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EURL-HM-22 Proficiency Test Report

Determination of total As, Cd, Pb, Hg, MeHg and inorganic As in fish

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European Union Reference Laboratory
Heavy Metals in Feed and Food

EURL-HM-22 Proficiency test report

Determination of total As, Cd, Pb, Hg, MeHg and inorganic As in fish

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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-22) for the determination of the mass fraction of total As, Cd, Pb, Hg, methyl Hg (MeHg) and inorganic As (iAs) in fish to support the Commission Regulation (EC) 1881/2006 setting maximum levels for certain contaminants in foodstuffs. This PT was open only to National Reference Laboratories (NRLs).

The reference material "IAEA-436" (Tuna fish flesh homogenate) was used as test item. The finely ground dry powder material was rebottled, relabelled and dispatched to the participants. The reference values of interest were provided by the IAEA, together with an informative value for total Pb. The University of Graz (Austria) was requested to analyse the mass fraction of iAs in the material and reported a truncated value ("less than" 0.005 mg kg^{-1}).

Forty two participants from 30 countries registered to the exercise (all EU Member States plus Iceland and Norway). Only one participant could not report results due to technical instrumental problems.

Laboratory results were rated using *z*- (*z'*- for MeHg) 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 Hg and MeHg; 15% for total As; and 22% for total Cd. No scoring was provided for total Pb and iAs.

More than 92% of the participating NRLs reported satisfactory results (according to the z-score) for total As, Cd, Hg and MeHg, thus confirming their ability in monitoring the maximum levels set by the European Regulation (EC) No 1881/2006 for fish commodities. However, only 9 (out of 41) participants reported results for MeHg.

Most of the laboratories provided realistic estimates of their measurement uncertainties.

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-22 for the determination of total arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), methyl mercury (MeHg) and inorganic Arsenic (iAs) mass fractions in a fish dry powder. This PT was agreed with the Directorate General for Health and Food Safety (DG SANTE) in the annual work programme 2016 of the EURL-HM.

This report summarises the outcome of this 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 in the determination of total As, Cd, Pb, Hg, MeHg and iAs mass fractions in a fish dry powder.

In addition, participants were asked to evaluate the conformity of the analysed fish material according to the maximum levels (MLs) set in Regulation (EC) No 1881/2006 [2].

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 [3].

This PT is identified as EURL-HM-22.

3 Set up of the exercise

3.1 Time frame

The organisation of the EURL-HM-22 exercise was agreed upon by the NRL network at the 10th EURL-HM Workshop held in Brussels on September 28-29, 2015. The exercise was announced on the JRC webpage on February 18, 2016 (Annex 2) and the same day an invitation letter was sent to all NRLs of the network via e-mail (Annex 3). The registration deadline was set to April 1, 2016. Samples were sent to participants on April 12, 2016. 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 May 13, 2016.

3.2 Confidentiality

The procedures used for the organisation of PTs, are accredited according to ISO 17043:2010 [3] and guarantee that the identity of the participants and the information provided by them is treated as confidential.

3.3 Distribution

Each participant received:

- One bottle of the test item (approx. 8 g of material);
- The "Test item accompanying letter" (Annex 4); and
- A "Confirmation of receipt form" to be sent back to JRC-Geel after receipt of the test item (Annex 5).

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, MeHg and iAs in a fish dry powder.

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

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 6).

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

The reference material "IAEA-436, *Tuna Fish Flesh Homogenate*" was used as the EURL-HM-22 test item. Sufficient number of IAEA-436 bottles were purchased from the International Atomic Energy Agency (IAEA).

The purchased material was rebottled and relabelled at the JRC-Geel. The material was pooled in an acid washed plastic drum, mixed in a DynaMIX CM200 mixer and the new vials were filled manually in a clean cell. These vials were previously cleaned with 2 % nitric acid and rinsed with Type 1 water and Milli-Q water, then air-dried in a clean cell. All the filled vials were labelled and kept at 4°C until dispatch.

The IAEA informed the EURL-HM that this material is currently being re-certified.

5 Assigned values

5.1 Reference values and corresponding uncertainties

The assigned values and expanded uncertainties (x_{pt} and $U(x_{pt})$) of four measurands (mass fractions of total As, Cd, Hg and MeHg in tuna fish finely ground dry powder), obtained in the frame of the ongoing re-certification exercise, were provided by the IAEA [4] together with an informative value for total Pb (Table 1).

Note: The values presented in Table 1 ("new" certified values - set as assigned values in the present exercise) may differ from the "old" *recommended values* presented on the IAEA website.

Furthermore, the EURL-HM requested the Institute of Chemistry of the University of Graz (Austria) to determine the mass fraction of iAs in the test item. This laboratory was selected based on its previously demonstrated measurement capabilities. Six independent measurements were performed and the laboratory reported a truncated value ("less than" 0.005 mg kg^{-1}). The following analytical procedure was applied:

> *For the iAs determination, 500 mg of the test item were weighed with a precision of 0.1 mg into 50 mL polypropylene tubes, and a solution (10 mL) of 100 mmol L^{-1} trifluoroacetic acid containing 1% (v/v) of a 30% H_2O_2 solution was added. The*

samples were extracted with a Gesellschaft fur Labortechnik GFL-1083 (Burkwedel, Germany) shaking water bath at 95°C for 60 minutes. After cooling to room temperature the extracts were centrifuged for 15 min at 4700 g. An aliquot of 1 mL was transferred to Eppendorf vials and centrifuged for 15 min at 21300 g. The supernatant was used directly for HPLC-ICPMS analysis using an Agilent 1100 series HPLC (Waldbronn, Germany).

5.2 Standard deviation of the proficiency test assessment, σ_{pt}

The relative standard deviations for PT assessment (σ_{pt}, in %) presented in Table 1 were calculated using the Horwitz equation modified by Thompson [5].

Table 1: Assigned value x_{pt} (referring to dry mass), corresponding expanded uncertainty $U(x_{pt})$ (k=2), and standard deviation for the PT assessment σ_{pt} The test item was the IAEA-436 reference material consisting of a finely ground dry powder of a tuna fish homogenate.

	$X_{pt} \pm U(x_{pt})$ in mg kg^{-1}	σ_{pt} in mg kg^{-1} (%)	$u(x_{pt})/\sigma_{pt}$ --
As	1.98 ± 0.20	0.30 (15%)	0.33
Cd	0.0490 ± 0.0043	0.0108 (22%)	0.20
Hg	4.26 ± 0.36	0.55 (13%)	0.33
MeHg *(a)*	3.62 ± 0.47	0.47 (13%)	0.50
Pb	(0.012) *(b)*	--	
iAs	--	--	

(a) expressed as Hg

(b) informative value

6 Evaluation of results

6.1 Scores and evaluation criteria

Individual laboratory performance was expressed in terms of z- and ζ-scores according to ISO 13528:2015 [6]:

$$z_i = \frac{x_i - x_{pt}}{\sigma_{pt}} \qquad \text{Eq. 1}$$

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

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 [6], when $u(x_{pt}) > 0.3\ \sigma_{pt}$ (as for MeHg, see Table 1) *the uncertainty of the assigned value can be taken into account by expanding the denominator of the z-score and calculating the z'-score,* as follows:

$$z'_i = \frac{x_i - x_{pt}}{\sqrt{\sigma_{pt}^2 + u^2(x_{pt})}} \qquad \text{Eq. 3}$$

The interpretation of the z-, z'- and ζ- scores is done according ISO 13528:2015 [3]:

|score| ≤ 2	satisfactory performance	(green in Annexes 7-10,14)
2 < |score| < 3	questionable performance	(yellow in Annexes 7-10,14)
|score| ≥ 3	unsatisfactory performance	(red in Annexes 7-10,14)

The z- and 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-score states 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 standard measurement uncertainty reported by the laboratory $u(x_i)$. The ζ-score includes all parts of a measurement result, namely the expected value (assigned value), the corresponding measurement uncertainty in the unit of the result as well as the standard uncertainty of the reported values. An unsatisfactory ζ-score can either be caused by an inappropriate estimation of the mass fraction, 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 √3, as recommended by Eurachem and CITAC [7].

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": $u_{min} \leq u_{lab} \leq u_{max}$). 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 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_{ref} 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 two NRLs from 30 countries registered to this PT, covering all Member States plus Iceland and Norway. One laboratory (L35) could not report any results due to technical problems with the instrumentation. The participants having reported results are listed in the "Acknowledgment" section.

Most of the laboratories reported results for As, Cd, Hg and Pb, while only nine results were reported for MeHg (Table 2).

Table 2: Overview of the number of reported results per measurand (out of 41)

	Reported Results	Comments
As	35 (85 %)	No results from L05; L11; L19; L29; L31; L32
Cd	41 (100 %)	
Pb	41 (100 %)	Of which 19 reported "*less than*" values
Hg	39 (95 %)	No results from L11; L19
MeHg	9 (22 %)	
iAs	21 (51 %)	Of which 10 reported "*less than*" values

6.3 Laboratory results and scorings

6.3.1 Performances

Annexes 7 to 12 present the reported results as tables and graphs for each measurand, where NRLs are denoted as "LXX". The corresponding Kernel density plots, obtained using the software available from the Statistical Subcommittee of the Analytical Methods Committee of the UK Royal Society of Chemistry [8] are also included.

The laboratory performance for the determination of total As, Cd and Hg were assessed using the z- and ζ-scores. However, the ISO 13528:2015 recommendation was applied for MeHg (for which $u(x_{pt}) > 0.3\ \sigma_{pt}$, see Table 1) and the z'-score was used instead of the z-score.

Having only an informative value provided by the IAEA for the total Pb and a truncated value ("less than") reported by the Graz University for iAs, no assigned values were established and therefore no performance scoring were computed for these two measurands.

Total As, Cd, Hg and MeHg

Figures 1 and 2 present the laboratory performances for total As, Cd, Hg and MeHg, assessed by the z- (z'- for MeHg) and ζ-scores. Most of the participants having reported results performed satisfactorily: above 92% for the z-score and 85% for the ζ-scores.

Twenty nine (out of 41) laboratories performed satisfactorily for the determination of three measurands (total As, Cd and Hg). Only nine laboratories analysed MeHg.

No direct correlations could be found between the analytical methods used by the participants (see Annex 14) and the quality of the reported results.

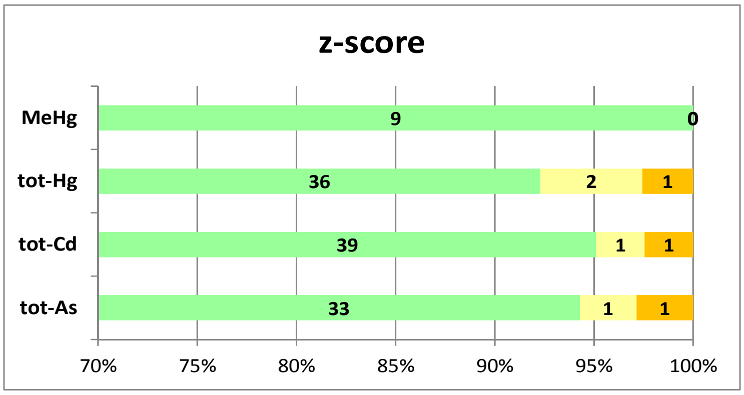

Figure 1:

Overview of laboratory performance per measurand according to z-scores (z'-score in the case of MeHg).

Corresponding number of laboratories indicated in the graph.

Satisfactory (green); Questionable (yellow) or Unsatisfactory (orange)

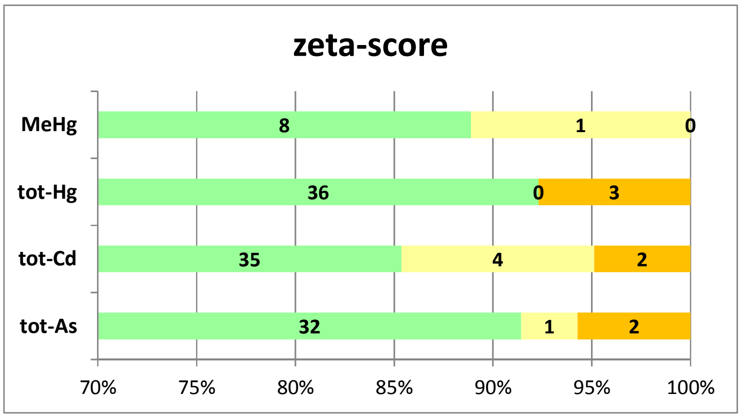

Figure 2:

Overview of laboratory performance per measurand according to ζ-scores.

Corresponding number of laboratories indicated in the graph.

Satisfactory (green); Questionable (yellow) or Unsatisfactory (orange)

Inorganic As

The laboratory performances for the determination of iAs were not assessed, since the selected expert laboratory reported a truncated value ("less than" 0.005 mg kg^{-1}).

From the 21 laboratories having performed the analysis, 10 laboratories reported "less than" values. The numerical values submitted (9 out of 11) range from 0.010 to 0.056 mg kg^{-1}, with ICP-MS results lower than the HG-AAS ones (Annex 12). However, these results are similar to the experimental data published by Sloth *et al.* [9], Raber *et al.* [10] and Muñoz *et al*. [11]. The scatter of results observed may be attributed to the different analytical approaches used and/or to interferences from methyl arsonate and arsenolipids present in the fish matrix [12]. Further investigation is required.

Total Pb

All 41 laboratories reported results for total Pb: 22 numerical results and 19 truncated "less than" values (mostly obtained with ICP-MS). The corresponding Kernel density plot (Annex 11) presents a bimodal distribution. Eight ICP-MS and AAS results (5+3) and seven truncated values are in the range of the indicative value of 0.012 mg kg^{-1} provided by the reference material producer. The higher reported mass fractions (of *ca*. 0.045 mg kg^{-1}) are similar to the overestimated results reported for lead in the frame of EURL-HM-20 [13] which were attributed to laboratory contamination. Such a contamination (of ca. 0.025 mg kg^{-1}) would not be detected when analysing samples with lead mass fractions close to the ML set in the legislation (0.3 mg kg^{-1}), as it would be covered by the measurement uncertainty.

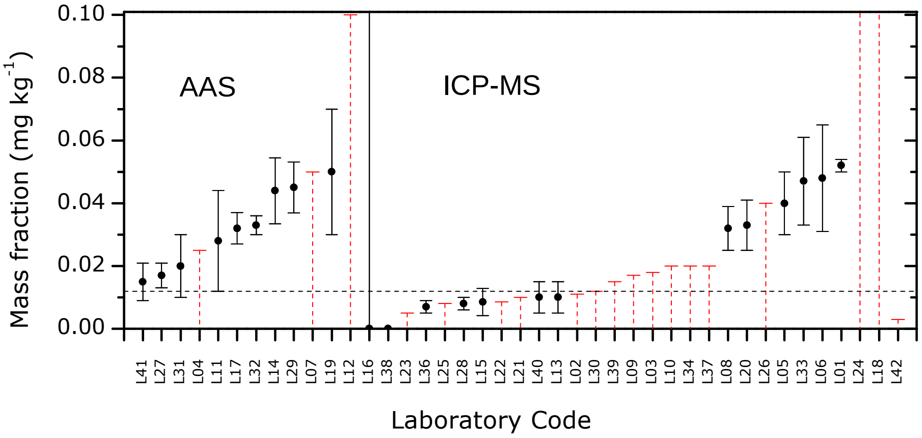

Figure 3: *Lead mass fractions reported by participants, sorted by techniques. The horizontal dashed line represents the "indicative value" provided by the IAEA, while the reported truncated values are presented by drop-down lines.*

6.3.2 Uncertainties

Figure 3 presents the uncertainty assessment per measurand. Most of the participants (around 60%) reported reasonable measurement uncertainty estimates (case "a": $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$). Those that were "mathematically" flagged as Case "c" ($u(x_i) > \sigma_{pt}$) reported uncertainties of the order of 15% for Hg or 17% for As, which were slightly above the corresponding σ_{pt} (set to 13% and 15%, respectively). L16 may have systematically reported uncertainties in percent (and not in mg kg^{-1}; uncertainties flagged in "orange" in Annexes 7-9). Four (out of the 13) questionable and unsatisfactory ζ-scores are due to underestimated uncertainties (Case "b" for L21-Cd; L12,L38-Hg; and L27-MeHg).

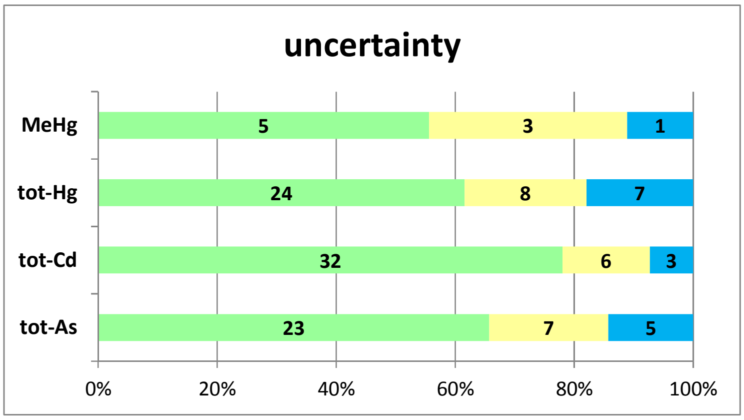

Figure 3:

Overview of uncertainties reported per measurand.

The corresponding number of laboratories indicated in the graph.

Case "a" (green): $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$;
Case "b" (yellow): $u(x_i) < u(x_{pt})$; and
Case "c" (blue): $u(x_i) > \sigma_{pt}$

6.3.3 Compliance

The following maximum levels (MLs) are set in the European regulation (EC) No 1881/2006 [2] for muscle meat of tuna, expressed as mg kg^{-1} wet weight: 0.3 for Pb; 0.10-0.15 for Cd; and 1.0 for Hg. In addition, a lower ML (0.5 mg kg^{-1}) is set for Hg in other fishery products and fish muscle meats.

The assigned values for Cd and Pb are well below the corresponding MLs mentioned above.

The assigned value for Hg in the investigated tuna dried powder of 4.26 ± 0.36 (k=2) mg kg^{-1} dry mass (cf. Table 1) would be equivalent to 0.85 ± 0.07 (k=2) mg kg^{-1} wet weight, assuming an average water content of 80% in the tuna meat. Since 0.85 + 0.07 is below 1.0 mg kg^{-1}, the tuna fish homogenate is to be considered as compliant. This would not be the case if the sample to be analysed would have been another fishery product or fish muscle meat (with the lower ML).

Participants were request to assess the compliance of the fish powder distributed, without knowing the type of fish they analysed. Thirty eight laboratories reported mass fraction above 3 mg kg^{-1} dry mass for total Hg. Most of them concluded that the test item was non-compliant, stating that their results (referred to dry mass) exceeded the MLs set in the legislation (Annex 13). Only four laboratories (L03, L09, L33, L34 and L36) stated correctly that compliance could not be properly assessed, due to the lack of information about the fish species analysed and the water content in the natural (non-lyophilised) fish. L03 submitted the correct reasoning but selected the lower ML for his assessment.

6.3.4 Additional information from the questionnaire

The questionnaire was answered by 35 (out of 41) participants. Several approaches were used to evaluate measurement uncertainties (Table 4). The majority of the NRLs (28 out of 42) report uncertainty to their customers. A total of 111 out of 124 results were assessed with satisfactory ζ-score, from which 77 corresponded to realistic uncertainty estimates (case "a"). 72% of the latter were obtained by laboratories reporting regularly measurement uncertainty to their customers.

Table 4: *Approaches used to estimate measurement uncertainties*
Multiple selections were possible.

Approach	**Number of labs.**
According to ISO-GUM	13
According to ISO 21748	1
Derived from a single-laboratory validation study	23
Determined as standard deviation of replicate measurements	11
Estimation based on judgment	1
Derived from inter-comparison data	10
According to the NORDTEST guidelines	1

Laboratories were asked to report the limits of detection (LODs) of the methods used for the determination of the six measurands. Annex 14 presents LODs, the general experimental conditions and the techniques used. Large discrepancies in reported LODs are observed even among laboratories using the same technique.

Thirty laboratories determined recovery factors ranging from 80 to 120 %. The few laboratories having reported recoveries lower than 80 % or higher than 120 % must be aware that such recoveries indicate a significant bias in their analytical method and that corrective actions must be undertaken. Two approaches for the determination of recoveries were used: spiking and use of reference materials.

All of the NRLs stated that they are accredited for one or more of the investigated measurands, according to ISO/IEC 17025.

No correlation between performance and experience (evaluated as number of analyses per year) on the specific analysis could be identified for any of the measurands.

7 Conclusion

The EURL-HM-22 PT was organised in 2016 to assess the analytical capabilities of the NRLs from the EU using the IAEA-436 (Tuna fish flesh homogenate) reference material as test item.

The overall performance of the participants in the determination of total As, Cd, Hg and MeHg was satisfactory. This confirms the analytical capabilities of the NRLs to enforce the European Regulation (EC) No 1881/2006 setting levels for certain contaminants in foodstuffs. However, only few laboratories performed the analyses for MeHg and reported results (9 out of 41).

Since there were no assigned values for total Pb and iAs, the laboratory performances could not be evaluated for these measurands.

Overall, NRLs reported good measurement uncertainty estimates, thus demonstrating the effectiveness of the various PTs and training courses organised by the EURL-HM in the past 10 years.

Acknowledgements

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 one laboratories listed hereafter are kindly acknowledged for their participation in the PT.

Organisation	***Country***
AGES GmbH	*Austria*
CODA-CERVA	*Belgium*
CLVCE	*Bulgaria*
Croatian National Institute of Public Health	*Croatia*
Croatian Veterinary Institute	*Croatia*
State General Laboratory	*Cyprus*
Central Institute for Supervising and Testing in Agriculture (UKZUZ)	*Czech Republic*
State Veterinary Institute Olomouc	*Czech Republic*
Danish Veterinary and Food Administration	*Denmark*
Agricultural Research Centre	*Estonia*
Veterinary and Food Laboratory	*Estonia*
Finnish Customs Laboratory	*Finland*
Finnish Food Safety Authority Evira	*Finland*
French Agency for food, Environmental and Occupational Health and safety (ANSES)	*France*
Laboratoire SCL de Bordeaux	*France*
Federal Office for Consumer Protection and Food Safety (BVL)	*Germany*
General Country State Laboratory	*Greece*
Veterinary Center of Athens	*Greece*
National Food Chain Office Food and Feed Safety	*Hungary*
National Food Chain Safety Office, Food and Feed Safety Directorate	*Hungary*
Matis	*Iceland*
Health Service Executive (HSE)	*Ireland*
Istituto Superiore Di Sanita' (ISS)	*Italy*
Istituto Zooprofilattico del Piemonte, Liguria e Valle d'Aosta	*Italy*
Institute of Food Safety, Animal Health and Environment	*Latvia*
National Food and Veterinary Risk Assessment Institute	*Lithuania*
Laboratoire National de Santé	*Luxembourg*
Public Health Laboratory	*Malta*
RIKILT	*Netherlands*
Alcontrol Stjørdal	*Norway*
National Institute of Nutrition and Seafood Research (NIFES)	*Norway*
National Institute of Public Health-National Institute of Hygiene	*Poland*
National Veterinary Research Institute in Pulawy	*Poland*
Instituto Português do Mar e da Atmosfera (IPMA)	*Portugal*
Institute for Hygiene and Veterinary Public Health	*Romania*
Sanitary Veterinary and Food Safety Directorate Bucharest	*Romania*
State veterinary and food institute Dolný Kubín, Veterinary and food institute Košice	*Slovakia*
National Laboratory of Health, Environment and Food (NLZOH)	*Slovenia*
Laboratorio Arbitral Agroalimentario (MAGRAMA)	*Spain*
National Food Agency	*Sweden*
FERA Science Ltd	*United Kingdom*

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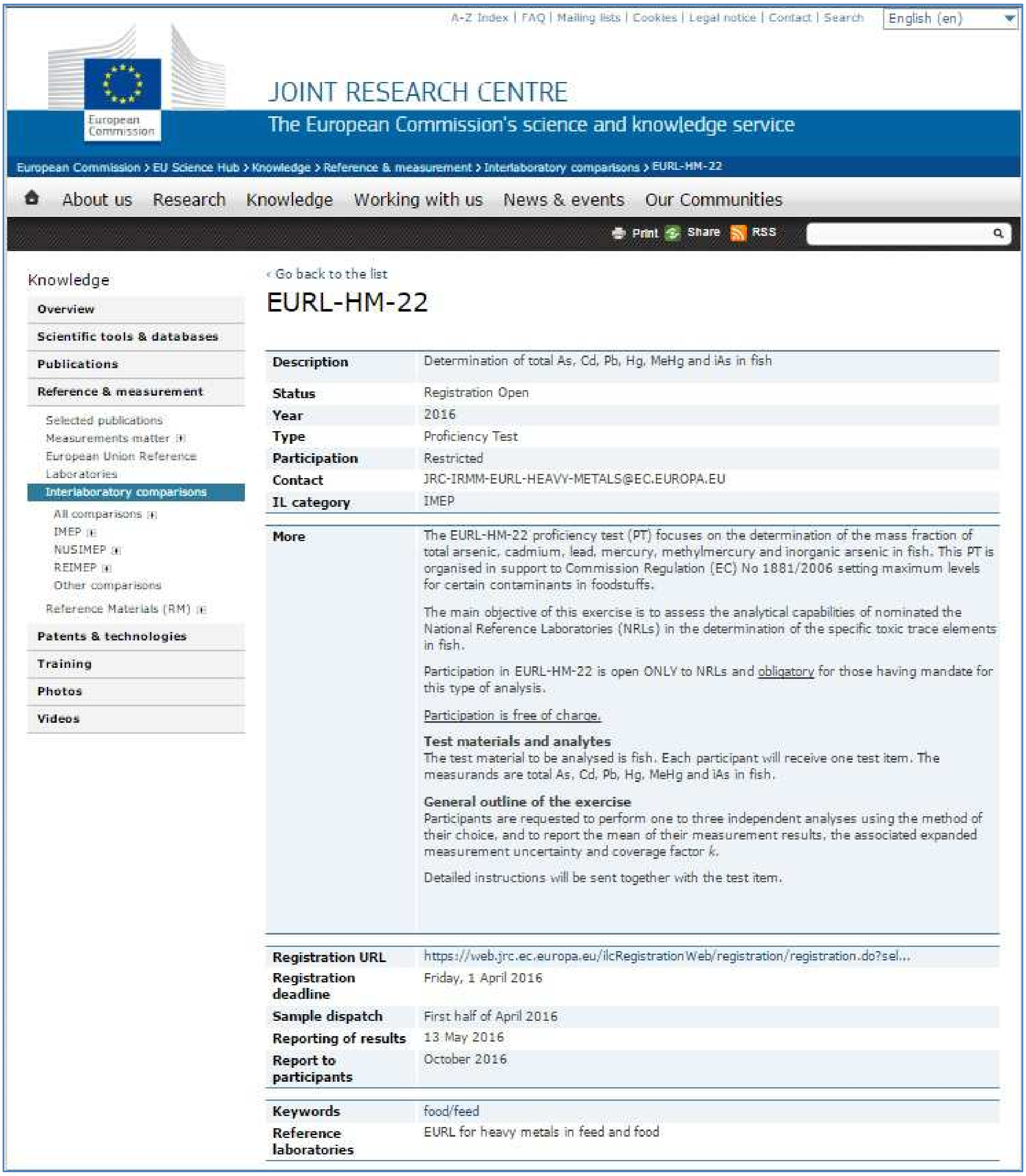
Annexes

Annex 1: List of abbreviations

AMC	Analytical Methods Committee of the Royal Society of Chemistry
CV-AAS	Cold Vapour Atomic Absorption Spectrometry
DG SANTE	Directorate General for Health and Food Safety
DMA	Direct Mercury Analyser (also called Elemental Mercury Analyzer, EMA)
EFSA	European Food Safety Authority
ET-AAS	Electro Thermal – Atomic Absorption Spectrometry (also called Graphite Furnace Atomic Absorption Spectroscopy, GF-AAS)
FIAS-AAS	Flow Injection Analysis System - Atomic Absorption Spectrometry
FIMS	Flow Injection Mercury System
GF-AAS	Graphite Furnace – 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-(Q)MS	Inductively Coupled Plasma –(Quadrupole) Mass Spectrometry
ID-GC-ICP-MS	Isotope Dilution – Gas Chromatography – ICP-MS
JRC	Joint Research Centre
LOD	Limit of detection
NRL	National Reference Laboratory
PT	Proficiency Test
Z-ET-AAS	Zeeman ET-AAS

Annex 2: JRC web announcement



EURL-HM-22

Description	Determination of total As, Cd, Pb, Hg, MeHg and iAs in fish
Status	Registration Open
Year	2016
Type	Proficiency Test
Participation	Restricted
Contact	JRC-IRMM-EURL-HEAVY-METALS@EC.EUROPA.EU
IL category	IMEP

More

The EURL-HM-22 proficiency test (PT) focuses on the determination of the mass fraction of total arsenic, cadmium, lead, mercury, methylmercury and inorganic arsenic in fish. This PT is organised in support to Commission Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs.

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

Participation in EURL-HM-22 is open ONLY to NRLs and obligatory for those having mandate for this type of analysis.

Participation is free of charge.

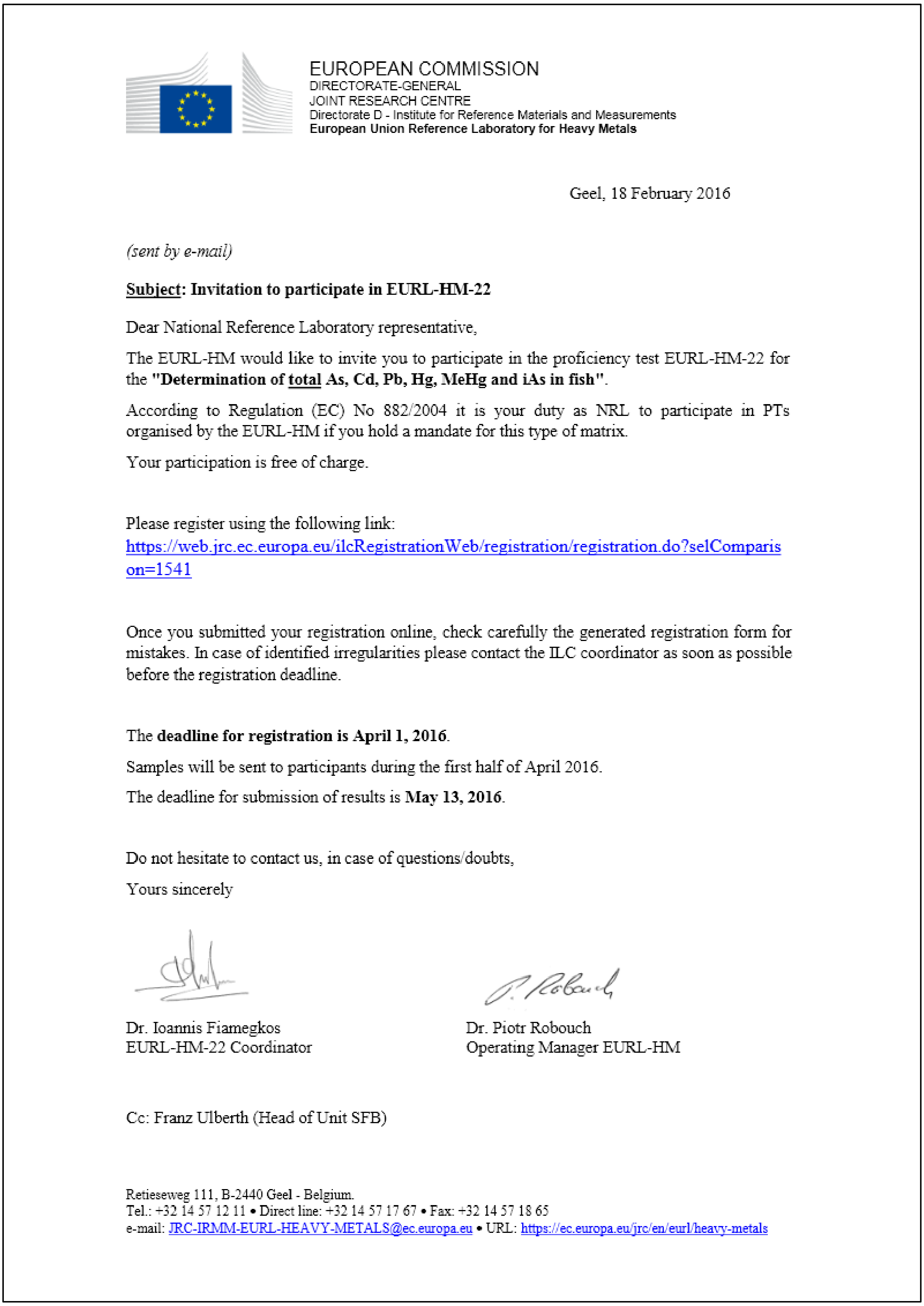
Test materials and analytes
The test material to be analysed is fish. Each participant will receive one test item. The measurands are total As, Cd, Pb, Hg, MeHg and iAs in fish.

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	Friday, 1 April 2016
Sample dispatch	First half of April 2016
Reporting of results	13 May 2016
Report to participants	October 2016
Keywords	food/feed
Reference laboratories	EURL for heavy metals in feed and food

Annex 3: Invitation letter to NRLs



EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
European Union Reference Laboratory for Heavy Metals

Geel, 18 February 2016

(sent by e-mail)

Subject: Invitation to participate in EURL-HM-22

Dear National Reference Laboratory representative,

The EURL-HM would like to invite you to participate in the proficiency test EURL-HM-22 for the **"Determination of total As, Cd, Pb, Hg, MeHg and iAs in 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=1541

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

The **deadline for registration is April 1, 2016**.

Samples will be sent to participants during the first half of April 2016.

The deadline for submission of results is **May 13, 2016**.

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

Yours sincerely

P. Robouch

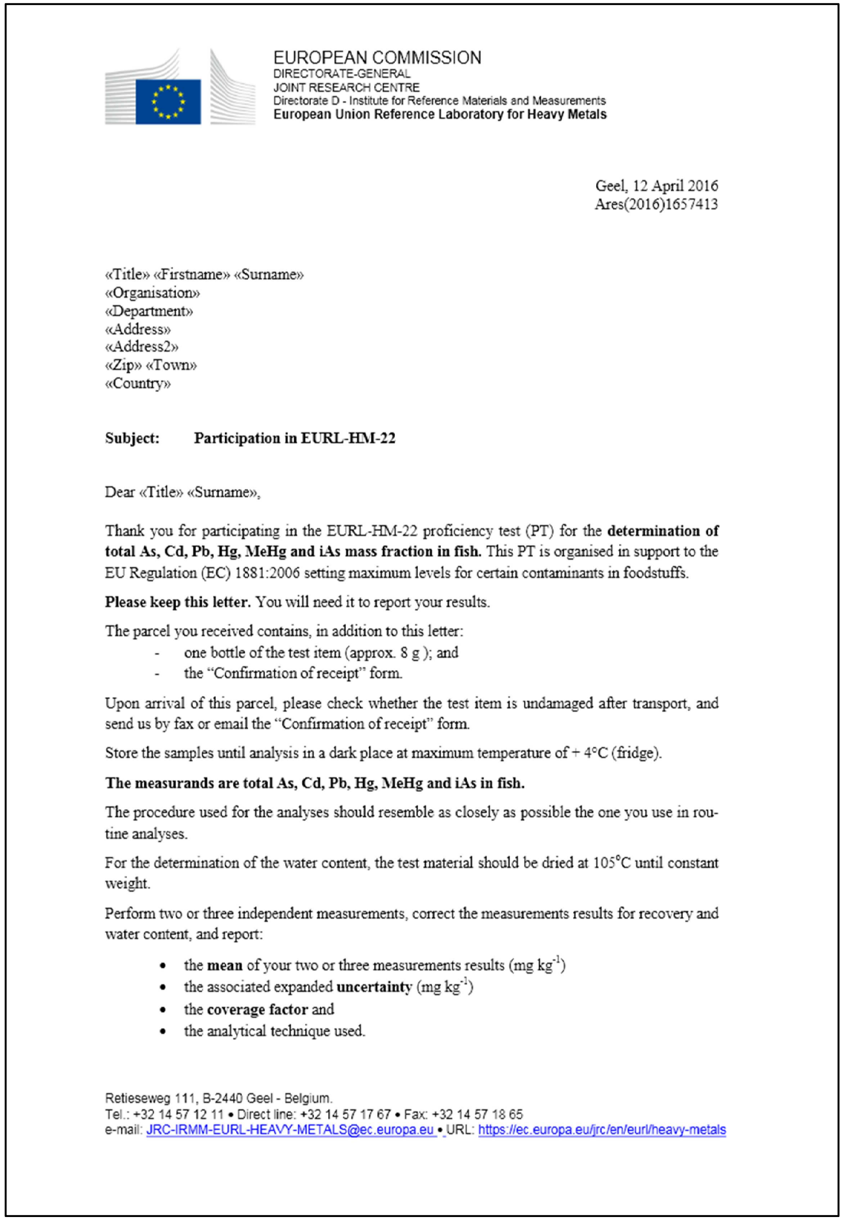
Dr. Ioannis Fiamegkos
EURL-HM-22 Coordinator

Dr. Piotr Robouch
Operating Manager EURL-HM

Cc: Franz Ulberth (Head of Unit SFB)

Retieseweg 111, B-2440 Geel - Belgium.
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 17 67 • Fax: +32 14 57 18 65
e-mail: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu • URL: https://ec.europa.eu/jrc/en/eurl/heavy-metals

Annex 4: "Test item accompanying letter"



EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
European Union Reference Laboratory for Heavy Metals

Geel, 12 April 2016
Ares(2016)1657413

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

Subject: Participation in EURL-HM-22

Dear «Title» «Surname»,

Thank you for participating in the EURL-HM-22 proficiency test (PT) for the **determination of total As, Cd, Pb, Hg, MeHg and iAs mass fraction in fish.** This PT is organised in support to the EU Regulation (EC) 1881:2006 setting maximum levels for certain contaminants in foodstuffs.

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

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

- one bottle of the test item (approx. 8 g); and
- the "Confirmation of receipt" form.

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 maximum temperature of + 4°C (fridge).

The measurands are total As, Cd, Pb, Hg, MeHg and iAs in fish.

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

For the determination of the water content, the test material should be dried at 105°C until constant weight.

Perform two or three independent measurements, correct the measurements results for recovery and water content, and report:

- the **mean** of your two or three measurements results (mg kg^{-1})
- the associated expanded **uncertainty** (mg kg^{-1})
- the **coverage factor** and
- the analytical technique used.

Retieseweg 111, B-2440 Geel - Belgium.
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 17 67 • Fax: +32 14 57 18 65
e-mail: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu • URL: https://ec.europa.eu/jrc/en/eurl/heavy-metals

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.**

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

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

The deadline for submission of results is **13/05/2016**.

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,

Ioannis Fiamegkos (PhD)
EURL-HM-22 Coordinator

Cc: F. Ulberth (Head of Unit, Standards for Food Bioscience)

Retieseweg 111, B-2440 Geel - Belgium.
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 17 67 • Fax: +32 14 57 18 65
e-mail: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu • URL: https://ec.europa.eu/jrc/en/eurl/heavy-metals
2

Annex 5: Confirmation of receipt form

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
European Union Reference Laboratory for Heavy Metals

Geel, 12 April 2016
Ares(2016)1657413

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

Subject: **"Confirmation receipt" form**
EURL-HM-22 - Heavy Metals in 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 ______________________

____

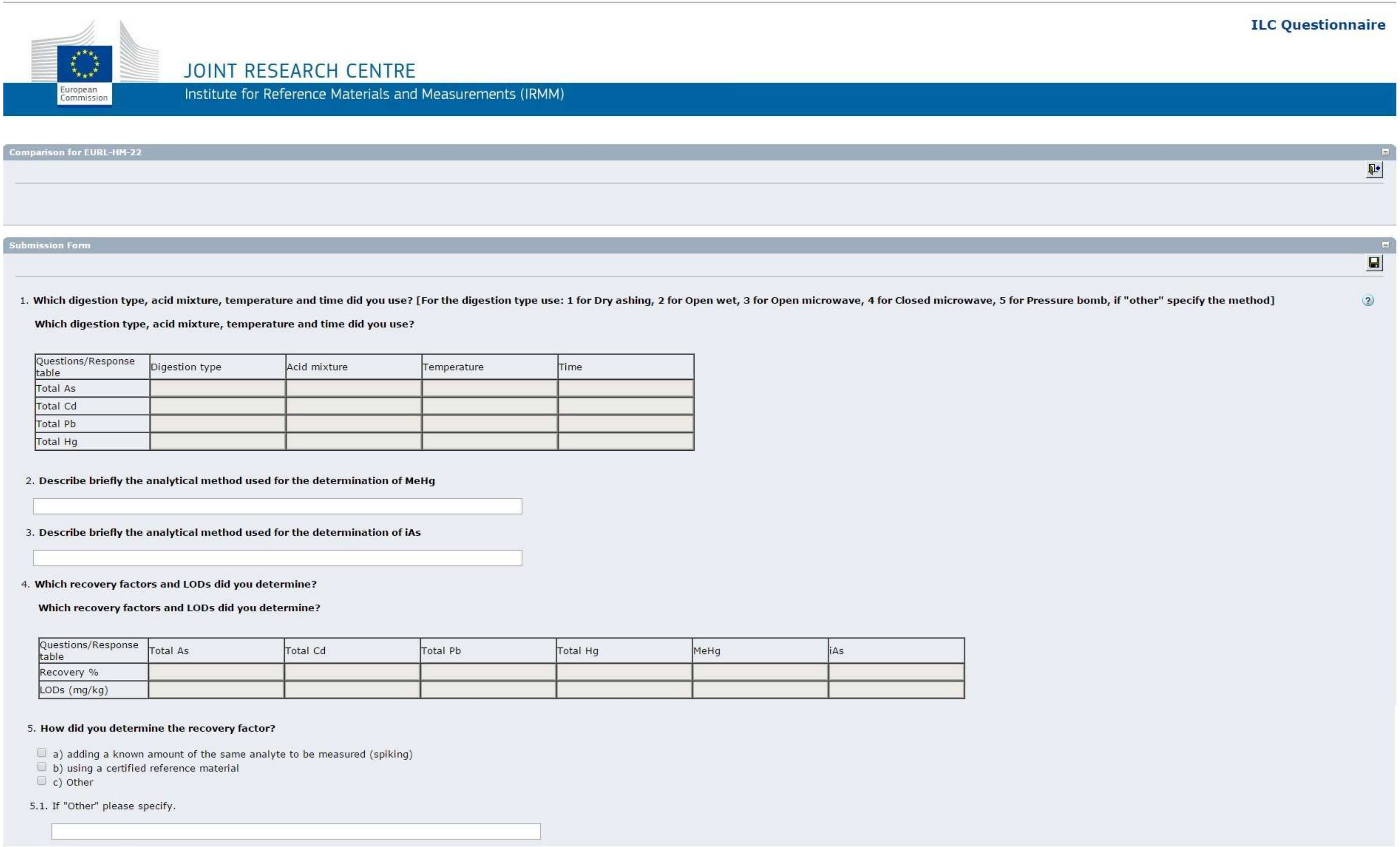
Signature ______________________

Thank you for returning this form by fax or email to:

Dr Ioannis Fiamegkos
EURL-HM-22 Coordinator
Fax : +32-14-571865
e-mail : JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu

Retieseweg 111, B-2440 Geel - Belgium.
Tel.: +32 14 57 12 11 • Direct line: +32 14 57 17 67 • Fax: +32 14 57 18 65
e-mail: JRC-IRMM-EURL-HEAVY-METALS@ec.europa.eu • URL: https://ec.europa.eu/jrc/en/eurl/heavy-metals

Annex 6: Questionnaire



ILC Questionnaire

JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements (IRMM)

Comparison for EURL-HM-22

Submission Form

1. Which digestion type, acid mixture, temperature and time did you use? [For the digestion type use: 1 for Dry ashing, 2 for Open wet, 3 for Open microwave, 4 for Closed microwave, 5 for Pressure bomb, if "other" specify the method]

Which digestion type, acid mixture, temperature and time did you use?

Questions/Response table	Digestion type	Acid mixture	Temperature	Time
Total As				
Total Cd				
Total Pb				
Total Hg				

2. Describe briefly the analytical method used for the determination of MeHg

3. Describe briefly the analytical method used for the determination of iAs

4. Which recovery factors and LODs did you determine?

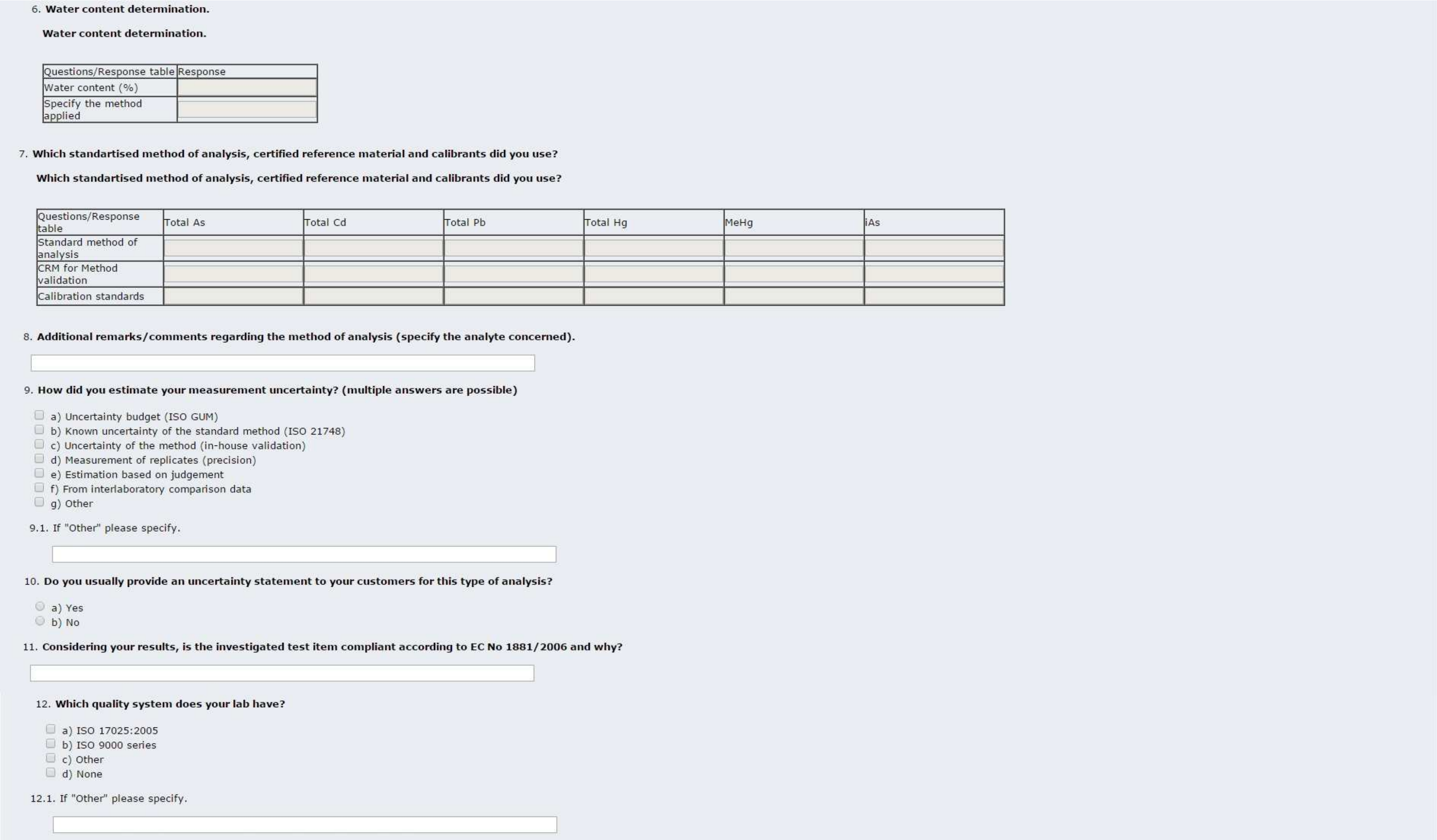
Which recovery factors and LODs did you determine?

Questions/Response table	Total As	Total Cd	Total Pb	Total Hg	MeHg	iAs
Recovery %						
LODs (mg/kg)						

5. How did you determine the recovery factor?

☐ a) adding a known amount of the same analyte to be measured (spiking)
☐ b) using a certified reference material
☐ c) Other

5.1. If "Other" please specify.



6. **Water content determination.**

Water content determination.

Questions/Response table	Response
Water content (%)	
Specify the method applied	

7. **Which standartised method of analysis, certified reference material and calibrants did you use?**

Which standartised method of analysis, certified reference material and calibrants did you use?

Questions/Response table	Total As	Total Cd	Total Pb	Total Hg	MeHg	iAs
Standard method of analysis						
CRM for Method validation						
Calibration standards						

8. **Additional remarks/comments regarding the method of analysis (specify the analyte concerned).**

9. **How did you estimate your measurement uncertainty? (multiple answers are possible)**

☐ a) Uncertainty budget (ISO GUM)
☐ b) Known uncertainty of the standard method (ISO 21748)
☐ c) Uncertainty of the method (in-house validation)
☐ d) Measurement of replicates (precision)
☐ e) Estimation based on judgement
☐ f) From interlaboratory comparison data
☐ g) Other

9.1. If "Other" please specify.

10. **Do you usually provide an uncertainty statement to your customers for this type of analysis?**

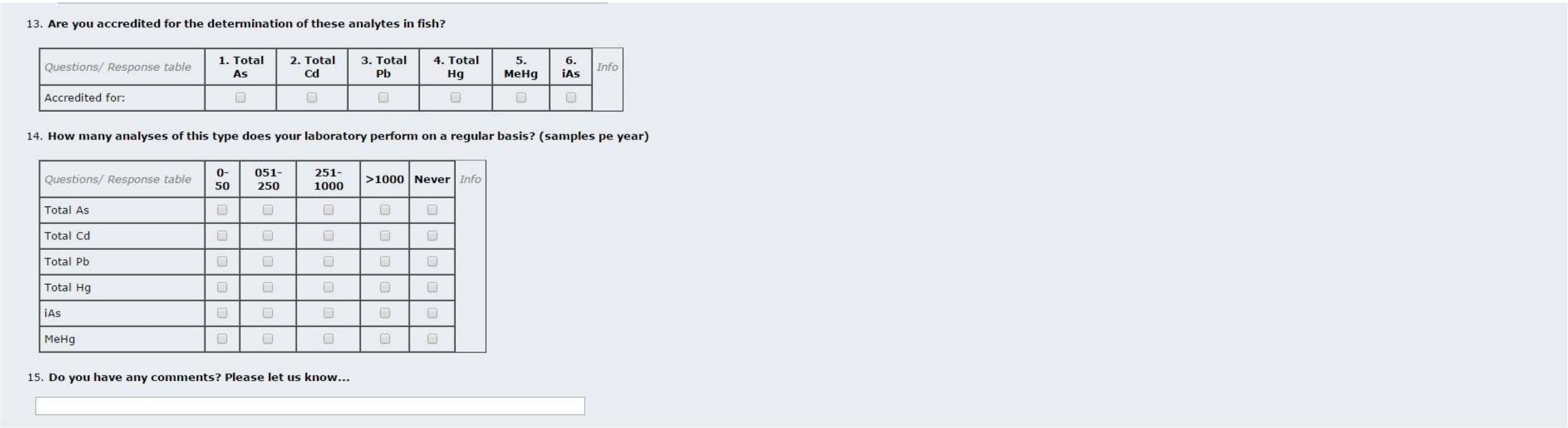
○ a) Yes
○ b) No

11. **Considering your results, is the investigated test item compliant according to EC No 1881/2006 and why?**

12. **Which quality system does your lab have?**

☐ a) ISO 17025:2005
☐ b) ISO 9000 series
☐ c) Other
☐ d) None

12.1. If "Other" please specify.



13. **Are you accredited for the determination of these analytes in fish?**

Questions/ Response table	**1. Total As**	**2. Total Cd**	**3. Total Pb**	**4. Total Hg**	**5. MeHg**	**6. iAs**	*Info*
Accredited for:	☐	☐	☐	☐	☐	☐	

14. **How many analyses of this type does your laboratory perform on a regular basis? (samples pe year)**

Questions/ Response table	**0-50**	**051-250**	**251-1000**	**>1000**	**Never**	*Info*
Total As	☐	☐	☐	☐	☐	
Total Cd	☐	☐	☐	☐	☐	
Total Pb	☐	☐	☐	☐	☐	
Total Hg	☐	☐	☐	☐	☐	
iAs	☐	☐	☐	☐	☐	
MeHg	☐	☐	☐	☐	☐	

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

Annex 7: Results for total As

Assigned values: x_{pt} = 1.98; $U(x_{pt})$ = 0.20 (k=2); and σ_{pt} = 0.297; all values in mg kg^{-1}, related to dry mass

Lab Code	x_i	$U(x_i)$	k[a]	technique	$u(x_i)$	z-score[b]	ζ-score	uncert.[c]
L01	2.04	0.10	2	ICP-MS	0.05	0.20	0.54	b
L02	2.47	0.21	2	ICP-MS	0.105	1.65	3.38	a
L03	1.92	0.38	2	ICP-MS	0.19	-0.20	-0.28	a
L04	2.13	0.21	2	HG-AAS	0.105	0.51	1.03	a
L05								
L06	1.4	0.6	2	ICP-MS	0.3	-1.95	-1.83	c
L07	1.871	0.187	2	HG-AAS	0.0935	-0.37	-0.80	b
L08	1.9	0.4	2	Z-ETA-AAS	0.2	-0.27	-0.36	a
L09	2.207	0.265	2	ICP-QMS	0.1325	0.76	1.37	a
L10	2.145	0.236	2	ICP-MS	0.118	0.56	1.07	a
L11								
L12	2.07	0.686	2	HG-AAS	0.343	0.30	0.25	c
L13	2.0	0.8	2	ICP-QMS	0.4	0.07	0.05	c
L14	1.99	0.55	2	HG-AAS	0.275	0.03	0.03	a
L15	2.1	0.12	2	ICP-QMS	0.06	0.40	1.03	b
L16	5.784	20	√3	ICP-MS	11.547	12.81	0.33	c
L17	1.8	0.4	2	ETAAS	0.2	-0.61	-0.80	a
L18	1.95	0.195	2	ICP-MS	0.0975	-0.10	-0.21	b
L19								
L20	2.14	0.54	2	ICP-MS	0.27	0.54	0.56	a
L21	2.05	0.37	2	ICP-MS	0.185	0.24	0.33	a
L22	2.2	0.5	2	ICP-QMS	0.25	0.74	0.82	a
L23	2.45	0.24	2	ICP-MS	0.12	1.58	3.01	a
L24	2.82	0.584	2	ICP-MS	0.292	2.83	2.72	a
L25	2.05	0.41	2	ICP-MS	0.205	0.24	0.31	a
L26	2.05	0.4	2	ICP-MS	0.2	0.24	0.31	a
L27	1.86	0.21	2	HG-AAS	0.105	-0.40	-0.83	a
L28	2.1	0.36	2	ICP-MS	0.18	0.40	0.58	a
L29								
L30	1.85	0.13	2	ICP-MS	0.065	-0.44	-1.09	b
L31								
L32								
L33	1.880	0.154	2	ICP-QMS	0.077	-0.34	-0.79	b
L34	1.9	0.60	2	ICP-MS	0.3	-0.27	-0.25	c
L36	2.05	0.32	2	ICP-MS	0.16	0.24	0.37	a
L37	2.1	0.4	2	HPLC-ICP-MS	0.2	0.40	0.54	a
L38	2.0	0.5	2	ICP-MS	0.25	0.07	0.07	a
L39	1.99	0.17	2	ICP-QMS	0.085	0.03	0.08	b
L40	1.850	0.342	2	ICP-MS	0.171	-0.44	-0.66	a
L41	2.05	0.47	2	ICP-MS	0.235	0.24	0.27	a
L42	1.82	0.346	2		0.173	-0.54	-0.80	a

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

[b] Score evaluation colors: satisfactory, questionable, unsatisfactory,

[c] *Case* "a": $u(x_{pt}) \le u(x_i) \le \sigma_{pt}$; *Case* "b": $u(x_i) < u(x_{pt})$; *and Case* "c" :$u(x_i) > \sigma_{pt}$

Annex 8: Results for total Cd

Assigned values: x_{pt} = 0.0490; $U(x_{pt})$ = 0.0043 (k=2); and σ_{pt} = 0.0108; all values in mg kg^{-1}, related to dry mass

Lab Code	x_i	$U(x_i)$	k[a]	technique	$u(x_i)$	z-score[b]	ζ-score	uncert.[c]
L01	0.046	0.003	2	ICP-MS	0.0015	-0.28	-1.14	b
L02	0.057	0.005	2	ICP-MS	0.0025	0.74	2.43	a
L03	0.0508	0.0127	2	ICP-MS	0.00635	0.17	0.27	a
L04	0.046	0.005	2	ETAAS	0.0025	-0.28	-0.91	a
L05	0.061	0.013	2	ICP-QMS	0.0065	1.11	1.75	a
L06	0.046	0.016	2	ICP-MS	0.008	-0.28	-0.36	a
L07	0.093	0.028	2	GF-AAS	0.014	4.08	3.11	c
L08	0.056	0.006	2	ICP-QMS	0.003	0.65	1.90	a
L09	0.0593	0.0101	2	ICP-QMS	0.00505	0.96	1.88	a
L10	0.053	0.006	2	ICP-MS	0.003	0.37	1.08	a
L11	0.042	0.007	2	GF-AAS	0.0035	-0.65	-1.70	a
L12	0.054	0.011	2	GF-AAS	0.0055	0.46	0.85	a
L13	0.053	0.021	2	ICP-QMS	0.0105	0.37	0.37	a
L14	0.047	0.0124	2	GF-AAS	0.0062	-0.19	-0.30	a
L15	0.053	0.0037	2	ICP-QMS	0.00185	0.37	1.41	b
L16	0.0494	30	√3	ICP-MS	17.32051	0.04	0.00	c
L17	0.053	0.007	2	ETAAS	0.0035	0.37	0.97	a
L18	0.051	0.013	2	ICP-MS	0.0065	0.19	0.29	a
L19	0.046	0.011	2	GF-AAS	0.0055	-0.28	-0.51	a
L20	0.053	0.013	2	ICP-MS	0.0065	0.37	0.58	a
L21	0.0408	0.0039	2	ICP-MS	0.00195	-0.76	-2.83	b
L22	0.058	0.011	2	ICP-QMS	0.0055	0.83	1.52	a
L23	0.058	0.005	2	ICP-MS	0.0025	0.83	2.73	a
L24	0.06	0.010	2	ICP-MS	0.005	1.02	2.02	a
L25	0.054	0.014	2	ICP-MS	0.007	0.46	0.68	a
L26	0.045	0.009	2	ICP-MS	0.0045	-0.37	-0.80	a
L27	0.051	0.002	2	ETAAS	0.001	0.19	0.84	b
L28	0.049	0.014	2	ICP-MS	0.007	0.00	0.00	a
L29	0.048	0.0082	2	GF-AAS	0.0041	-0.09	-0.22	a
L30	0.049	0.006	2	ICP-MS	0.003	0.00	0.00	a
L31	0.05	0.01	2	GF-AAS	0.005	0.09	0.18	a
L32	0.047	0.005	2	GF-AAS	0.0025	-0.19	-0.61	a
L33	0.052	0.014	2	ICP-QMS	0.007	0.28	0.41	a
L34	0.064	0.026	2	ICP-MS	0.013	1.39	1.14	c
L36	0.050	0.008	2	ICP-MS	0.004	0.09	0.22	a
L37	0.060	0.012	2	ICP-MS	0.006	1.02	1.73	a
L38	0.052	0.004	2	ICP-MS	0.002	0.28	1.02	b
L39	0.050	0.0042	2	ICP-QMS	0.0021	0.09	0.33	b
L40	0.045	0.012	2	ICP-MS	0.006	-0.37	-0.63	a
L41	0.022	0.010	2	GF-AAS	0.005	-2.50	-4.96	a
L42	0.056	0.011	2		0.0055	0.65	1.19	a

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

[b] Score evaluation colors: satisfactory, questionable, unsatisfactory,

[c] *Case* "a": $u(x_{pt}) \le u(x_i) \le \sigma_{pt}$; *Case* "b": $u(x_i) < u(x_{pt})$; *and Case* "c" : $u(x_i) > \sigma_{pt}$

Annex 9: Results for total Hg

Assigned values: x_{pt} = 4.26; $U(x_{pt})$ = 0.36 (k=2); and σ_{pt} = 0.55; all values in mg kg^{-1}, related to dry mass

Lab Code	x_i	$U(x_i)$	k[a]	technique	$u(x_i)$	z-score[b]	ζ-score	uncert.[c]
L01	4.56	0.01	2	DMA	0.005	0.54	1.67	b
L02	4.34	0.38	2	ICP-MS	0.19	0.14	0.31	a
L03	4.27	0.85	2	ICP-MS	0.425	0.02	0.02	a
L04	4.2	0.4	2	DMA	0.2	-0.11	-0.22	a
L05	4.7	0.5	2	FIMS	0.25	0.79	1.43	a
L06	4.4	1.3	2	DMA	0.65	0.25	0.21	c
L07	3.623	0.543	2	CV-AAS	0.2715	-1.15	-1.96	a
L08	4.5	0.7	2	DMA	0.35	0.43	0.61	a
L09	4.755	0.476	2	ICP-QMS	0.238	0.89	1.66	a
L10	3.846	0.405	2	DMA	0.2025	-0.75	-1.53	a
L11								
L12	3.47	0.246	2	CV-AAS	0.123	-1.43	-3.62	b
L13	4.2	1.68	2	ICP-QMS	0.84	-0.11	-0.07	c
L14	4.420	0.860	2	CV-AAS	0.43	0.29	0.34	a
L15	4.3	0.45	2	ICP-QMS	0.225	0.07	0.14	a
L16	3.046	20	√3	CV-AFS	11.55	-2.19	-0.11	c
L17	3.7	0.6	2	FIAS-AAS	0.3	-1.01	-1.60	a
L18	4.160	0.624	2	DMA	0.312	-0.18	-0.28	a
L19								
L20	4.53	1.13	√3	ICP-MS	0.65	0.49	0.40	c
L21	4.11	0.66	2	DMA	0.33	-0.27	-0.40	a
L22	4.0	0.5	2	DMA	0.25	-0.47	-0.84	a
L23	1.50	0.15	2	CV-AAS	0.075	-4.98	-14.15	b
L24	4.58	1.25	2	ICP-MS	0.625	0.58	0.49	c
L25	4.2	1.2	2	ICP-MS	0.6	-0.11	-0.10	c
L26	4.127	0.8	2	ICP-MS	0.4	-0.24	-0.30	a
L27	4.30	0.102	2	DMA	0.051	0.07	0.21	b
L28	4.4	0.88	2	DMA	0.44	0.25	0.29	a
L29	3.91	0.695	2	CV-AAS	0.3475	-0.63	-0.89	a
L30	4.26	0.26	2	DMA	0.13	0.00	0.00	b
L31	4.7	0.4	2	DMA	0.2	0.79	1.64	a
L32	4.393	0.502	2	CV-AAS	0.251	0.24	0.43	a
L33	4.180	0.167	2	DMA	0.0835	-0.14	-0.40	b
L34	5.6	2.2	2	ICP-MS	1.1	2.42	1.20	c
L36	4.20	0.60	2	ICP-MS	0.3	-0.11	-0.17	a
L37	4.2	0.8	2	ICP-MS	0.4	-0.11	-0.14	a
L38	5.1	0.306	2	DMA	0.153	1.52	3.56	b
L39	4.6	0.56	2	CV-AAS	0.28	0.61	1.02	a
L40	3.716	0.488	2	ICP-MS	0.244	-0.98	-1.79	a
L41	4.1	1.1	2	CV-AAS	0.55	-0.29	-0.28	a
L42	3.95	0.198	2		0.099	-0.56	-1.51	b

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

[b] Score evaluation colors: satisfactory, questionable, unsatisfactory,

[c] *Case* "a": $u(x_{pt}) \le u(x_i) \le \sigma_{pt}$; *Case* "b": $u(x_i) < u(x_{pt})$; *and Case* "c" :$u(x_i) > \sigma_{pt}$

Annex 10: Results for Total Pb

Informative value: $x_{pt} \approx 0.012$ mg kg^{-1}

Lab Code	X_i	$U(x_i)$	k	technique
L01	0.052	0.002	2	ICP-MS
L02	<0.011			ICP-MS
L03	<0.018			ICP-MS
L04	<0.025			ETAAS
L05	0.04	0.01	2	ICP-QMS
L06	0.048	0.017	2	ICP-MS
L07	<0.050			GF-AAS
L08	0.032	0.007	2	ICP-QMS
L09	<0.017			ICP-QMS
L10	<0.020			ICP-MS
L11	0.028	0.016	2	GF-AAS
L12	<0.1			GF-AAS
L13	0.010	0.005	2	ICP-QMS
L14	0.044	0.0105	2	GF-AAS
L15	0.0085	0.0043	2	ICP-QMS
L16	0	20		ICP-MS
L17	0.032	0.005	2	ETAAS
L18	<0.3			ICP-MS
L19	0.05	0.02	2	GF-AAS
L20	0.033	0.008		ICP-MS
L21	<0.010			ICP-MS
L22	<0.0085			ICP-QMS
L23	<0.005			ICP-MS
L24	<0.12			ICP-MS
L25	<0.008			ICP-MS
L26	<0.040			ICP-MS
L27	0.017	0.004	2	ETAAS
L28	0.008	0.002	2	ICP-MS
L29	0.045	0.0081	2	GF-AAS
L30	<0.012			ICP-MS
L31	0.02	0.01	2	GF-AAS
L32	0.033	0.003	2	GF-AAS
L33	0.047	0.014	2	ICP-QMS
L34	<0.02			ICP-MS
L36	0.007	0.002	2	ICP-MS
L37	<0.02			ICP-MS
L38	0	0	2	ICP-MS
L39	<0.015			ICP-QMS
L40	0.010	0.005	2	ICP-MS
L41	0.015	0.006	2	GF-AAS
L42	<0.003			

all values in mg kg^{-1}, related to dry mass

Annex 11: Results for MeHg (expressed as Hg)

Assigned values: x_{pt} = 3.62; $U(x_{pt})$ = 0.47 ($k=2$); and σ_{pt} = 0.47; all values in mg of Hg kg^{-1} related to dry mass

Lab Code	x_i	$U(x_i)$	k[a]	technique	$u(x_i)$	z'-score[b]	ζ-score	uncert.[c]
L02	4.15	0.29	2	ID GC-ICP-MS	0.145	0.80	1.92	b
L04	0	0	0					
L08	4.27	0.73	2	DMA	0.365	0.98	1.50	a
L09	4.163	0.500	2	HPLC-ICP-MS	0.250	0.82	1.58	a
L13	4.1	2.05	2	ICP-IDMS	1.025	0.72	0.46	c
L15	3.8	0.76	2	HPLC-ICP-MS	0.38	0.27	0.40	a
L27	4.26	0.08	2	DMA	0.04	0.96	2.68	b
L28	3.7	0.63	2	DMA	0.315	0.12	0.20	a
L30	4.18	0.34	2	HPLC-ICP-MS	0.17	0.84	1.93	b
L37	3.8	0.8	2	HPLC-ICP-MS	0.4	0.27	0.39	a

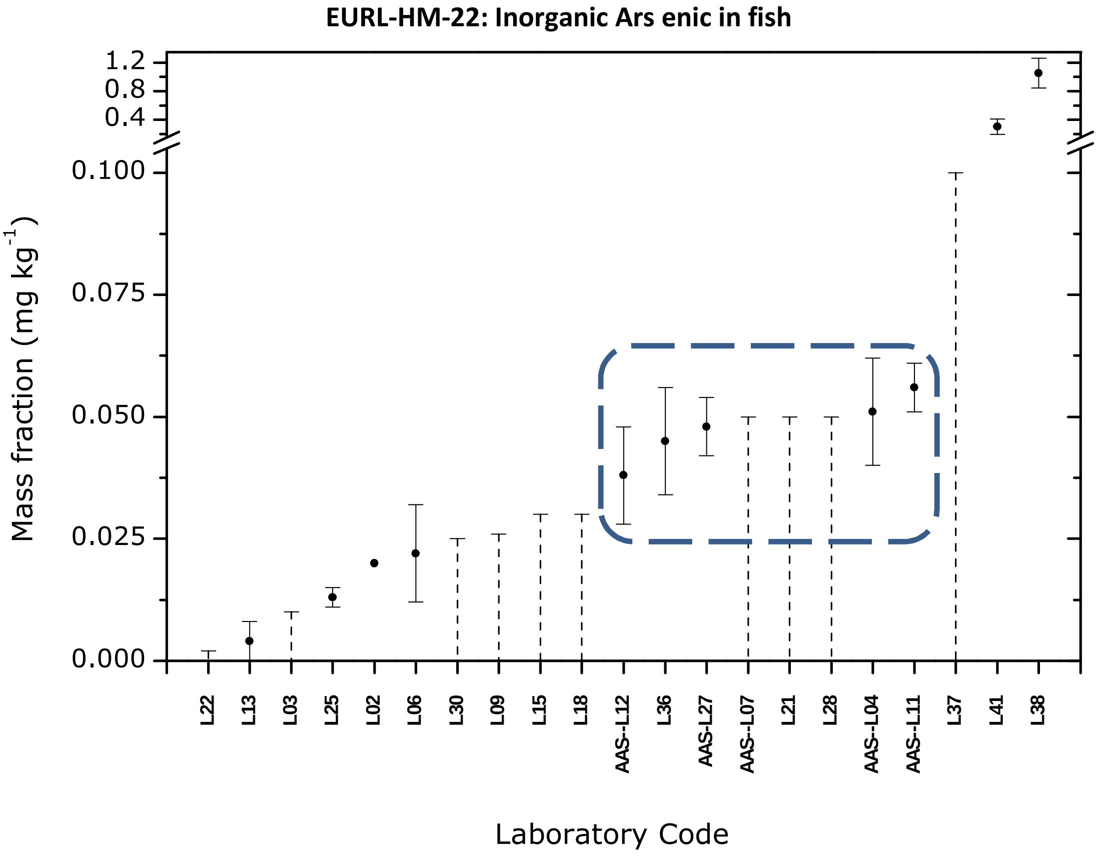
[a] Score evaluation colors: satisfactory, questionable, unsatisfactory,

[b] *Case* "a": $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$; *Case* "b": $u(x_i) < u(x_{pt})$; *and Case* "c" :$u(x_i) > \sigma_{pt}$

Annex 12: Results for iAs

Lab Code	X_i	$U(x_i)$	k	technique
L02	0.02		2	HPLC-ICP-MS
L03	<0.01			HPLC-ICP-MS
L04	0.051	0.011	2	HG-AAS
L06	0.022	0.010	2	HPLC-ICP-MS
L07	<0.05			HG-AAS
L09	<0.026			HPLC-ICP-MS
L11	0.056	0.005	2	HG-AAS
L12	0.038	0.010	2	HG-AAS
L13	0.0040	0.004	2	HPLC-ICP-MS
L15	<0.03			HPLC-ICP-MS
L18	<0.03			HPLC-ICP-MS
L21	<0.05			ICP-MS
L22	<0.002			HPLC-ICP-MS
L25	0.013	0.002	2	HPLC-ICP-MS
L27	0.048	0.006	2	HG-AAS
L28	<0.05			IC-ICP-MS
L30	<0.025			HPLC-ICP-MS
L36	0.045	0.011	2	ICP-MS
L37	<0.1			IC-ICP-MS
L38	1.055	0.211	2	HPLC-ICP-MS
L41	0.30	0.11	2	

all values in mg kg^{-1}, related to dry mass



Annex 13: Conformity of the test item to the EC Regulation 1881/2006, as expressed by the participants

Lab code	Compliance Statement
L02	The mercury result is higher than the ML set by the regulation EC 1881/2006, the present **test item isn't in compliance** with the (UE) regulation
L03	**No**, considering a water content of 80 % of the fish before freeze drying and that the fish is not one of the under 3.3.2 listed species the calculated content of mercury is well above the ML for fish (0.5 mg/kg).
L04	**No**. Content of mercury is higher than maximum levels for fish set in Regulation 1881/2006
L05	**Mercury exceeds maximum level** for this food matrix.
L06	**Depends on the fish species for the mercury content** (0.5 mg/kg or 1.0 mg/kg) . For an average of 80% (water content) in fresh fish, the mercury content is 0.92 mg/kg (wet weight). Our NRL is specialized in food from plant origin only.
L08	Results Hg is **not compliant** to the regulation limit
L09	Regarding Cd and Pb it is certainly compliant, **for Hg it depends on the fish species** and the dry matter content of the fresh sample
L10	**No** because of high concentration of Hg.
L11	It is compliant for Cd and and Pb since the respective reported values are lower than the MLs recorded in EC No 1881/2006 and modifications. *(note of the author: L11 did not analyse Hg)*
L12	The tested item is **not compliant** since the level of mercury exceeds the maxium level specified in EC No 1881/2006.
L14	Yes for Pb and Cd; **No for Hg**, taking into account the specifications from the paper of test in which you mentioned that the sample is fish, not taking into account the presentation form of sample analysis.
L17	**NON COMPLIANT** ACCORDING TO EC 1881/2006 DUE TO MERCURY
L18	**NO**, because of exceeding the ML for total Hg (0,5 or 1 mg/kg in fresh material)set by the legislation
L21	test item is **not compliant**, Hg is over maximum level
L22	No: **not compliant** due to the Hg concentration: 4.0 mg/kg -0.5 mg/kg > all MLs for fish (the exact fish species was not indicated)
L23	**No**
L24	**Not Compliant** because of high Mercury level
L25	**No** the Hg level is to high when assuming that the water content in the original fish sample is 80 % and using the ML 0,5 mg/kg
L28	**No**, because the result, after subtracting the uncertainty value is 3.5mg/kg, which is over the maximum limit for all the fish species.
L29	Pb is compliant with Reg 1881/2006 because the value is under maximum level- 0.3mg/kg-(point 3.1.5). Cd is compliance with Reg 1881/2006 because the value is under maximum leve(0.050mg.kg)l-(point 3.2.5). **Hg is non-compliance** with Reg 1881/2006 because the value is higher then maximum level 0.5mg/kg (point 3.3.1). Conclusion: the sample is not compliant according with Reg EC 1881/2006
L30	The investigate test item is **not compliant** according to EC No 1881/2006 - result of Hg exceeds the maximum level (results of Cd and Pb does not exceed the ML) as laid down in EC No 1881/2006 taking account the expanded measurement uncertainty.
L31	**No**, total Hg concentration higher than the limit proposed for fish (0.5 or 1.0 mg/kg). However, the limits proposed by the Regulation (Hg, Cd, Pb) are for **wet sample and not lyophilized sample**...
L33	Regulation EC No 1881/2006 refers to the maximum levels of toxic elements in mg/kg of wet weight. Although the **level of mercury exceed the ML**, the test item is lyophilized and cannot be judged according to this regulation.
L34	Test item is compliant for Pb, As and Cd. **Hg might be non-compliant**, but it depends on the water content and fish species of the original fish from which the powder is made of. The maximum levels are for the wet weight (fresh fish).
L36	EU Regulation 1881/2006 limits are based on fresh weight and sample was supplied as dry powder. Both Cd and Pb are compliant even without moisture correction. Hg cannot be assessed as the fish species is unknown. Assuming a moisture content of 75%, and allowing for UM error, the fish would have 0.9 mg/kg FW. This would be compliant for fish in section 3.3.2 but **non-compliant for fish in 3.3.1**
L38	Concentration of **Hg is over the maximum level**, Pb and Cd are under the maximum level.
L39	**No** because Hg is above the ML according to EC No 1881/2006
L40	**no**, Hg content is over 1.0 mg/kg
L41	**No**, Hg result are bigger than MRL
L42	**No** because mercury is not compliant to that document

Annex 14: Experimental details *(as provided by participants)*

LCode	Measurand	Digestion type	Acid mixture	Temperature (°C)	Time (min)	Recovery (%)	LOD (mg/kg)	Std method used	CRM used	Calibrants	Technique
L01	As	Closed microwave	HNO3/H2O2	180	15	80-100	1	ICP-MS	Liver (offal)	0-100 µg/l	ICP-MS
L01	Cd	Closed microwave	HNO3/H2O2	180	15	80-100	0.5	ICP-MS	Liver (offal)	0-100 µg/l	ICP-MS
L01	Hg	DMA				80-100	0.005	DMA	Liver (offal)	0-800 ng of Hg	DMA
L01	iAs	Not performed				/	/	/	/	/	
L01	MeHg	Not performed				/	/	/	/	/	
L01	Pb	Closed microwave	HNO3/H2O2	180	15	80-100	0.1	ICP-MS	Liver (offal)	0-100 µg/l	ICP-MS
L02	As	Closed microwave	HNO3	180	20		0.009	in house method	ERM 278k	external calib 0-20 µg/l	ICP-MS
L02	Cd	Closed microwave	HNO3	180	20		0.002	in house method	ERM 278k	external calib 0-20 µg/l	ICP-MS
L02	Hg	Closed microwave	HNO3	180	20		0.009	in house method	ERM 278k	external calib 0-20 µg/l	ICP-MS
L02	iAs	Closed microwave.	H2O				0.011	in house method	BC 211	external calib 0-20 µg/l	HPLC-ICP-MS
L02	MeHg	0.2 g of sample were spiked with appropriate amount of 201Hg enriched MeHg+ 3ml TMAH for the digestion. The mixture was rotate during 24h. After that, the pH was adjusted with pH5 sodium acetate/acetic acid buffer, the derivatisation of the mixture was done by ethylatyon with Na2BEt4.					0.008	NF EN 16801	Nist 2976 + BCR 436	external calib 0-20 µg/l	ID-GC-ICP-MS
L02	Pb	Closed microwave	HNO3	180	20		0.005	in house method	ERM 278k	external calib 0-20 µg/l	ICP-MS
L03	As	Closed microwave	HNO3	230	20	100	0.023	EN 15763	TORT 2, NIST 1547	Merck	ICP-MS
L03	Cd	Closed microwave	HNO3	230	20	100	0.005	EN 15763	TORT 2, NIST 1547	Merck	ICP-MS
L03	Hg	Closed microwave	HNO3	230	20	100	0.011	EN 15763	TORT 2, NIST 1547	Merck	ICP-MS
L03	iAs	Extraction	HNO3/H2O2			100	0.01	EN 16802	IMEP 107	Merck	HPLC-ICP-MS
L03	MeHg										
L03	Pb	Closed microwave	HNO3	230	20	100	0.018	EN 15763	TORT 2, NIST 1547	Merck	ICP-MS
L04	As	Dry Ashing	HNO3			95	0.025	EN	NIST 1566b	GUM	HG-AAS
L04	Cd	Closed microwave	HNO3/H2O2			94.4	0.002	EN	1566b CTA-OTL-1	GUM	ETAAS
L04	Hg	direct analysis				102	0.0002		1566B, 1568B, BCR-422	GUM	DMA

LCode	Measurand	Digestion type	Acid mixture	Temperature (°C)	Time (min)	Recovery (%)	LOD (mg/kg)	Std method used	CRM used	Calibrants	Technique
L04	iAs	Sample was hydrolysed using concentrated hydrochloric acid. After reduction by hydrobromic acid and hydrazine sulfate, inorganic arsenic was extracted into chloroform, then back-extracted into 1M HCl, dry-ashed, and quantified by HG-AAS				90	0.027	1568b			HG-AAS
L04	MeHg	-				-	-				
L04	Pb	Closed microwave	HNO3/H2O2			93	0.012	EN	1566b, CTA-OTL-1	GUM	ETAAS
L05	As										
L05	Cd	Closed microwave	HNO3/H2O2	180	30	97	0.0001	EN15763:2009	DORM 4	RM 1 g/l	ICP-QMS
L05	Hg	Closed microwave	HNO3/H2O2	180	30	96.7	0.003	EN 13806:2002	DORM 4	RM 1 g/l	FIMS
L05	iAs										
L05	MeHg										
L05	Pb	Closed microwave	HNO3/H2O2	180	30	104	0.0005	EN15763:2009	DORM 4	RM 1 g/l	ICP-QMS
L06	As	Closed microwave	HNO3	200	20	110%	0.05	internal method	internal control+ERM	Techlab	ICP-MS
L06	Cd	Closed microwave	HNO3	200	20	102%	0.01	internal method	internal control+ERM	Techlab	ICP-MS
L06	Hg	direct analysis	-	-	-	99%	0.010	internal method	internal control+ERM	Techlab	DMA
L06	iAs	Closed microwave	H2O	90	15	100%	0.02	internal method	FAPAS	Sigma	HPLC-ICP-MS
L06	MeHg	-									
L06	Pb	Closed microwave	HNO3	200	20	82%	0.01	internal method	internal control+ERM	Techlab	ICP-MS
L07	As	Closed microwave, Dry ashing	HNO3/H2O2	200 ; 425	25' ; 1h	86	0.050	MSZ EN 16206		SCP Science	HG-AAS
L07	Cd	Closed microwave	HNO3/H2O2	200	25	110	0.050	MSZ EN 15550		CPA Chem	GF-AAS
L07	Hg	Closed microwave	HNO3/H2O2	200	25	100	0.050	MSZ EN 16277		CPA Chem	CV-AAS
L07	iAs	MSZ EN 16278					0.050	MSZ EN 16278			HG-AAS
L07	MeHg										
L07	Pb	Closed microwave	HNO3/H2O2	200	25	90	0.050	MSZ EN 15550		CPA Chem	GF-AAS
L08	As	Closed microwave	HNO3/H2O2	200	28	99.3	0.0004	ISTISAN 1996/34	DOLT3,DOLT5,	standard addition	Z-ETA-AAS
L08	Cd	Closed microwave	HNO3/H2O2	200	28	100.8	0.009	in house method	DOLT4	external calibration	ICP-QMS
L08	Hg					98.25	0.003	in house method	SRM1566b, BCR463, DORM2	external calibration	DMA
L08	iAs										
L08	MeHg	Report EUR 25830 EN				84.45	-	Report EUR 25830EN	SRM1566b,SRM2974a ,TORT2	external calibration	DMA
L08	Pb	Closed microwave	HNO3/H2O2	200	28	97.4	0.008	in house method	BROWN BREAD BCR191	external calibration	ICP-QMS
L09	As	Closed microwave	HNO3	220	30	97	0.005	no	EURL CEFAO 23th PT	Merck	ICP-QMS

LCode	Measurand	Digestion type	Acid mixture	Temperature (°C)	Time (min)	Recovery (%)	LOD (mg/kg)	Std method used	CRM used	Calibrants	Technique
L09	Cd	Closed microwave	HNO3	220	30	98	0.001	no	EURL CEFAO 23th PT	Merck	ICP-QMS
L09	Hg	Closed microwave	HNO3	220	30	97	0.003	no	EURL CEFAO 23th PT	Merck	ICP-QMS
L09	iAs	according to EN16802				106	0.026	EN16802	DORM-4	Merck	HPLC-ICP-MS
L09	MeHg	Extraction with cysteine, separation by LC on C18 column				98	0.045	no	DOLT-4 TORT-2	Alfa Aesar	HPLC-ICP-MS
L09	Pb	Closed microwave	HNO3	220	30	102	0.017	no	EURL CEFAO 23th PT	Merck	ICP-QMS
L10	As	Closed microwave	HNO3/H2O2	1400 W	15	98,81	0.004	In house	DORM-4		ICP-MS
L10	Cd	Closed microwave	HNO3/H2O2	1400 W	15	98,81	0.008	In house	DORM-4		ICP-MS
L10	Hg					99,71	0.001	In house	DORM-4		DMA
L10	iAs	-						-			
L10	MeHg	-						-			
L10	Pb	Closed microwave	HNO3/H2O2	1400 W	15	99,45	0.008	In house	DORM-4		ICP-MS
L11	As										
L11	Cd	Closed microwave	HNO3	200	25		0.003	Graphite furnace - AAS	BCR 610, BCR191	2 ppb	GF-AAS
L11	Hg										
L11	iAs	Hydride generation - atomic spectroscopy					0.008	Hydride generation-AAS	Schema 7169	10 ppb	HG-AAS
L11	MeHg										
L11	Pb	Closed microwave	HNO3	200	25		0.008	Graphite furnace - AAS	BCR713, BCR191	25 ppb	GF-AAS
L12	As	Dry Ashing	HNO3	425	17 h	96.4	0.0625	EN 14546:2005	DORM2	0.5 - 3 ppb	HG-AAS
L12	Cd	Open wet	HNO3/H2O2	170	1 h	91.0	0.0063		EURL-CEFAO 23rd PT	0.1 - 1.6 ppb	GF-AAS
L12	Hg	Open wet	HNO3/H2O2	170	1 h	88.8	0.0625		EURL-CEFAO 23rd PT	1 - 16 ppb	CV-AAS
L12	iAs	Solubilisation in 9M HCl; Reduction by HBr and hydrazine sulfate; Chloroform extraction; Back extraction in 1M HCl; Dry ashing.				83.7	0.0063		DORM2	0.5 - 3 ppb	HG-AAS
L12	MeHg										
L12	Pb	Open wet	HNO3/H2O2	170	1 h		0.0625		EURL-CEFAO 23rd PT	1 - 16 ppb	GF-AAS
L13	As										ICP-QMS
L13	Cd										ICP-QMS
L13	Hg										ICP-QMS
L13	iAs										HPLC-ICP-MS
L13	MeHg										ICP-IDMS
L13	Pb										ICP-QMS

LCode	Measurand	Digestion type	Acid mixture	Temperature (°C)	Time (min)	Recovery (%)	LOD (mg/kg)	Std method used	CRM used	Calibrants	Technique
L14	As	Dry Ashing	HCl /HNO3	450	12 h	106.11	0.100	SR EN 14546	BCR 32	0.002-0.010	HG-AAS
L14	Cd	Dry Ashing	HCl /HNO3	450	24 h	97.48	0.0005	SR EN 14082		0.001-0.005	GF-AAS
L14	Hg	Closed microwave	HNO3	180	50	99.5	0.003	SR EN 13806		0.002-0.010	CV-AAS
L14	iAs										
L14	MeHg										
L14	Pb	Dry Ashing	HCl /HNO3	450	24 h	93.71	0.005	SR EN 14082		0.010-0.050	GF-AAS
L15	As	Closed microwave	HNO3	200	20	98	0,009	DS/EN 15763	Mussel tissue SRM 2976	Std curve	ICP-QMS
L15	Cd	Closed microwave	HNO3	200	20	101	0,003	DS/EN 15763	Mussel Tissue CRM 2976	Std curve	ICP-QMS
L15	Hg	Closed microwave	HNO3	200	20	99	0,002	DS/EN 15763	Mussel Tissue SRM 2976	Std curve	ICP-QMS
L15	iAs	Extration on waterbath with diluted nitric acid and hydrogen peroxide. Measurement using anion exchange HPLC coupled on-line to an ICP-MS					0,030	EN 16802	Rice ERM-BC 211	Std curve	HPLC-ICP-MS
L15	MeHg	Extration with diluted HCl by sonification. Detemination by HPLC-ICP-MS						In house method	Tort-2	Std curve	HPLC-ICP-MS
L15	Pb	Closed microwave	HNO3	200	20	97	0,006	DS/EN 15763	Mussel tissue SRM 2976	Std curve	ICP-QMS
L16	As										ICP-MS
L16	Cd										ICP-MS
L16	Hg										CV-AFS
L16	iAs										
L16	MeHg										
L16	Pb										ICP-MS
L17	As	Closed microwave	HNO3/H2O2	200	35	97.4	0.072	IN HOUSE	DORM3	1-50 ng/ml	ETAAS
L17	Cd	Closed microwave	HNO3/H2O2	200	35	100.9	0.0016	IN HOUSE	DORM3	0.2-2 ng/ml	ETAAS
L17	Hg	Closed microwave	HNO3/H2O2	200	35	100.3	0.0017	IN HOUSE	CRM278R	1-20 ng/ml	FIAS-AAS
L17	iAs										
L17	MeHg										
L17	Pb	Closed microwave	HNO3/H2O2	200	35	98.8	0.015	IN HOUSE	DORM3	1-50 ng/ml	ETAAS
L18	As	Open microwave	HNO3	190	10	98-102	0,006	EN 15763:2009	GBW 7604	CZ 9003 (1 N)	ICP-MS
L18	Cd	Open microwave	HNO3	190	10	98-102	0,006	EN 15763:2009	GBW 7604	CZ9010(1N)	ICP-MS
L18	Hg	dry combustion in oxygen - AMA 254				98-102	0,0003		GBW 7604	CZ 9024(1N)	DMA
L18	iAs	closed microwave extraction in mixture 0,06M HCl in 3% H2O2, temperature 90 C, determination HPLC-ICP-MS					0,01		IMEP 112,IMEP 116	dissolutin salts AsIII,V	HPLC-ICP-MS

LCode	Measurand	Digestion type	Acid mixture	Temperature (°C)	Time (min)	Recovery (%)	LOD (mg/kg)	Std method used	CRM used	Calibrants	Technique
L18	MeHg	method has not been optimized , we perform only feedingstuffs analysis and this parameter has not been optimized yet									
L18	Pb	Open microwave	HNO3	190	10	98-102	0,09	EN 15763: 2009	GBW 7604	CZ 9041(1N)	ICP-MS
L19	As										
L19	Cd										GF-AAS
L19	Hg										
L19	iAs										
L19	MeHg										
L19	Pb										GF-AAS
L20	As	closed microwavw	HNO3/H2O2	230	50		0.01	EN 15763	SRM 1568b	Fluka	ICP-MS
L20	Cd	closed microwave	HNO3/H2O2	230	50		0.01	EN 15763	SRM 1568b	Fluka	ICP-MS
L20	Hg	closed microwave	HNO3/H2O2	230	50		0.01	EN 15763	SRM 1568b	Fluka	ICP-MS
L20	iAs										
L20	MeHg										
L20	Pb	closed microwave	HNO3/H2O2	230	50		0.02	EN 15763	ERM-BD151	Fluka	ICP-MS
L21	As	microwave digestion	HNO3/H2O2	200	20	99.8	0.050	SIST EN 15763	DORM-3	MERCK VI	ICP-MS
L21	Cd	microwave digestion	HNO3/H2O2	200	20	103.3	0.010	SIST EN 15763	DORM-3	MERCK VI	ICP-MS
L21	Hg	-	-	850	150 s	106	0.010	EPA 7473	DORM-3	-	DMA
L21	iAs	microwave extraction, separation SPE, ICP-MS determination (SIST EN 16278:2012, modif.)				102.9	0.050	SIST EN 16278:2012, modif	SRM 1568b	MERCK VI	ICP-MS
L21	MeHg	-				-	-	-	-	-	
L21	Pb	microwave digestion	HNO3/H2O2	200	20	101.7	0.020	SIST EN 15763	DORM-3	MERCK VI	ICP-MS
L22	As	Closed microwave	HNO3	180	30	98-101%	0.0003	-	DOLT5	CZ9090 Mix010	ICP-QMS
L22	Cd	Closed microwave	HNO3	180	30	99-101%	0.00042	-	DOLT5	CZ9090 Mix010	ICP-QMS
L22	Hg	Direct mercury analysis				99-101%	0.0001	-	NIST2976, DOLT5	-	DMA
L22	iAs	Acid mixture: HNO3 + H2O2; digestion in closed microwave at 90°C for 20 minutes				95%	0.0006	-	NMIJ7532a	CGAS(5)1	HPLC-ICP-MS
L22	MeHg	MeHg not determined									
L22	Pb	Closed microwave	HNO3	180	30	95-101%	0.0024	-	DOLT5	CZ9090 Mix010	ICP-QMS
L23	As	Closed microwave	HNO3/H2O2/ H2O	150/180	15/15.	100	0.005	In-house Validated Method	QMAS	Merck ICP	ICP-MS
L23	Cd	Closed microwave	HNO3/H2O2/ H2O	150/180	15/15	100	0.005	In-house Validated Method	QMAS	Sigma-Aldrich ICP	ICP-MS
L23	Hg	Open wet	H2SO4	200	15	100	0.02	AAC 971.21	EURL PT	Sigma-Aldrich ICP	CV-AAS
L23	iAs										

LCode	Measurand	Digestion type	Acid mixture	Temperature (^{o}C)	Time (min)	Recovery (%)	LOD (mg/kg)	Std method used	CRM used	Calibrants	Technique
L23	MeHg										
L23	Pb	Closed microwave	HNO3/H2O2/ H2O	150/180	15/15	100	0.005	In-house Validated Method	QMAS	Sigma-Aldrich ICP	ICP-MS
L24	As	Closed microwave	HNO3/H2O2	170	22	93.0	0.05	In House Mrthod	LGC7162 Strawberry Leaves	VWR Stock Calibn.Solution	ICP-MS
L24	Cd	Closed microwave	HNO3/H2O2	170	22	91.5	0.003	In House Method	LGC 7162 Strawberry Leave	VWR Stock Calibn Solution	ICP-MS
L24	Hg	Closed Microwave	HNO3/H2O2	170	22	92.0	0.01	In House Method	TORT3 Lobster	VWR Stock Calibn. Solutio	ICP-MS
L24	iAs										
L24	MeHg										
L24	Pb	Closed Microwave	HNO3/H2O2	170	22	84.6	0.03	In House Method	LGC 7162 Strawberry Leave	VWR Stock Calibn. Solutio	ICP-MS
L25	As	Closed microwave	HNO3+HCl	200	30	NA	0,010	EN 15763:2009	DORM-2 NRCC	Spectrascan, Teknolab	ICP-MS
L25	Cd	Closed microwave	HNO3+HCl	200	30	NA	0,003	EN 15763:2009	DORM-2	Spectrascan, Teknolab	ICP-MS
L25	Hg	Closed microwave	HNO3+HCl	200	30	NA	0,019	EN 15763:2009	NIST 1566	Spectrascan, Teknolab	ICP-MS
L25	iAs	EN 16802:2016	HNO3/H2O2	90	60	NA	0,002	EN 16802:2016	DORM 4	CGAS1 Inorganic Ventures	HPLC-ICP-MS
L25	MeHg	Not analysed				NA	NA				
L25	Pb	Closed microwave	HNO3/HCl	200	30	NA	0,004	EN 15763:2009	DORM-2	Spectrascan, Teknolab	ICP-MS
L26	As										ICP-MS
L26	Cd										ICP-MS
L26	Hg										ICP-MS
L26	iAs										
L26	MeHg										
L26	Pb										ICP-MS
L27	As	Dry Ashing	HNO3/HCl	450	12 h	94	0.01		IAEA 436		HG-AAS
L27	Cd	Closed microwave	HNO3	200	30	99	0.006		NIST 2976		ETAAS
L27	Hg	direct				95	0.0005		IAEA 436		DMA
L27	iAs	extraction with chloroform (IMEP 41)				93	0.01		DORM 4		HG-AAS
L27	MeHg	A double liquid-liquid extraction ((toluene)				100	0.01		NIST 2976		DMA
L27	Pb	Closed microwave	HNO3	200	30	108	0.01		BCR 191		ETAAS
L28	As	Closed microwave	HNO3/H2O2	200	40	99	0.010		DORM/DOLT		ICP-MS
L28	Cd	Closed microwave	HNO3/H2O2	200	40	97	0.002		ORM/DOLT		ICP-MS
L28	Hg	no digestion				105	0.010		ORM/DOLT		DMA

LCode	Measurand	Digestion type	Acid mixture	Temperature (°C)	Time (min)	Recovery (%)	LOD (mg/kg)	Std method used	CRM used	Calibrants	Technique
L28	iAs	extraction: acid mixture HNO3 0.3% + 4% H2O2: Close microwave 95ºC 50 min / HPLC-ICP-MS				105	0.050		ORM/DOLT		IC-ICP-MS
L28	MeHg	SOP IMEP115				91	0.070	SOP IMEP 115	ORM/DOLT		DMA
L28	Pb	Closed microwave	HNO3/H2O2	200	40	96	0.006		ORM/DOLT		ICP-MS
L29	As	-	-	-	-	-	-	-	-	-	
L29	Cd	Dry Ashing	HNO3/HCl	450	10 h	92	0.001	SR14082/2003	IRMM-804	Scharlab	GF-AAS
L29	Hg	Closed microwave	HNO3/H2O2	180	40	92	0.02	SR 13806/2003	BCR 463	Merck	CV-AAS
L29	iAs	-				-	-	-	-	-	
L29	MeHg	-				-	-	-	-	-	
L29	Pb	Dry Ashing	HNO3/HCl	450	10 h	90	0.005	SR 14082/2003	IRMM-804	Scharlab	GF-AAS
L30	As	Closed microwave	HNO3/H2O2	150/180	20/10	95	0.0009		DORM-4		ICP-MS
L30	Cd	Closed microwave	HNO3/H2O2	150/180	20/10	98	0.0003		DORM-4		ICP-MS
L30	Hg	without digestion	-	-	-	110	0.0001		ERM CE464		DMA
L30	iAs	Determination of iAs by HPLC-ICP-MS after microwave assisted extraction with mixture HCl + H2O2.				96	0.006		IMEP 32-3		HPLC-ICP-MS
L30	MeHg	Determination of MeHg by HPLC-ICP-MS after specific enzymatic hydrolysis with L-cystein.				75	0.021		ERM CE464		HPLC-ICP-MS
L30	Pb	Closed microwave	HNO3/H2O2	150/180	20/10	100	0.004		DORM-4		ICP-MS
L31	As										
L31	Cd	Closed microwave	HNO3	210	35	100	0.003	Standard NP EN 14084	DORM 4		GF-AAS
L31	Hg					100	0.005	Standard US EPA 7473	DORM 4		DMA
L31	iAs										
L31	MeHg										
L31	Pb	Closed microwave	HNO3	210	35	100	0.02	Standard NP EN 14084	DORM 4		GF-AAS
L32	As										
L32	Cd										GF-AAS
L32	Hg										CV-AAS
L32	iAs										
L32	MeHg										
L32	Pb										GF-AAS
L33	As	Closed microwave	HNO3/H2O2	190	15	92	0,0009	-	SRM2976	VAR-CAl-71	ICP-QMS
L33	Cd	Closed microwave	HNO3/H2O2	190	15	100	0,0008	-	DORM-3	VAR-CAl-71	ICP-QMS
L33	Hg	Dry Ashing	1			102	0,001	-	DORM-3	1000 mg/kg J.T.Baker	DMA

LCode	Measurand	Digestion type	Acid mixture	Temperature ($^{\circ}$C)	Time (min)	Recovery (%)	LOD (mg/kg)	Std method used	CRM used	Calibrants	Technique
L33	iAs										
L33	MeHg										
L33	Pb	Closed microwave	HNO3/H2O2	190	15	100	0,0012	-	DORM-3	VAR-CAl-71	ICP-QMS
L34	As	Closed microwave	HNO3/H2O2	180	15	87	0.007	EN 15763:2009 modified	DORM-4	Accu Standard	ICP-MS
L34	Cd	Closed microwave	HNO3/H2O2	180	15	82	0.003	EN 15763:2009 modified	BCR-191	Accu Standard	ICP-MS
L34	Hg	Closed microwave	HNO3/H2O2	180	15	88	0.02	EN 15763:2009 modified	DORM-4	Accu Standard	ICP-MS
L34	iAs										
L34	MeHg										
L34	Pb	Closed microwave	HNO3/H2O2	180	15	84	0.007	EN 15763:2009 modified	BCR-191	Fluka	ICP-MS
L35	As										
L35	Cd										
L35	Hg										
L35	iAs										
L35	MeHg										
L35	Pb										
L36	As	Closed microwave	HNO3/HCl	240	15	100	0.001	In-house	CE278K, DORM4, NIST1566b	0.05 to 50	ICP-MS
L36	Cd	Closed microwave	HNO3/HCl	240	15	101	0.0003	In-house	CE278K, DORM4, NIST1566b	0.05 to 50	ICP-MS
L36	Hg	Closed microwave	HNO3/HCl	240	15	103	0.02	In-house	CE278K, DORM4, NIST1566b	0.01 to 10	ICP-MS
L36	iAs	Solubilised in HCl, reduced and extracted into CCl4, back extracted into dilute HCl				77	0.006	In-house	NMIJ7503a, DORM4	0.10 to 100	ICP-MS
L36	MeHg	Not analysed - Currently adapting cysteine method to our ICPMS and requires validation									
L36	Pb	Closed microwave	HNO3/HCl	240	15	105	0.001	In-house	CE278K, DORM4, NIST1566b	0.05 to 50	ICP-MS
L37	As										HPLC-ICP-MS
L37	Cd										ICP-MS
L37	Hg										ICP-MS
L37	iAs										IC-ICP-MS
L37	MeHg										HPLC-ICP-MS
L37	Pb										ICP-MS
L38	As	Closed microwave	HNO3/H2O2	200	10	109	0.0006	in-house method	SRM 2976	Romil FS9 ME1754	ICP-MS
L38	Cd	Closed microwave	HNO3/H2O2	200	10	104	0.0002	in-house method	SRM 2976	Romil FS9 ME1754	ICP-MS

LCode	Measurand	Digestion type	Acid mixture	Temperature (°C)	Time (min)	Recovery (%)	LOD (mg/kg)	Std method used	CRM used	Calibrants	Technique
L38	Hg	Dry Ashing		650	8	97	0.001	in-house method	ERM BB-422	PerkinElmer	DMA
L38	iAs	Digestion type "closed microwave"; acid mixture HNO3+H2O2; temperature 80 C; time 30 min; sample analysed with HPLC-ICP-MS (solvent H2O+ammoniumcarbonate (grad.), column Hamilton PRP-X100 (250x4.6 mm; 5 µm))				93	0.02	in-house method	BCR-627	Merck	HPLC-ICP-MS
L38	MeHg	not analysed									
L38	Pb	Closed microwave	HNO3/H2O2	200	10	105	0.004	in-house method	SRM 2976	Romil FS9 ME1754	ICP-MS
L39	As	Closed microwave	HNO3/H2O2	200	65	103.7	0.0043	AOAC Vol 96 No 5 2013.06	IAEA 436	0-20 ng/ml	ICP-QMS
L39	Cd	Closed microwave	HNO3/H2O2	200	65	98	0.0008	AOAC Vol 96 No 5 2013.06	IAEA 436	0-20 ng/ml	ICP-QMS
L39	Hg	Closed microwave	HNO3/H2O2	200	65	104	0.016	AOAC 974.14 2005	IAEA 436	0-20 ng/ml	CV-AAS
L39	iAs										
L39	MeHg										
L39	Pb	Closed microwave	HNO3/H2O2	200	65	87.9	0.0044	AOAC Vol 96 No 5 2013.06	IAEA 436	0-20 ng/ml	ICP-QMS
L40	As	Closed microwave	HNO3/H2O2	180	30	96	0.020	EN 15763:2010			ICP-MS
L40	Cd	Closed microwave	HNO3/H2O2	180	30	102	0.002	EN 15763:2010			ICP-MS
L40	Hg	Closed microwave	HNO3/H2O2	180	30	85	0.020	EN 15763:2010			ICP-MS
L40	iAs										
L40	MeHg										
L40	Pb	Closed microwave	HNO3/H2O2	180	30	101	0.005	EN 15763:2010			ICP-MS
L41	As	Closed microwave	HNO3/H2O2	200	60	90-110	0.01	LST EN 15763:2010	Residue of PT	1000 mg/l	ICP-MS
L41	Cd	Closed microwave	HNO3/H2O2	200	60	90-110	0.002	LST EN 14084:2003	Residue of PT	1000 mg/l	GF-AAS
L41	Hg	Closed microwave	HNO3/H2O2	200	60	90-110	0.002	LST EN 13806:2002	Residue of PT	1000 mg/l	CV-AAS
L41	iAs	LST EN 16278:2012				90-110	0.09	LST EN 16278:2012	-	1000 mg/l	
L41	MeHg										
L41	Pb	Closed microwave	HNO3/H2O2	200	60	90-110	0.015	LST EN 14084:2003	Residue of PT	1000 mg/l	GF-AAS
L42	As	Open microwave	HNO3/H2O2	max.190		70-130	0.0023				
L42	Cd	Open microwave	HNO3/H2O2	max.190		70-13	0.0016				
L42	Hg					70-130	0,0001				
L42	iAs										
L42	MeHg										
L42	Pb	Open microwave	HNO3/H2O2	max.190		70-130	0.0015				

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