 L24 L01 L05 L19 L36 L40 L41 L42 L02 L37 L43 L11 L12 L09 L08 L16 L45 L17 L32
Measurement result range reported by participants
Assigned value (x_{pt}): solid black line; Assigned range ($x_{pt} \pm U_{pt}$ (k=2)): dashed blue lines; Acceptance range ($x_{pt} \pm 2\ \sigma_{pt}$): dotted red lines.
Kernel Density Plot
Total Pb
0
0.5
1
1.5
2
0
1
2
3
4

Annex 10: Results for mercury (Hg)

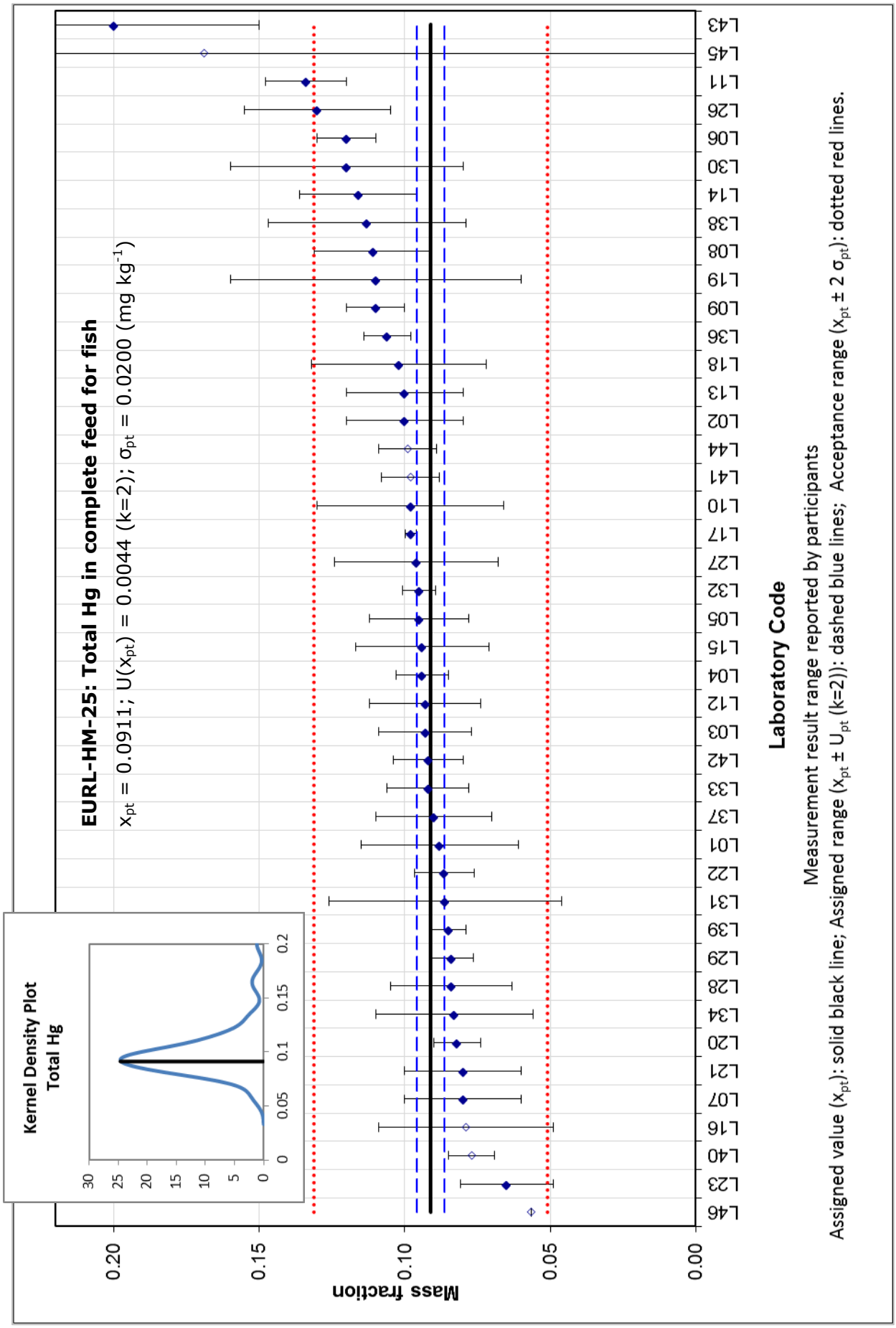
Assigned range: x_{pt} = 0.0911; $U(x_{pt})$ (k = 2.0) = 0.0044; σ_{pt} = 0.0200 (all values in mg kg^{-1})

Lab	x_i	U_i	k [a]	u_i	Technique	z score [b]	ζ score [b]	Unc [c]
L01	0.088	0.027	2	0.0135	CV-AAS	-0.15	-0.23	a
L02	0.10	0.02	2	0.01	DMA	0.44	0.87	a
L03	0.093	0.016	2	0.008	DMA	0.09	0.23	a
L04	0.094	0.009	2	0.0045	DMA	0.14	0.57	a
L05	0.095	0.017	2	0.0085	DMA	0.19	0.44	a
L06	0.12	0.01	2	0.005	ICP-MS	1.44	**5.25**	a
L07	0.08	0.02	2	0.01	ICP-MS	-0.55	-1.08	a
L08	0.111	0.02	2	0.01	DMA	0.99	1.94	a
L09	0.11	0.01	2	0.005	ICP-MS	0.94	**3.43**	a
L10	0.098	0.032	2	0.016	ICP-MS	0.34	0.43	a
L11	0.134	0.014	2	0.007	CV-AAS	**2.14**	**5.82**	a
L12	0.093	0.019	2	0.0095	CV-AFS	0.09	0.19	a
L13	0.1	0.02	2	0.01	DMA	0.44	0.87	a
L14	0.116	0.02	2	0.01	DMA	1.24	**2.43**	a
L15	0.094	0.023	2	0.0115	ICP-MS	0.14	0.25	a
L16	0.079	0.03	2	0.015	DMA	-0.60	-0.80	a
L17	0.0979	0.0019	2	0.00095	DMA	0.34	**2.73**	b
L18	0.102	0.03	2	0.015	ICP-MS	0.54	0.72	a
L19	0.11	0.05	2	0.025	ICP-MS	0.94	0.75	c
L20	0.082	0.008	2	0.004	DMA	-0.45	-1.97	a
L21	0.08	0.02	2	0.01	ICP-MS	-0.55	-1.08	a
L22	0.0864	0.0104	2	0.0052	CV-AFS	-0.23	-0.83	a
L23	0.065	0.016	2	0.008	HG-AAS	-1.30	**-3.14**	a
L26	0.13	0.025	2	0.0125	HG-AAS	1.94	**3.06**	a
L27	0.096	0.028	2	0.014	ICP-MS	0.24	0.35	a
L28	0.084	0.021	2	0.0105	ICP-MS	-0.35	-0.66	a
L29	0.0841	0.007569	√3	0.00437	DMA	-0.35	-1.42	a
L30	0.12	0.04	2	0.02	GA-UV detection	1.44	1.44	a
L31	0.0861	0.04	2	0.02	DMA	-0.25	-0.25	a
L32	0.0951	0.00571	2	0.002855	DMA	0.20	1.09	a
L33	0.092	0.014	2	0.007	ICP-MS	0.04	0.12	a
L34	0.083	0.027	2	0.0135	GA-UV detection	-0.40	-0.59	a
L36	0.106	0.008	2	0.004	CV-AAS	0.74	**3.23**	a
L37	0.09	0.02	2	0.01	DMA	-0.05	-0.11	a
L38	0.113	0.034	2	0.017	ICP-MS	1.09	1.28	a
L39	0.085	0.006	2	0.003	ICP-MS	-0.30	-1.61	a
L40	0.077	0.008	2	0.004	FI-Hg system	-0.70	**-3.06**	a
L41	0.098	0.01	1	0.01	CV-AAS	0.34	0.67	a
L42	0.092	0.012	2	0.006	CV-AAS	0.04	0.14	a
L43	0.2	0.05	2	0.025	CV-AAS	**5.43**	**4.34**	c
L44	0.099	0.01	2	0.005	CV-AAS	0.39	1.44	a
L45	0.169	**56**	2	28	CV-AAS	**3.89**	0.00	c
L46	0.0566			0	HG-AAS	-1.72	**-15.00**	b

[a] √3 is set by the ILC coordinator when no coverage factor k is reported. The reported uncertainty was assumed to have a rectangular distribution with k = √3,

[b] performance: satisfactory, questionable, unsatisfactory,

[c] a : $u_{min}(u(x_{pt})) \leq u_i \leq u_{max}(\sigma_{pt})$; b : $u_i < u(x_{pt})$; and c : $u_i > \sigma_{pt}$


EURL-HM-25: Total Hg in complete feed for fish
x_{pt} = 0.0911; U(x_{pt}) = 0.0044 (k=2); σ_{pt} = 0.0200 (mg kg^{-1})
Mass fraction
0.20
0.15
0.10
0.05
0.00
Laboratory Code
L43 L45 L11 L26 L06 L30 L14 L38 L08 L19 L09 L36 L18 L13 L02 L44 L41 L10 L17 L27 L32 L05 L15 L04 L12 L03 L42 L33 L37 L01 L22 L31 L39 L29 L28 L34 L20 L21 L07 L16 L40 L23 L46
Kernel Density Plot
Total Hg
30 25 20 15 10 5 0
0 0.05 0.1 0.15 0.2
Measurement result range reported by participants
Assigned value (x_{pt}): solid black line; Assigned range ($x_{pt} \pm U_{pt}$ (k=2)): dashed blue lines; Acceptance range ($x_{pt} \pm 2\ \sigma_{pt}$): dotted red lines.

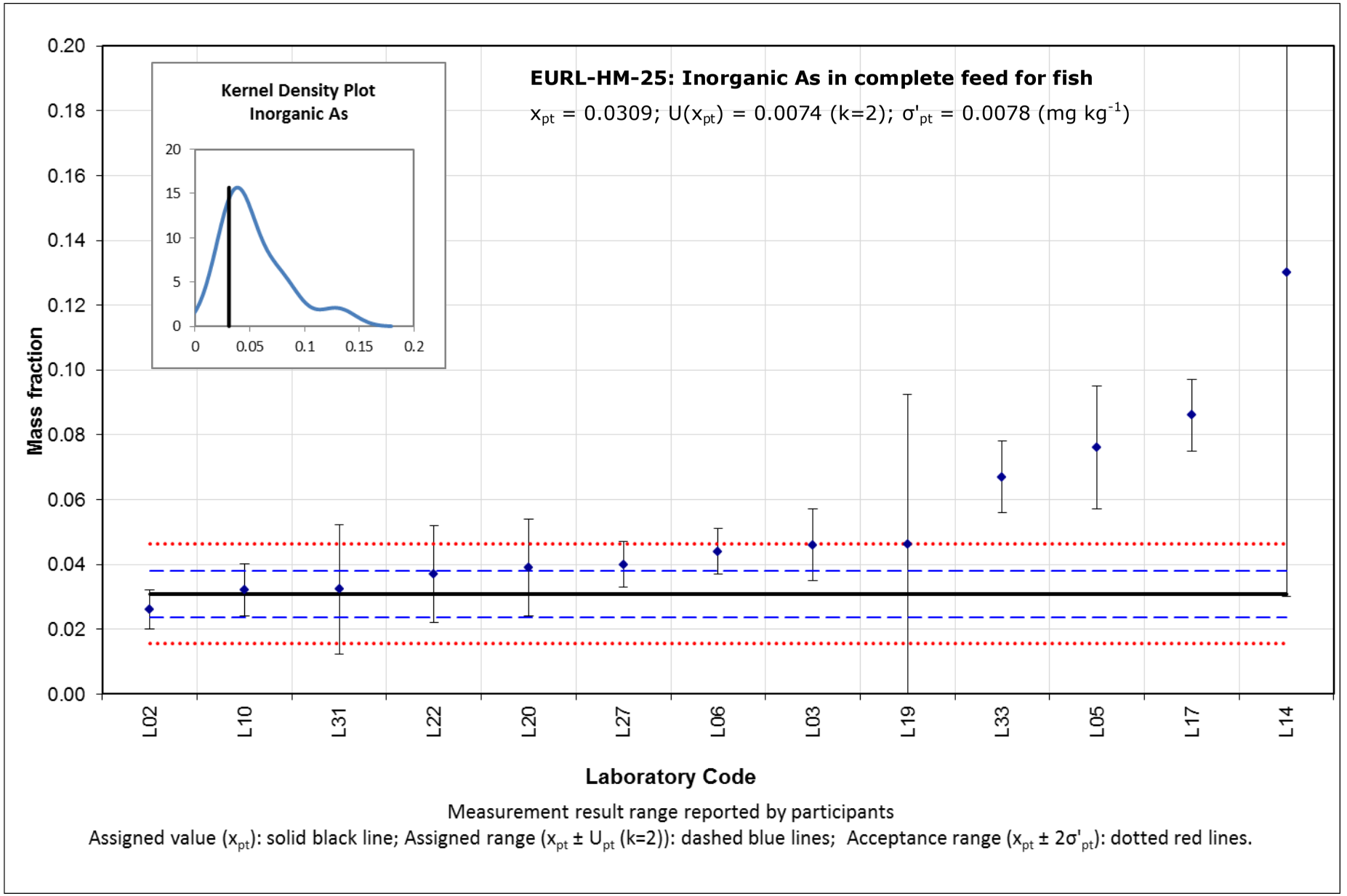
Annex 11: Results for inorganic arsenic (iAs)

Assigned range: x_{pt} = 0.0309; $U(x_{pt})$ (k = 2.0) = 0.0074; σ'_{pt} = 0.0078 (all values in mg kg^{-1})

Lab	x_i	U_i	k	u_i	Technique	z' score [a]	ζ score [a]	Unc [b]
L01	< 0.1				LC-ICP-MS			
L02	0.026	0.006	2	0.003	LC-ICP-MS	-0.65	-1.00	b
L03	0.046	0.011	2	0.0055	LC-ICP-MS	1.94	**2.21**	a
L04	< 0.040				LC-ICP-MS			
L05	0.076	0.019	2	0.0095	ICP-MS	**5.81**	**4.37**	c
L06	0.044	0.007	2	0.0035	LC-ICP-MS	1.68	**2.45**	b
L10	0.0322	0.0081	2	0.00405	LC-ICP-MS	0.15	0.21	a
L14	0.13	0.1	2	0.05	LC-ICP-MS	**12.77**	1.97	c
L17	0.086	0.011	2	0.0055	HG-GF AAS	**7.10**	**8.09**	a
L19	0.0462	0.0462	2	0.0231	LC-ICP-MS	1.96	0.65	c
L20	0.039	0.015	2	0.0075	LC-ICP-MS	1.03	0.94	a
L22	0.037	0.015	2	0.0075	LC-ICP-MS	0.77	0.71	a
L27	0.04	0.007	2	0.0035	LC-ICP-MS	1.16	1.69	b
L31	0.0323	0.02	2	0.01	LC-ICP-MS	0.17	0.12	c
L33	0.067	0.011	2	0.0055	ICP-MS	**4.65**	**5.29**	a
L43	< 0.3				HG-AAS			

[a] performance: satisfactory, questionable, unsatisfactory,

[b] a : $u_{min}(u(x_{pt})) \leq u_i \leq u_{max}(\sigma'_{pt})$; b : $u_i < u(x_{pt})$; and c : $u_i > \sigma'_{pt}$ $(\sigma'_{pt} = \sqrt{(\sigma^2_{pt} + u^2(x_{pt}))}$

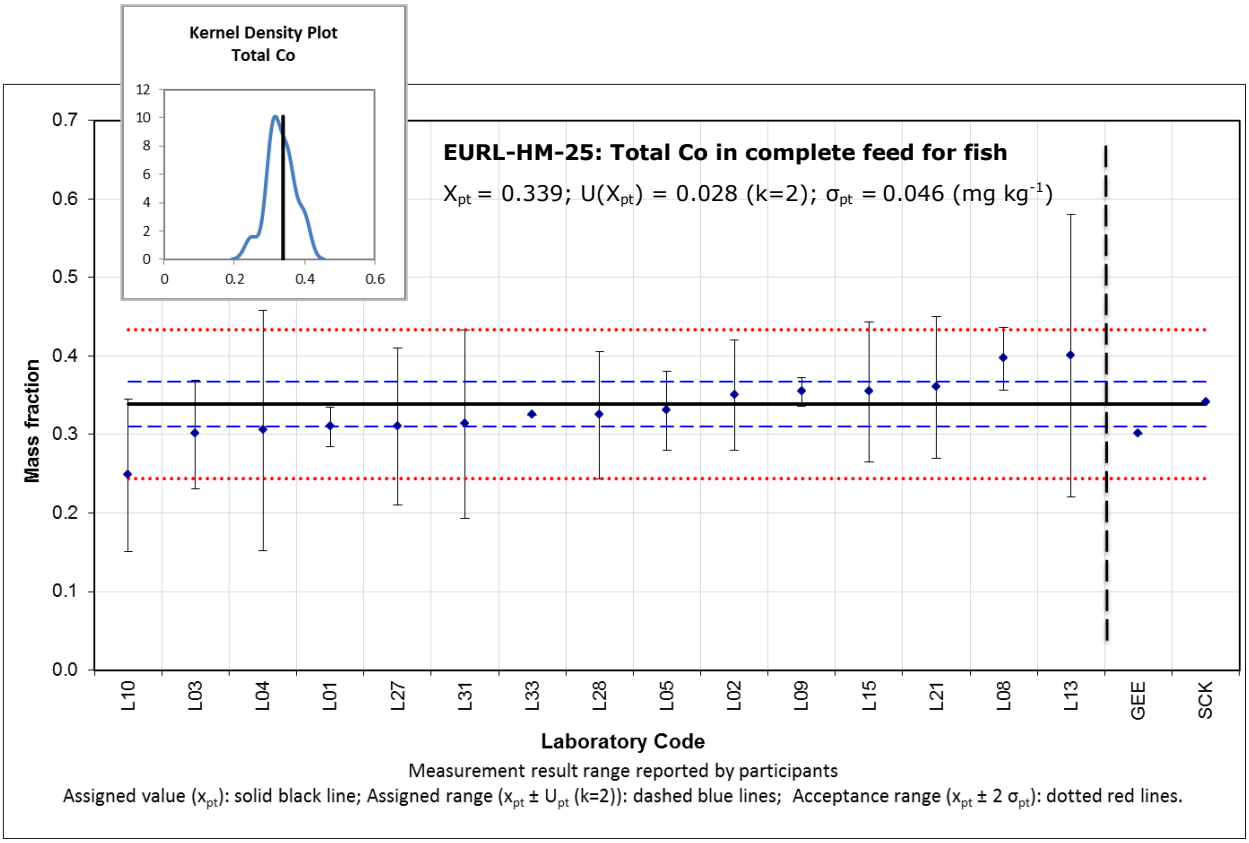

EURL-HM-25: Inorganic As in complete feed for fish
x_{pt} = 0.0309; U(x_{pt}) = 0.0074 (k=2); σ'$_{pt}$ = 0.0078 (mg kg^{-1})
Kernel Density Plot
Inorganic As
Mass fraction
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
L02
L10
L31
L22
L20
L27
L06
L03
L19
L33
L05
L17
L14
Laboratory Code
Measurement result range reported by participants
Assigned value (x_{pt}): solid black line; Assigned range (x_{pt} ± U_{pt} (k=2)): dashed blue lines; Acceptance range (x_{pt} ± 2σ'$_{pt}$): dotted red lines.

Annex 12: Results for cobalt (Co)

Assigned range: x_{pt} = 0.339; $U(x_{pt})$ (k = 2.0) = 0.028; σ_{pt} = 0.046 (all values in mg kg^{-1})

Lab	x_i	U_i	k	u_i	Technique	z score [a]	ζ score [a]
L01	0.31	0.025	2	0.0125	ICP-MS	-0.61	-1.55
L02	0.35	0.07	2	0.035	ICP-MS	0.23	0.29
L03	0.30	0.069	2	0.035	ICP-MS	-0.82	-1.05
L04	0.305	0.153	2	0.077	ICP-MS	-0.72	-0.44
L05	0.33	0.05	2	0.025	ICP-MS	-0.19	-0.31
L08	0.396	0.04	2	0.02	ICP	1.20	**2.33**
L09	0.354	0.018	2	0.009	ICP-MS	0.32	0.90
L10	0.248	0.097	2	0.049	ICP-MS	-1.92	-1.80
L13	0.4	0.18	2	0.09	ICP-MS	1.29	0.67
L15	0.354	0.089	2	0.045	ICP-MS	0.32	0.32
L21	0.36	0.09	2	0.045	ICP-MS	0.44	0.45
L27	0.31	0.1	2	0.05	ICP-MS	-0.61	-0.56
L28	0.324	0.081	2	0.0405	ICP-MS	-0.32	-0.35
L31	0.313	0.12	2	0.06	ICP-MS	-0.55	-0.42
L33	0.324			0	ICP-MS	-0.32	-1.07

[a] performance: satisfactory, questionable, unsatisfactory.

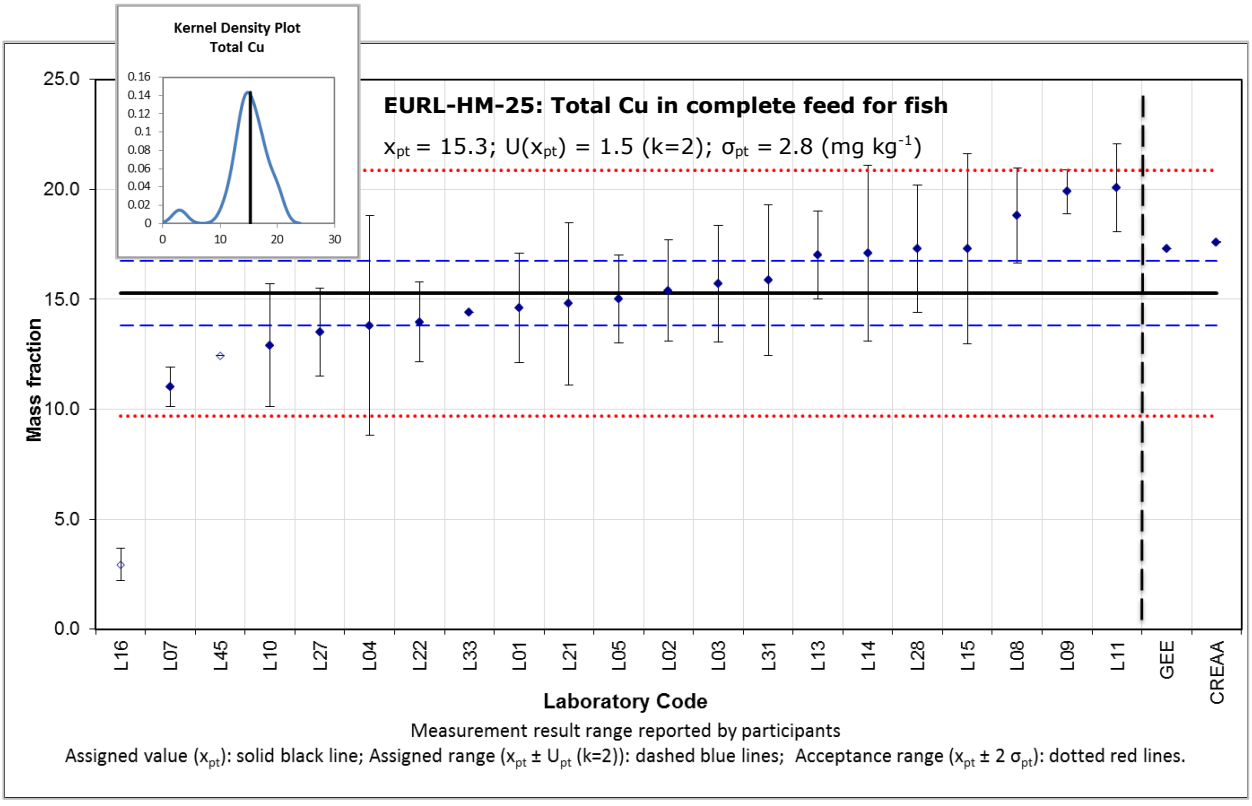


Annex 13: Results for copper (Cu)

Assigned range: x_{pt} = 15.3; $U(x_{pt})$ (k = 2.0) = 1.5; σ_{pt} = 2.8 (all values in mg kg^{-1})

Lab	x_i	U_i	k	u_i	Technique	z score [a]	ζ score [a]
L01	14.6	2.5	2	1.25	ICP-MS	-0.25	-0.48
L02	15.4	2.3	2	1.15	ICP-OES	0.04	0.08
L03	15.7	2.66	2	1.33	ICP-MS	0.15	0.27
L04	13.8	5.0	2	2.5	ICP-OES	-0.54	-0.57
L05	15	2	2	1	ICP-MS	-0.11	-0.23
L07	11	0.9	2	0.45	ICP-MS	-1.56	**-5.00**
L08	18.809	2.163	2	1.082	ICP-MS	1.28	**2.70**
L09	19.9	1	2	0.5	ICP-MS	1.68	**5.21**
L10	12.9	2.8	2	1.4	ICP-MS	-0.87	-1.51
L11	20.08	2	2	1	AAS	1.74	**3.87**
L13	17	2	2	1	AAS	0.62	1.38
L14	17.09	4	2	2	ICP-MS	0.65	0.85
L15	17.31	4.328	2	2.164	ICP-MS	0.73	0.88
L16	2.923	0.731	2	0.366	AAS	**-4.49**	**-15.15**
L21	14.8	3.7	2	1.85	ICP-MS	-0.18	-0.25
L22	13.96	1.81	2	0.91	ICP-MS	-0.48	-1.14
L27	13.5	2	2	1	ICP-MS	-0.65	-1.45
L28	17.3	2.9	2	1.45	ICP	0.73	1.24
L31	15.881	3.42	2	1.71	ICP-MS	0.21	0.32
L33	14.4			0	ICP-MS	-0.32	-1.22
L45	12.43			0	AAS	-1.04	**-3.92**

[a] performance: satisfactory, questionable, unsatisfactory.

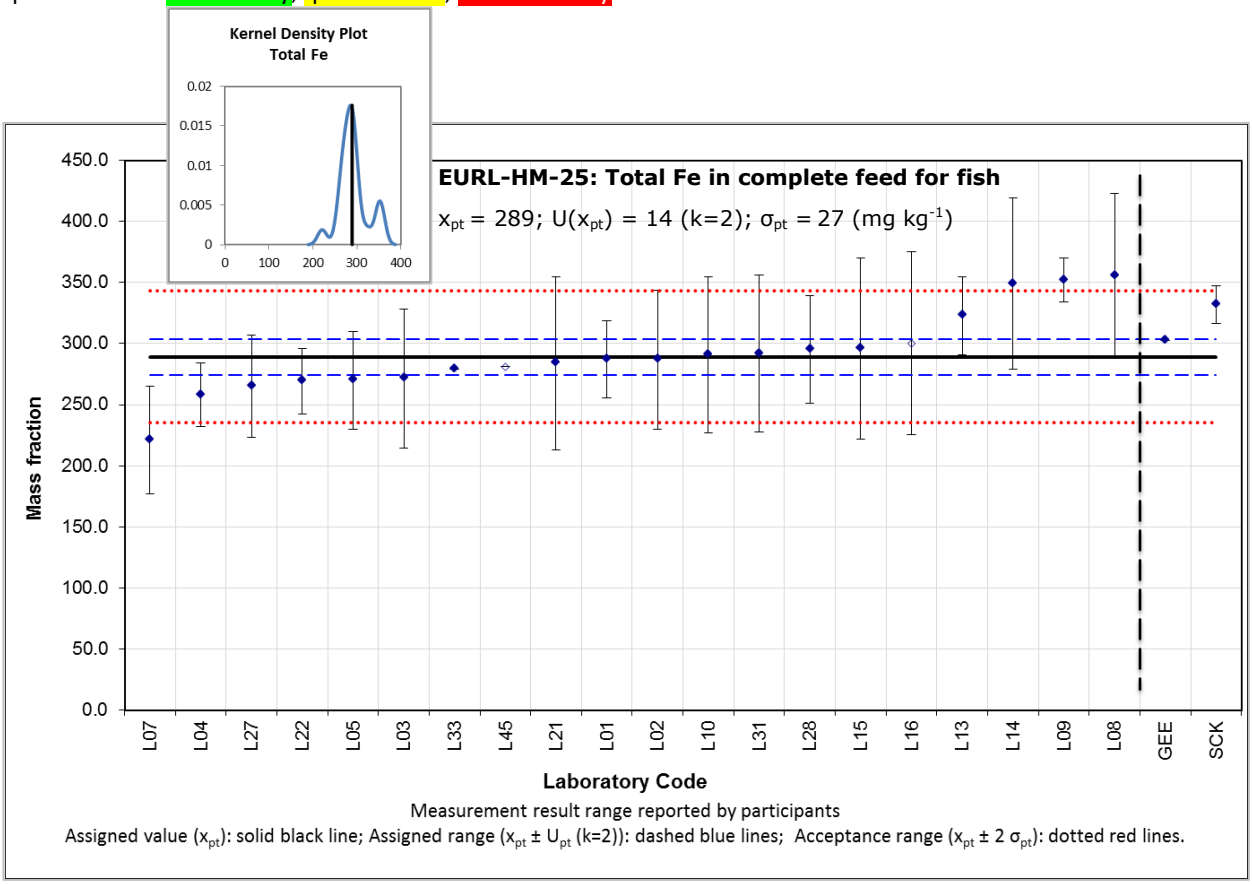


Annex 14: Results for iron (Fe)

Assigned range: x_{pt} = 289; $U(x_{pt})$ (k = 2.0) = 14; σ_{pt} = 27 (all values in mg kg^{-1})

Lab	x_i	U_i	k	u_i	Technique	z score [a]	ζ score [a]
L01	287	31.6	2	15.8	ICP-MS	-0.08	-0.12
L02	287	57	2	28.5	ICP-OES	-0.08	-0.07
L03	271.6	57	2	28.5	ICP-MS	-0.67	-0.59
L04	258.1	25.8	2	12.9	ICP-OES	-1.19	**-2.09**
L05	270	40	2	20	AAS	-0.73	-0.89
L07	221	44	2	22	ICP-MS	**-2.61**	**-2.94**
L08	355.385	67.523	2	33.7615	ICP-MS	**2.55**	1.92
L09	352	18	2	9	ICP-MS	**2.42**	**5.47**
L10	291	64	2	32	ICP-MS	0.08	0.06
L13	323	32	2	16	AAS	1.31	1.94
L14	349	70	2	35	ICP-MS	**2.31**	1.68
L15	296	74	2	37	ICP-MS	0.27	0.19
L16	300.182	75.045	2	37.5225	AAS	0.43	0.29
L21	284	71	2	35.5	ICP-MS	-0.19	-0.14
L22	269.3	26.9	2	13.45	FAAS	-0.76	-1.29
L27	265	42	2	21	ICP-MS	-0.92	-1.08
L28	295	44	2	22	ICP	0.23	0.26
L31	291.846	64.53	2	32.265	ICP-MS	0.11	0.09
L33	279			0	ICP-MS	-0.38	-1.39
L45	281			0	AAS	-0.31	-1.11

[a] performance: satisfactory, questionable, unsatisfactory.

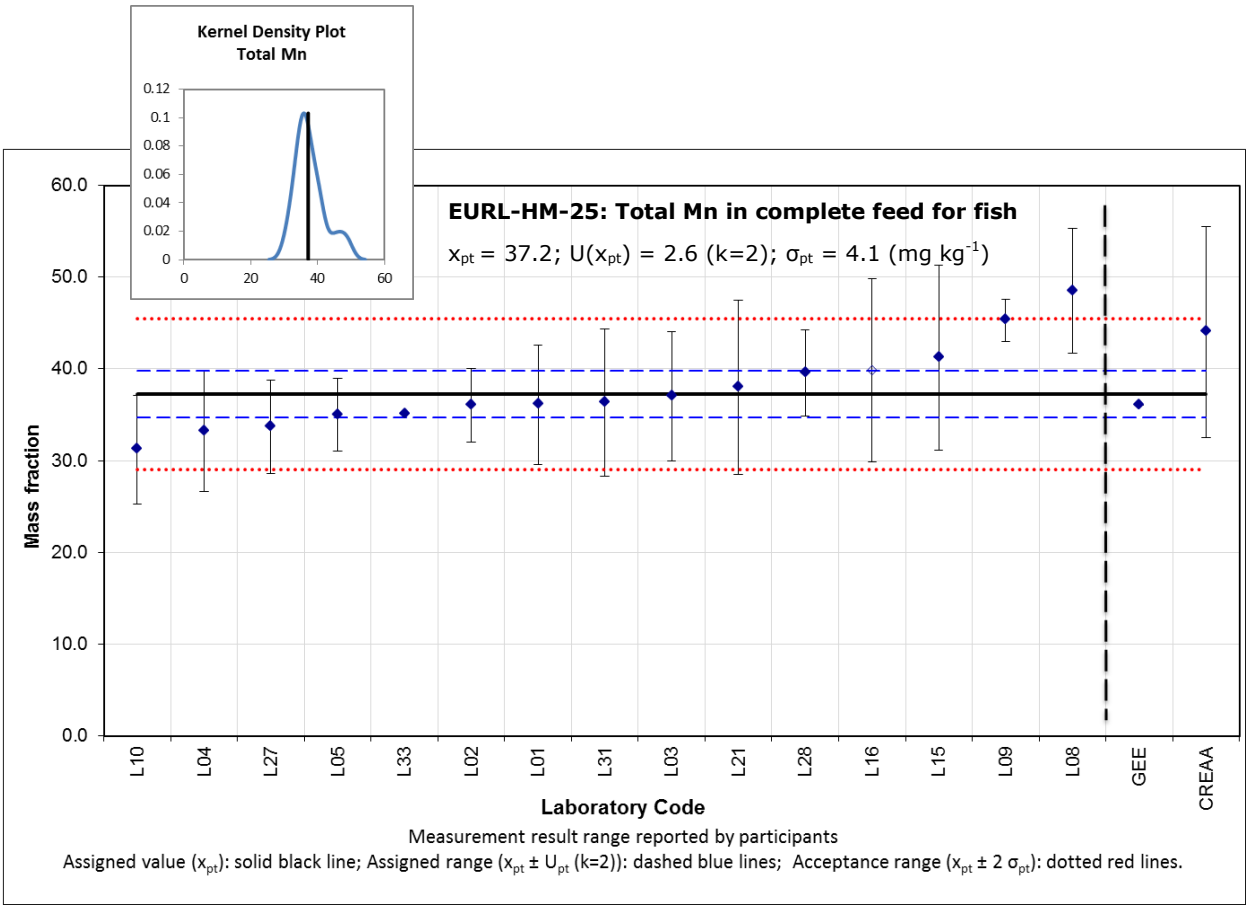


Annex 15: Results for manganese (Mn)

Assigned range: x_{pt} = 37.2; $U(x_{pt})$ (k = 2.0) = 2.6; σ_{pt} = 4.1 (all values in mg kg^{-1})

Lab	x_i	U_i	k	u_i	Technique	z score [a]	ζ score [a]
L01	36.1	6.5	2	3.25	ICP-MS	-0.27	-0.31
L02	36	4	2	2	ICP-OES	-0.29	-0.50
L03	37.0	7.03	2	3.515	ICP-MS	-0.05	-0.05
L04	33.2	6.6	2	3.3	ICP-OES	-0.98	-1.13
L05	35	4	2	2	ICP-MS	-0.54	-0.92
L08	48.515	6.792	2	3.396	ICP-MS	**2.77**	**3.11**
L09	45.3	2.3	2	1.15	ICP-MS	1.98	**4.67**
L10	31.2	5.9	2	2.95	ICP-MS	-1.47	-1.86
L15	41.22	10.1	2	5.05	ICP-MS	0.98	0.77
L16	39.87	9.968	2	4.984	AAS	0.65	0.52
L21	38	9.5	2	4.75	ICP-MS	0.20	0.16
L27	33.7	5.1	2	2.55	ICP-MS	-0.86	-1.22
L28	39.6	4.7	2	2.35	ICP	0.59	0.89
L31	36.319	8.04	2	4.02	ICP-MS	-0.22	-0.21
L33	35.1			0	ICP-MS	-0.51	-1.62

[a] performance: satisfactory, questionable, unsatisfactory.

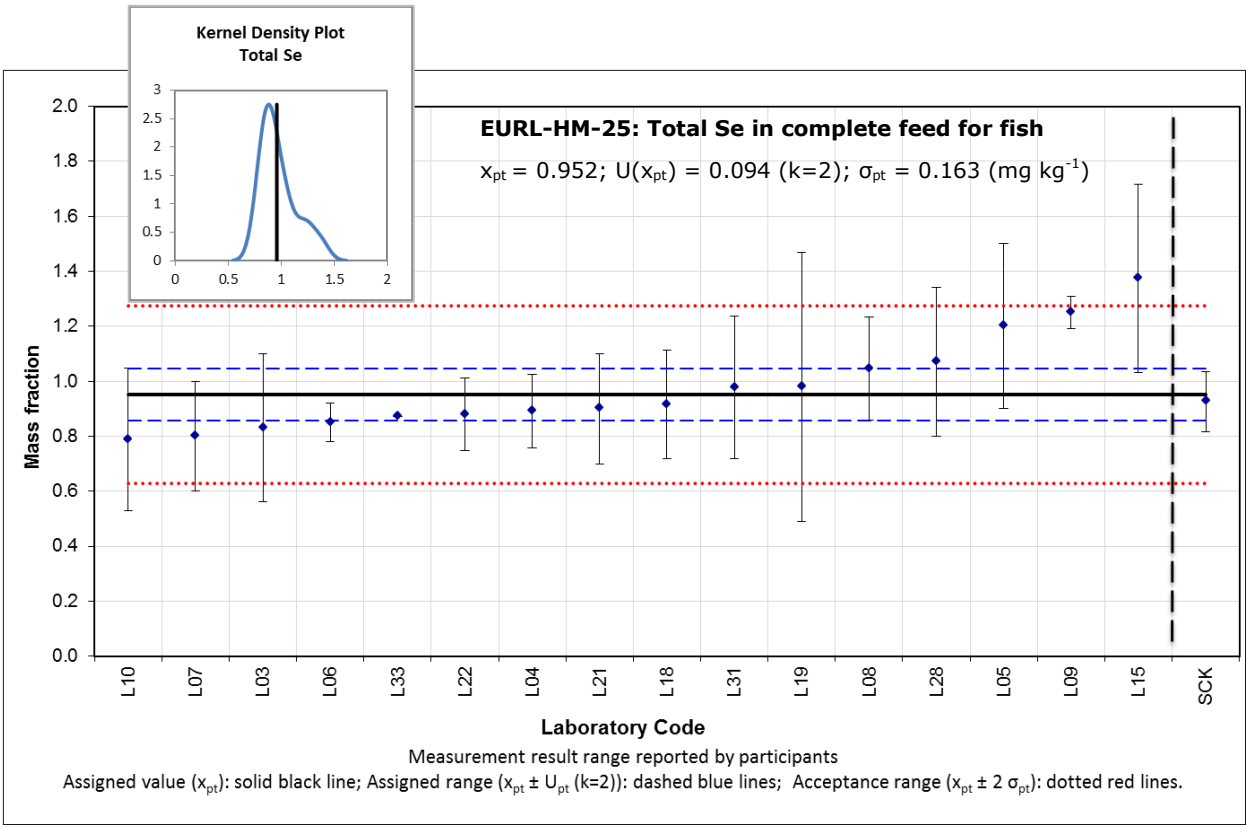


Annex 16: Results for selenium (Se)

Assigned range: x_{pt} = 0.952; $U(x_{pt})$ (k = 2.0) = 0.094; σ_{pt} = 0.163 (all values in mg kg^{-1})

Lab	x_i	U_i	k	u_i	Technique	z score [a]	ζ score [a]
L01	< 0.75				ICP-MS		
L03	0.83	0.27	2	0.135	ICP-MS	-0.75	-0.85
L04	0.891	0.134	2	0.067	ICP-MS	-0.38	-0.75
L05	1.2	0.3	2	0.15	ICP-MS	1.53	1.58
L06	0.85	0.07	2	0.035	ICP-MS	-0.63	-1.74
L07	0.8	0.2	2	0.1	ICP-MS	-0.94	-1.38
L08	1.046	0.188	2	0.094	ICP-MS	0.58	0.89
L09	1.25	0.06	2	0.03	ICP-MS	1.84	**5.34**
L10	0.788	0.26	2	0.13	ICP-MS	-1.01	-1.19
L15	1.374	0.344	2	0.172	ICP-MS	**2.61**	**2.37**
L18	0.915	0.198	2	0.099	ICP-MS	-0.23	-0.34
L19	0.98	0.49	2	0.245	ICP-MS	0.17	0.11
L21	0.9	0.2	2	0.1	ICP-MS	-0.32	-0.47
L22	0.879	0.132	2	0.066	ICP-MS	-0.45	-0.90
L28	1.07	0.27	2	0.135	ICP-MS	0.73	0.83
L31	0.977	0.26	2	0.13	ICP-MS	0.15	0.18
L33	0.871			0	ICP-MS	-0.50	-1.72

[a] performance: satisfactory, questionable, unsatisfactory.

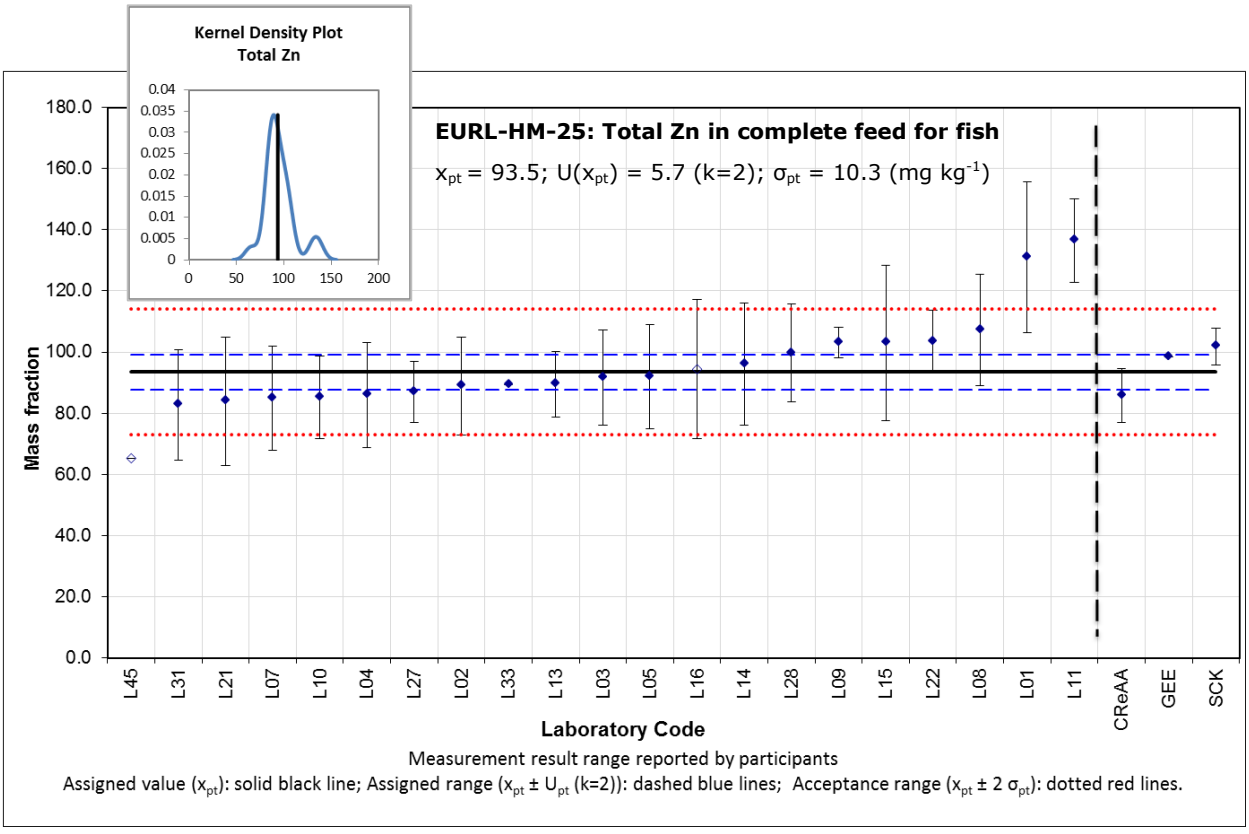


Annex 17: Results for zinc (Zn)

Assigned range: x_{pt} = 93.5; $U(x_{pt})$ (k = 2.0) = 5.7; σ_{pt} = 10.3 (all values in mg kg^{-1})

Lab	x_i	U_i	k	u_i	Technique	z score [a]	ζ score [a]
L01	131	24.8	2	12.4	ICP-MS	**3.64**	**2.94**
L02	89	16	2	8	ICP-OES	-0.44	-0.53
L03	91.7	15.6	2	7.8	ICP-MS	-0.18	-0.22
L04	86.0	17.2	2	8.6	ICP-OES	-0.73	-0.83
L05	92	17	2	8.5	ICP-MS	-0.15	-0.17
L07	85	17	2	8.5	ICP-MS	-0.83	-0.95
L08	107.103	18.207	2	9.104	ICP-MS	1.32	1.42
L09	103	5	2	2.5	ICP-MS	0.92	**2.49**
L10	85.2	13.6	2	6.8	ICP-MS	-0.81	-1.13
L11	136.5	13.6	2	6.8	AAS	**4.18**	**5.82**
L13	89.5	10.7	2	5.35	AAS	-0.39	-0.66
L14	96	20	2	10	ICP-MS	0.24	0.24
L15	103	25.5	2	12.75	ICP-MS	0.92	0.73
L16	94.421	22.682	2	11.341	AAS	0.09	0.08
L21	84	21	2	10.5	ICP-MS	-0.93	-0.87
L22	103.4	10.3	2	5.15	ICP-MS	0.96	1.68
L27	87	10	2	5	ICP-MS	-0.63	-1.13
L28	99.6	16	2	8	ICP	0.59	0.72
L31	82.753	18.04	2	9.02	ICP-MS	-1.05	-1.14
L33	89.3			0	ICP-MS	-0.41	-1.47
L45	65.3			0	AAS	**-2.74**	**-9.83**

[a] performance: satisfactory, questionable, unsatisfactory.



Annex 18: Experimental details and performance (expressed as z scores)

Lab		Accredited	Standard method	Recovery (%)	LOD (mg/kg)	CRM for validation of measurement procedure	CRM for instrument calibration	Digestion type	Digestion mixture	Digestion time (min)	Digestion Temp. (°C)	Samples /year	Technique	Measurement uncertainty evaluation
L01	As	Yes	No	105	0.031							250-999	AAS	From in-house method validation
	Cd	Yes	No	82	0.0035							250-999	AAS	
	Pb	Yes	No	93	0.014							250-999	AAS	
	Hg	Yes	No	109	0.01							250-999	CV-AAS	
	iAs	Yes	No	92	0.051							50-249	LC-ICP-MS	
L02	As		No	96-110	0.0012	DORM-4, TORT-2, BCR185r		CMW	HNO_3	30	180	0-49	ICP-MS	From in-house method validation
	Cd		No	94-108	0.0003	DORM-4, TORT-2, BCR185r		CMW	HNO_3	30	180	0-49	ICP-MS	
	Pb		No	99-103	0.0018	DORM-4, TORT-2, BCR185r		CMW	HNO_3	30	180	0-49	ICP-MS	
	Hg		No	102	0.0001	DORM4, BCR150, IAEA407						0-49	DMA	
	iAs		No	92-93	0.0012	NMIJ7532a, NMIJ7406a		CMW	HNO_3, H_2O_2	20	90	0-49	LC-ICP-MS	
L03	As	Yes	No	96	0.033	Dolt-4		MW	HNO_3, H_2O_2	30	200	> 1000	ICP-MS	From in-house method validation
	Cd	Yes	No	102	0.003	Dolt-4		MW	HNO_3, H_2O_2	30	200	> 1000	ICP-MS	
	Pb	Yes	No	94	0.002	Dolt-4		MW	HNO_3, H_2O_2	30	200	> 1000	ICP-MS	
	Hg	Yes	No	111	0.003	Dorm-2		NA	NA	NA	NA	> 1000	DMA	
	iAs	No	No	97	0.015	rice		MW	0.3 % HNO_3, H_2O_2	50	95	0-49	LC-ICP-MS	
L04	As	Yes	Yes	95-105	0,006	GBW 7604,7603,7602	Astasol, Analytika(CZ)	OMW	HNO_3	20	210	50-249	ICP-MS	Uncertainty budget (ISO GUM), From in-house method validation, From measurement of replicates (precision)
	Cd	Yes	Yes	98-102	0,006	GBW 7604,7603,7602	Astasol, Analytika(CZ)	OMW	HNO_3	20	210	50-249	ICP-MS	
	Pb	Yes	Yes	98-102	0,060	GBW 7604,7603,7602	Astasol, Analytika(CZ)	OMW	HNO_3	20	210	50-249	ICP-MS	
	Hg	Yes	No	98-102	0,0003	IRM PT UKZUZ(CZ)	Astasol, Analytika(CZ)	DA	no acids		550	50-249	DMA	
	iAs		No	90-110	0,012	NIST rice flour1568b	saltsAsIII,V SigmaAldrich	CMW	0,07M HCl, 3% H_2O_2	25	90	0-49	LC-ICP-MS	
L05	As		Yes	99.8	0.05	DORM 4	MERCK ICP st. VI	CMW	HNO_3, H_2O_2	20	20	0-49	ICP-MS	Uncertainty budget (ISO GUM), From in-house method validation
	Cd		Yes	100.2	0.005	DORM 4	MERCK ICP st. VI	CMW	HNO_3, H_2O_2	20	20	0-49	ICP-MS	
	Pb		Yes	99.6	0.01	DORM 4	MERCK ICP st. VI	CMW	HNO_3, H_2O_2	20	20	0-49	ICP-MS	
	Hg		Yes	97.1	0.002	DORM 4	-	DA	-	3	850	0-49	DMA	
	iAs		**Yes**	**109**	**0.05**	**SRM 1568b**	**MERCK ICP st. VI**	**CMW**	**HCl, H_2O_2**	**25**	**90**	**0-49**	**ICP-MS**	
L06	As	Yes	Yes	106	0,003	Multi Nist SRM 695	Std-curve	CMW	Conc HNO_3	30	200	250-999	ICP-MS	From in-house method validation
	Cd	Yes	Yes	101	0,001	Multi Nist SRM 695	Std-curve	CMW	Conc HNO_3	30	200	250-999	ICP-MS	
	Pb	Yes	Yes	95	0,002	Multi Nist SRM 695	Std-curve	CMW	Conc HNO_3	30	200	250-999	ICP-MS	
	Hg	Yes	Yes	102	0,002	Multi Nist SRM 695	Std-curve	CMW	Conc HNO_3	30	200	250-999	ICP-MS	
	iAs	Yes	Yes	100	0,030	ERM-BC-211	Std-curve	Extraction	HNO_3, H_2O_2	60	90	0-49	LC-ICP-MS	
L07	As	Yes	Yes		0.01	DORM/TORT/Hijiki	DORM	MW	HNO_3	20	200	250-999	ICP-MS	From in-house method validation
	Cd	Yes	Yes		0.02	DORM/TORT/Hijiki	DORM	MW	HNO_3	20	200	250-999	ICP-MS	
	Pb	Yes	Yes		0.02	DORM/TORT/Hijiki	DORM	MW	HNO_3	20	200	250-999	ICP-MS	
	Hg	Yes	Yes		0.06	DORM/TORT/Hijiki	DORM	MW	HNO_3	20	200	250-999	ICP-MS	
	iAs													

Lab		Accredited	Standard method	Recovery (%)	LOD (mg/kg)	CRM for validation of measurement procedure	CRM for instrument calibration	Digestion type	Digestion mixture	Digestion time (min)	Digestion Temp. (°C)	Samples /year	Technique	Measurement uncertainty evaluation
L08	As	Yes	No	86.4	0.001	IMEP119	IV-ICPMS-71A	MW	HNO_3, HCl, H_2O_2	45	230	250-999	ICP-MS	Uncertainty budget (ISO GUM)
	Cd	Yes	No	93	0.001	IMEP119	IV-ICPMS-71A	MW	HNO_3, HCl, H_2O_2	45	230	250-999	ICP-MS	
	Pb	Yes	No	98.1	0.001	IMEP119	IV-ICPMS-71A	MW	HNO_3, HCl, H_2O_2	45	230	250-999	ICP-MS	
	Hg	Yes	No	97.6	0.001	IMEP119	IV-ICPMS-71A					250-999	DMA	
	iAs		No	-								0-49		
L09	As	Yes	No	100	0.005	Yes	Yes	CMW	HNO_3, H_2O_2	30	180	0-49	ICP-MS	From interlaboratory comparison
	Cd	Yes	No	100	0.005	Yes	Yes	CMW	HNO_3, H_2O_2	30	180	0-49	ICP-MS	
	Pb	Yes	No	100	0.01	Yes	Yes	CMW	HNO_3, H_2O_2	30	180	0-49	ICP-MS	
	Hg	Yes	No	100	0.001	Yes	Yes	CMW	HNO_3	30	180	0-49	ICP-MS	
	iAs		No											
L10	As	Yes	Yes	100	0.025	Yes	No	MW	HNO_3, HCl	60	230	250-999	ICP-MS	From interlaboratory comparison, Other
	Cd	Yes	Yes	100	0.006	Yes	No					250-999	ICP-MS	
	Pb	Yes	Yes	100	0.02	Yes	No					250-999	ICP-MS	
	Hg	Yes	Yes	100	0.013	Yes	No					250-999	ICP-MS	
	iAs	Yes	Yes	100	0.007	Yes	No					50-249	LC-ICP-MS	
L11	As													From in-house method validation
	Cd	**Yes**	**No**	**96.6**	**0.05**	**Yes**	**Yes**	**CMW**	**HNO_3, H_2O_2**	**35**	**175**	**0-49**	**ET-AAS**	
	Pb	Yes	No	99.6	0.5	Yes	Yes	CMW	HNO_3, H_2O_2	35	175	0-49	ET-AAS	
	Hg	**Yes**	**No**	**100.8**	**0.09**	**Yes**	**Yes**	**CMW**	**HNO_3, HCl**	**35**	**175**	**0-49**	**CV-AAS**	
	iAs													
L12	As	Yes											ICP-MS	
	Cd	Yes											ICP-MS	
	Pb	Yes											ICP-MS	
	Hg	Yes											CV-AFS	
	iAs													
L13	As													Uncertainty budget (ISO GUM), From in-house method validation, From measurement of replicates (precision)
	Cd	Yes	No	88.7	0.07	ULVA LACTUCA BCR279		CMW	HNO_3, H_2O_2, HF	28	200	50-249	ET-AAS	
	Pb	Yes	No	95.5	0.5	TEA LEAVES INCT-TL-1		CMW	HNO_3, H_2O_2, HF	28	200	50-249	ET-AAS	
	Hg	Yes	No	95.5	0.01	Tomato leaves NIST1573A						50-249	DMA	
	iAs													
L14	**As**		**Yes**	**80-120**	**0.01**	**Yes**		**MW**	**HNO_3, H_2O_2**	**30**	**180**	**250-999**	**ICP-MS**	From in-house method validation
	Cd	Yes	Yes	80-120	0.02	Yes		MW	HNO_3, H_2O_2	30	180	250-999	ICP-MS	
	Pb	Yes	Yes	80-120	0.01	Yes		MW	HNO_3, H_2O_2	30	180	250-999	ICP-MS	
	Hg		Yes	80-120	0.01	Yes		DMA				250-999	DMA	
	iAs		**Yes**	**80-120**	**0.1**	**Yes**		**wather bath**	**HNO_3, H_2O_2 diluted**	**60**	**95**	**0-49**	**LC-ICP-MS**	

Lab		Accredited	Standard method	Recovery (%)	LOD (mg/kg)	CRM for validation of measurement procedure	CRM for instrument calibration	Digestion type	Digestion mixture	Digestion time (min)	Digestion Temp. (°C)	Samples /year	Technique	Measurement uncertainty evaluation
L15	As	Yes	No	99,5	0,001			MW	HNO_3	75	<200	0-49	ICP-MS	From measurement of replicates (precision)
	Cd	Yes	No	99,6	0,001			MW	HNO_3	75	<200	0-49	ICP-MS	
	Pb	Yes	No	98,8	0,001			MW	HNO_3	75	<200	0-49	ICP-MS	
	Hg	Yes	No	99,3	0,001			MW	HNO_3	75	<200	0-49	ICP-MS	
	iAs		No					MW	HNO_3	75	<200	0-49		
L16	**As**	**Yes**	**No**	**69**	**0,025**			**MW**	**1ml H_2O + 4ml HNO_3**	**55**	**220**	**50-249**	**AAS**	Uncertainty budget (ISO GUM), From known uncertainty of standard method (ISO 21748), From in-house method validation, From measurement of replicates (precision), Based on judgment,
	Cd	Yes	No	87	0,025			MW	1ml H_2O + 4ml HNO_3	55	220	50-249	AAS	
	Pb	**Yes**	**No**	**121**	**0,025**			**MW**	**1ml H_2O + 4ml HNO_3**	**55**	**220**	**50-249**	**AAS**	
	Hg	Yes	No	96	0,012							50-249	DMA	
	iAs													
L17	As	Yes		104	0,01	NIST 2976 mussle	Merck RF	s s		12	425	Never	HG-GFAAS	From measurement of replicates (precision)
	Cd	Yes	Yes	94	0,006	NIST 1570	Merck RF	MW	HNO_3, H_2O_2			0-49	ET-AAS	
	Pb	**Yes**	**Yes**	**90**	**0,02**	**NIST 1570**	**Merck RF**	**MW**	**HNO_3, H_2O_2**			**0-49**	**ET-AAS**	
	Hg	Yes		98	0,005	NIST 1570	Merck RF	dir				0-49	DMA	
	iAs	**Yes**			**0,01**	**NIST1568 b**	**Merck RF**	**Extraction**		**12**	**425**	**0-49**	**HG-GFAAS**	
L18	As		Yes	91-109	0.05		1000 mg/l	MW	HNO_3, H_2O_2	60	210	0-49	ICP-MS	Based on judgment
	Cd		Yes	93-114	0.01		1000 mg/l	MW	HNO_3, H_2O_2	60	210	0-49	ICP-MS	
	Pb		Yes	95-113	0.01		1000 mg/l	MW	HNO_3, H_2O_2	60	210	0-49	ICP-MS	
	Hg		Yes	103-109	0.005		1000 mg/l	MW	HNO_3, H_2O_2	60	210	0-49	ICP-MS	
	iAs													
L19	As	Yes	Yes									250-999	ICP-MS	From in-house method validation, From measurement of replicates (precision), From interlaboratory comparison
	Cd	Yes	Yes									250-999	ICP-MS	
	Pb	Yes	Yes									250-999	ICP-MS	
	Hg	Yes	Yes									250-999	ICP-MS	
	iAs		**Yes**									**250-999**	**LC-ICP-MS**	
L20	As	Yes	No	116	0.0009	DORM4		MW	HNO_3, H_2O_2	20/10	150/180	50-249	ICP-MS	Uncertainty budget (ISO GUM), From in-house method validation
	Cd	Yes	No	101	0.0003	DORM4		MW	HNO_3, H_2O_2	20/10	150/180	50-249	ICP-MS	
	Pb	Yes	No	85	0.004	DORM4		MW	HNO_3, H_2O_2	20/10	150/180	50-249	ICP-MS	
	Hg	Yes	No	100	0.0002	IAEA336		without digestion	-	-	-	50-249	DMA	
	iAs	Yes	No	119	0.005	SRM1568b		MW-extr	HCl, H_2O_2	25	90	0-49	LC-ICP-MS	
L21	As	Yes		88.3	0.0083			MW	HNO_3, HCl, H_2O_2	40	115	50-249	ICP-MS	From in-house method validation
	Cd	Yes		89.9	0.0007			MW	HNO_3, HCl, H_2O_2	40	115	50-249	ICP-MS	
	Pb	Yes		102.7	0.0185			MW	HNO_3, HCl, H_2O_2	40	115	50-249	ICP-MS	
	Hg	Yes		98.1	0.0146			MW	HNO_3, HCl, H_2O_2	40	115	50-249	ICP-MS	
	iAs											Never		

Lab		Accredited	Standard method	Recovery (%)	LOD (mg/kg)	CRM for validation of measurement procedure	CRM for instrument calibration	Digestion type	Digestion mixture	Digestion time (min)	Digestion Temp. (°C)	Samples /year	Technique	Measurement uncertainty evaluation
L22	As	Yes	No	107	0.005		DORM-4	MW	HNO_3, HF	30	220	50-249	ICP-MS	From in-house method validation, Based on judgment
	Cd	Yes	No	98	0.001		DORM-4	MW	HNO_3, HF	30	220	50-249	ICP-MS	
	Pb	Yes	No	95	0.002		DORM-4	MW	HNO_3, HF	30	220	50-249	ICP-MS	
	Hg	Yes	No	104	0.0012		DORM-4	MW	HNO_3, HF	30	220	50-249	CV-AFS	
	iAs	Yes	Yes	102	0.0076		DORM-4	water bath	HNO_3, H_2O_2	60	90	50-249	LC-ICP-MS	
L23	As	Yes	No	80-110	0.067	HM-23		CMW	HNO_3, H_2O_2	20	180	50-249	AAS	From in-house method validation
	Cd	Yes	No	80-110	0.0033	HM-23		CMW	HNO_3, H_2O_2	20	180	50-249	AAS	
	Pb	Yes	No	80-110	0.17	HM-23		CMW	HNO_3, H_2O_2	20	180	50-249	AAS	
	Hg	Yes	No	80-110	0.007	HM-23		CMW	HNO_3, H_2O_2	20	180	0-49	HG-AAS	
	iAs													
L24	As		Yes	94		CRM		MW	HNO_3, H_2O_2	60	200	0-49	HG-AAS	Other
	Cd		Yes	90		CRM		MW	HNO_3, H_2O_2	60	200	0-49	AAS	
	Pb		Yes	95		CRM			HNO_3, H_2O_2	60	200	0-49	AAS	
	Hg											Never		
	iAs											Never		
L26	As													Other
	Cd	**Yes**	**Yes**	**106**	**0,040**			**MW**	**HNO_3, H_2O_2**	**20**	**200**	**50-249**	**ET-AAS**	
	Pb	Yes	Yes	94	0,040			MW	HNO_3, H_2O_2	20	200	50-249	ET-AAS	
	Hg	Yes	Yes	96	0,040			MW	HNO_3, H_2O_2	20	200	50-249	HG-AAS	
	iAs													
L27	As	Yes	Yes	94,0	0,011	Durum wheat NIST 8436		MW assisted	6 ml HNO_3+1ml HCl	25	220	0-49	ICP-MS	Uncertainty budget (ISO GUM), From in-house method validation, From interlaboratory comparison
	Cd	Yes	Yes	96,6	0,0018	Durum wheat NIST 8436		MW assisted	6 ml HNO_3+1ml HCl	25	220	250-999	ICP-MS	
	Pb	Yes	Yes	104,1	0,0047	Durum wheat NIST 8436		MW assisted	6 ml HNO_3+1ml HCl	25	220	250-999	ICP-MS	
	Hg	Yes	Yes	94,8	0,031	Durum wheat NIST 8436		MW assisted	6 ml HNO_3+1ml HCl	25	220	0-49	ICP-MS	
	iAs	Yes	Yes	105,7	0,0025	Durum wheat NIST 8436		Extraction	HNO_3, H_2O_2	60	90	50-249	LC-ICP-MS	
L28	As	Yes	Yes		0.01			MW		50	220	0-49	ICP-MS	Other
	Cd	Yes	Yes		0.01			MW	HNO_3, H_2O_2	50	220	0-49	ICP-MS	
	Pb	Yes	Yes		0.02			MW	HNO_3, H_2O_2	50	220	0-49	ICP-MS	
	Hg	Yes	Yes		0.01			MW	HNO_3, H_2O_2	50	220	0-49	ICP-MS	
	iAs											Never		
L29	As	Yes	Yes	19	0.0023			MW	HNO_3, H_2O_2	47	190	> 1000	ICP-MS	From in-house method validation, From measurement of replicates (precision)
	Cd	Yes	Yes	19	0.0016			MW	HNO_3, H_2O_2	47	190	> 1000	ICP-MS	
	Pb	Yes	Yes	20	0.0014			MW	HNO_3, H_2O_2	47	190	> 1000	ICP-MS	
	Hg	Yes	Yes	9	0.0001			direct analysis				> 1000	DMA	
	iAs													

Lab		Accredited	Standard method	Recovery (%)	LOD (mg/kg)	CRM for validation of measurement procedure	CRM for instrument calibration	Digestion type	Digestion mixture	Digestion time (min)	Digestion Temp. (°C)	Samples /year	Technique	Measurement uncertainty evaluation
L30	As		Yes	100	0,013							0-49	ICP-MS	
	Cd		Yes	100	0,013							0-49	ICP-MS	
	Pb		Yes	100	0,013							0-49	ICP-MS	
	Hg		Yes	100	0,005							0-49	GA-UV Det.	
	iAs													
L31	As		No	97,96	0,005	1568 b		MW	HNO_3, H_2O_2	25	210	0-49	ICP-MS	From in-house method validation
	Cd		No	98,81	0,003	1568 b		MW	HNO_3, H_2O_2	25	210	0-49	ICP-MS	
	Pb		No	94,71	0,004	1568 b		MW	HNO_3, H_2O_2	25	210	0-49	ICP-MS	
	Hg		No	97,30	0,001	1568 b						0-49	DMA	
	iAs		No	89,11	0,004	bc 211						Never	LC-ICP-MS	
L32	As													From in-house method validation
	Cd	Yes	No		0.163			DA				250-999	AAS	
	Pb	Yes	No		1			DA				250-999	AAS	
	Hg	Yes	No		0.0005	BCR 463						250-999	DMA	
	iAs													
L33	As	Yes	No	90	0	MPH-2		CMW	HNO_3, HCl	35.5	240	> 1000	ICP-MS	From interlaboratory comparison
	Cd	Yes	No	104	0	MPH-2		CMW	HNO_3, HCl	35.5	240	> 1000	ICP-MS	
	Pb	Yes	No	101	0.001	MPH-2		CMW	HNO_3, HCl	35.5	240	> 1000	ICP-MS	
	Hg	Yes	No	102	0.001	MPH-2		CMW	HNO_3, HCl	35.5	240	> 1000	ICP-MS	
	iAs	**Yes**	**No**	**88**	**0.003**	**IMEP112**		**other**	**HCl**	**~ 18 hrs**	**ambient**	**50-249**	**ICP-MS**	
L34	**As**		**No**	**90**	**0.1**	**no**	**No**	**MW**	**HNO_3, H_2O_2**	**10**	**200**	**50-249**	**ET-AAS**	From known uncertainty of standard method (ISO 21748)
	Cd	Yes	Yes	101	0.01	no	No	MW	HNO_3, H_2O_2	10	200	50-249	ET-AAS	
	Pb	Yes	Yes	101	0.3	no	No		HNO_3, H_2O_2	10	200	50-249	ET-AAS	
	Hg		No	97	0.0003	no	No		no one			50-249	GA-UV Det.	
	iAs													
L37	As													From in-house method validation
	Cd		Yes	100	0.002		Dorm4	MW	HNO_3, H_2O_2	20+15	210	250-999	ET-AAS	
	Pb		Yes	100	0.02		Dorm4	MW	HNO_3, H_2O_2	20+15	210	250-999	ET-AAS	
	Hg		Yes	100	0.004		Dorm4					250-999	DMA	
	iAs													
L38	As	Yes	No	100	0.008	Yes	No	MW	HNO_3, H_2O_2	20	200	50-249	ICP-MS	From in-house method validation
	Cd	Yes	No	89	0.002	Yes	No	MW	HNO_3, H_2O_2	20	200	50-249	ICP-MS	
	Pb	Yes	No	100	0.005	Yes	No	MW	HNO_3, H_2O_2	20		50-249	ICP-MS	
	Hg	Yes	No	84	0.008	Yes	No	MW	HNO_3, H_2O_2	20	175	50-249	ICP-MS	
	iAs										175			

Lab		Accredited	Standard method	Recovery (%)	LOD (mg/kg)	CRM for validation of measurement procedure	CRM for instrument calibration	Digestion type	Digestion mixture	Digestion time (min)	Digestion Temp. (°C)	Samples /year	Technique	Measurement uncertainty evaluation
L39	As		Yes	88	0.01	standard solution	standard solution	MW assisted	HNO_3, H_2O_2	30	175	0-49	ICP-MS	From measurement of replicates (precision)
	Cd		Yes	92	0.002	standard solution	standard solution	MW assisted	HNO_3, H_2O_2	30	175	0-49	ICP-MS	
	Pb		Yes	94	0.005	standard solution	standard solution	MW assisted	HNO_3, H_2O_2	30		0-49	ICP-MS	
	Hg		Yes	92	0.01	standard solution	standard solution	MW assisted	HNO_3, H_2O_2	30		0-49	ICP-MS	
	iAs													
L40	**As**		**Yes**	**100.2**	**0.003**	**FAPAS 07199**	**Merck**	**wet**	**HNO_3, H_2O_2**	**960**	**120**	**0-49**	**ET-AAS**	Uncertainty budget (ISO GUM)
	Cd	Yes	Yes	89.93	0.008	BCR 186	Merck	wet	HNO_3, H_2O_2	960	120	0-49	ET-AAS	
	Pb	Yes	Yes	118.79	0.093	BCR 186	Merck	wet	HNO_3, H_2O_2	960	120	0-49	ET-AAS	
	Hg		Yes	91.9	0.001	FAPAS 07199	Merck	wet	HNO_3, H_2O_2	960	120	0-49	FI-Hg syst.	
	iAs													
L41	As		Yes	89	0.115	Yes	No	CMW	HNO_3, H_2O_2	20		50-249	HG-AAS	From in-house method validation
	Cd	Yes	Yes	109	0.023	Yes	No	CMW	HNO_3, H_2O_2	20		50-249	ET-AAS	
	Pb	Yes	Yes	102	0.229	Yes	No	CMW	HNO_3, H_2O_2	20		50-249	ET-AAS	
	Hg		Yes	102	0.027	Yes	No	CMW	HNO_3, H_2O_2	20		0-49	CV-AAS	
	iAs													
L42	As	Yes	Yes	97.91	0.12		SRM 2976	DA	HCl, HNO_3	24 h	450	50-249	HG-AAS	Uncertainty budget (ISO GUM), From in-house method validation
	Cd	Yes	Yes	91.1	0.001		SRM 2976	DA, CMW	HCl, HNO_3	48 h, 50 min	450, 180	50-249	ET-AAS	
	Pb	Yes	Yes	93.12	0.006		-	DA, CMW	HCl, HNO_3	48 h, 50 min	450, 180	50-249	ET-AAS	
	Hg	Yes	Yes	98.36	0.003		SRM 2976	CMW	HNO_3	50 min	180	50-249	CV-AAS	
	iAs													
L43	As		Yes	85.6	0.125	EHMURL--23		DA	HNO_3	1440	440	0-49	HG-AAS	From interlaboratory comparison
	Cd		**No**	**113.3**	**0.005**	**TORT2**		**OW**	**HNO_3**	**60**	**170**	**50-249**	**ET-AAS**	
	Pb		No	96.6	0.05	TORT2		OW	HNO_3	60	170	50-249	ET-AAS	
	Hg		**No**	**107.4**	**0.05**	**TORT2**		**OW**	**HNO_3**	**60**	**170**	**50-249**	**CV-AAS**	
	iAs		No			EURL-HM-23		DA	HNO_3	1020	440	0-49	HG-AAS	
L44	As													From measurement of replicates (precision)
	Cd													
	Pb													
	Hg		No	92	0.025	Yes	No	Heating	HCl, HNO_3	90	80	0-49	CV-AAS	
	iAs													
L45	**As**	**Yes**	**Yes**	**98**	**0.0001**			**MW**	**HNO_3, H_2O_2, H_2O**	**25**	**70-180**	**50-249**	**HG-AAS**	From known uncertainty of standard method (ISO 21748)
	Cd	Yes	Yes	108	0.0003			MW	HNO_3, H_2O_2, H_2O	60	80-230	50-249	AAS	
	Pb	**Yes**	**Yes**	**85**	**0.002**			**MW**	**HNO_3, H_2O_2, H_2O**	**60**	**80-230**	**50-249**	**AAS**	
	Hg	**Yes**	**Yes**	**51**	**0.0004**			**MW**	**HNO_3, H_2O_2, H_2SO_4**	**20**	**180**	**50-249**	**CV-AAS**	
	iAs											Never		

MW refers to microwave, CMW closed microwave, DA to dry ashing, OW to open wet.

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