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IMEP-39: Determination of total cadmium, lead, arsenic, mercury and inorganic arsenic in mushrooms

Interlaboratory Comparison Report

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IMEP®

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Executive summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme (IMEP). One of its core tasks is to organise proficiency tests (PTs) in support to European Union (EU) policies. This report presents the results of a PT, IMEP-39, focussed on the determination of total cadmium, lead, arsenic, mercury and inorganic arsenic in mushrooms. The exercise was organised in support to the European Commission Regulation (EC) No 1881/2006 which sets the maximum levels for certain contaminants in foodstuffs.

Seventy one participants from thirty six countries registered to the exercise (32 % from non-European Union countries), of which sixty two reported results.

The test item used was a blend of mushrooms of the variety shiitake (*Lentinula edodes*). Five laboratories with demonstrated measurement capability in the field provided results to establish the assigned values (X_{ref}). The standard uncertainties associated to the assigned values (u_{ref}) were calculated by combining the uncertainty of the characterisation (u_{char}) with a contribution for homogeneity (u_{bb}) and for stability (u_{st}). u_{char} was calculated following ISO 13528.

Participants were invited to report their measurement uncertainties. This was done by the majority of laboratories having submitted results in this exercise.

Laboratory results were rated with *z*- and zeta (ζ-) scores in accordance with ISO 13528 and ISO 17043. The z-score compares the participant's deviation from the reference value with the standard deviation for proficiency assessment (σ_p) used as common quality criterion, the ζ-score states if the laboratory result agrees with the assigned value within the respective uncertainty. The standard deviation for the proficiency assessment, σ_p, for total Pb (20 % of X_{ref}) and inorganic arsenic (19 % of X_{ref}) were calculated using the Horwitz equation as modified by Thompson. For the rest of the measurands, on the basis of previous experience on similar measurands, σ_p was set by the advisory board of this PT to 15 % of X_{ref} for total As and Hg and to 10 % of X_{ref} for total Cd.

The percentage of satisfactory z-scores ranged from 64 % (inorganic arsenic) to 84 % (total cadmium).

1 Introduction

Mushrooms are excellent sources of nutrients (proteins, fibre, vitamins and essential minerals). However, edible portions of mushrooms are also known to accumulate high levels of inorganic contaminants such as cadmium, lead, arsenic and mercury from the soil [1]. Among the many edible mushrooms species, *Lentinula edodes* (Shiitake) is the most cultivated and consumed worldwide, thus deserving a particular attention from the analytical point of view as regards their content in certain trace elements, considered as toxic contaminants, if above certain limits set by the European legislation [2].

To protect consumers from any potential toxic effect, maximum levels for heavy metals in mushrooms have been laid down in Regulation (EC) No 1881/2006 [2] and its amendments [3,4].

The proficiency test IMEP-39, organised by the Joint Research Centre, aimed to assess the performance of food control laboratories in the determination of the total mass fraction of cadmium, lead, arsenic, mercury and inorganic arsenic in mushrooms. This proficiency test was carried out in collaboration with the European Union Reference Laboratory for Heavy Metals in Feed and Food (EURL-HM), who organised in parallel the PT IMEP-116 for its network of National Reference Laboratories (NRLs) using the same proficiency test item and the same criteria for performance evaluation. This report does not discuss the outcome of the IMEP-116.

This report summarises and evaluates the outcome of IMEP-39.

2 IMEP support to EU policy

The International Measurement Evaluation Programme (IMEP) is hold by the Joint Research Centre - Institute for Reference Materials and Measurements. IMEP provides support to the European measurement infrastructure in the following ways:

IMEP disseminates metrology from the highest level down to the field laboratories. These laboratories can benchmark their measurement result against the IMEP certified reference value. This value is established according to metrological best practice.

IMEP helps laboratories to assess their estimate of measurement uncertainty. Participants are invited to report the uncertainty on their measurement results. IMEP integrates the estimate into the scoring, and provides assistance for the interpretation.

IMEP supports EU policies by organising interlaboratory comparisons (ILCs) in the frame of specific EU Directives or on request of a specific EC Directorate-General. In the case of IMEP-39 it was organised to support the Directorate General for Health and Consumers (DG SANCO) with the implementation of the European Commission Regulation (EC) No 1881/2006 [2]. Furthermore, IMEP-39 provided support to the following stakeholders:

- The **European Cooperation for Accreditation** (EA) in the frame of a Memorandum of Understanding on a number of metrological issues, including the organisation of interlaboratory comparisons. National accreditation bodies were invited to nominate a limited number of laboratories for free participation in IMEP-39. Mrs. Annika Nordling, from the Swedish Board for Accreditation and Conformity Assessment (SWEDAC) liaised between EA and IMEP for this ILC. This report does not discern the EA nominees from the other participants. Their results are however summarised in a separate report to EA.

- The **Asia Pacific Laboratory Accreditation Cooperation** (APLAC), in the frame of the collaboration with APLAC. Mr. Aparna Dhawan (APLAC PT Committee) liaised between APLAC and IMEP, announcing the exercise to the accreditation bodies in the APLAC network.

- The **InterAmerican Accreditation Cooperation** (IAAC). Mrs. Barbara Belzer liaised between IAAC and IMEP. She was invited to announce the exercise to the accreditation bodies in the IAAC network.

3 Scope and aim

The aim of the present PT exercise was to assess the performance of food control laboratories on the determination of total Cd, Pb, As, Hg and inorganic As mass fractions in mushrooms.

The assessment of the measurement results is undertaken on the basis of requirements laid down in European legislation [2], and follows the administrative and logistic procedures of the IMEP of the Institute of Reference Materials and Measurements of the European Commission Directorate General Joint Research Centre (EC-JRC). IRMM is accredited according to ISO/IEC 17043:2010 [5].

4 Set-up of the exercise

4.1 Time frame

The exercise was announced via the IRMM web page on the 13th of March 2013 (Annex 1). Additionally, the exercise was announced to the European Cooperation for Accreditation (EA), to the Asian Pacific Laboratory Accreditation Cooperation (APLAC) and to the InterAmerican Accreditation Cooperation (IAAC). These announcements were made on the 4 and 5 March 2013 (Annexes 2 - 4).

Registration was opened till the 30th April 2013. The deadline for reporting results was the 22nd June 2013. Dispatch was followed by the messenger's parcel tracking system on the internet.

4.2 Confidentiality

The following confidentiality statement was made to EA, IAAC and APLAC: *"Confidentiality of the participants and their results towards third parties is guaranteed".* In the case of EA the following was added: "*However, IMEP will disclose details of the participants that have been nominated by EA to you. The EA accreditation bodies may wish to inform the nominees of this disclosure".*

4.3 Distribution

Proficiency test items were dispatched on the 15th of May 2013. Each participant received one package containing:

- One bottle containing approximately 2.5 g of the proficiency test item,
- The "*Sample accompanying letter*" (Annex 5),
- A *"Confirmation of Receipt"* form (Annex 6).

4.4 Instructions to participants

Participants were asked to perform two or three independent measurements, correct their measurements for recovery and for the moisture content (protocol provided in the sample accompanying letter) and report their calculated mean (expressed on a dry mass) and its associated measurement uncertainty (u_{lab}).

Participants received an individual code to access the online reporting interface, to report their measurement results and to complete the related questionnaire. The questionnaire was used to extract all relevant information related to measurements and laboratories (Annex 7).

Participants were asked to follow their routine procedures for the analysis and to report results in the same way (e.g. number of significant figures) as they would report to their customers.

5 Proficiency test item

5.1 Preparation

An amount of approximately 5 kg of fresh shiitake mushrooms (*Lentinula edodes*) was screened for the measurands covered in IMEP-39 and provided by the University of Barcelona (Spain). Fresh mushrooms were cleaned by hand of soil, moss, etc. The end of the stalk that had been in contact with soil was cut off using a stainless steel knife. Mushrooms were cut into pieces, which were air dried in a batch-type drying chamber at room temperature for 24 hours and dried in an oven at 40 °C for 24-48 hours. Dried mushrooms were minced using a commercial stainless steel mincer (Multiquick 5 Hand

Processor, Braun) until completely homogenised and were packaged and dispatched immediately to IRMM under refrigerated conditions [6].

Once received, the material was stored at -20 °C until processing. At the time of processing the mushrooms were cut up frozen in smaller pieces using an UMC-12 model cutter/mixer from Stephan (Hameln, Germany).

The material was freeze dried in two cycles using a freeze dryer from Martin Christ model Epsilon 2-10D (Osterode, Germany). Five trays were filled with about 500 g each of pre-cut mushrooms per cycle. In total 5.27 kg was dried, given 570 g of dried mushroom, respectively. These values correspond to a mass loss of about 89 %.

Dried mushrooms were cryogenically milled using a Palla VM-KT vibrating mill from Humboldt-Wedag (Köln, Germany). All grinding elements in this system are made of high purity titanium to avoid contamination of the test item. After milling, this material was sieved over a 250 µm stainless steel sieve resulting in 522 g available for final mixing and homogenisation. Mixing was performed in a Dynamix CM-200 (WAB, Basel, Switzerland). The material available for filling was checked for water content and particle size distribution using Karl Fischer titration and laser diffraction, respectively. Final water content was 4 % (m/m) with a top particle size below 200 µm.

Finally, portions of 2.5 g were filled using an automatic filling machine (Allfill, Sandy, United Kingdom) into 20 ml amber glass acid-washed vials. The vials were closed with an acid washed insert and an aluminium cap.

Each vial was uniquely identified (labelled following the IMEP procedures) which includes a unique number and the name of the PT.

5.2 Homogeneity and stability studies

Homogeneity and stability studies were performed by ALS Scandinavia AB using inductively coupled plasma sector field mass spectrometry (ICP-SFMS) after sample digestion with a mixture of HNO_3/HF. Homogeneity was evaluated according to ISO 13528:2005 [7]. The material proved to be adequately homogeneous for the total mass fraction of As, Cd, Pb and Hg.

The stability study was conducted following an isochronous experimental design [8, 9]. The material proved to be adequately stable for the eight weeks that elapsed between the dispatch of the samples and the deadline for submission of results for all the four investigated elements (As, Cd, Pb and Hg).

It was assumed, on the basis of previous experience (IMEP-107), that, if adequately homogeneous and stable for the total mass fraction of As, it should also be for the inorganic form of that element (iAs).

The contributions due to homogeneity (u_{bb}) and to stability (u_{st}) to the uncertainty of the assigned value (u_{ref}) were calculated using SoftCRM [10]. For iAs identical

contributions were calculated using the same percentage (of the mean value) as estimated for the mass fraction of total As.

The analytical results and the statistical evaluation of the homogeneity and stability studies are provided in Annex 8.

6 Reference values, uncertainties and σ_p

6.1 Assigned value, X_{ref}

The total Cd, Pb, As and Hg and inorganic As mass fractions were determined by five expert laboratories (certifiers, listed below) in order to assign a reference value:

- Federal Institute for Materials Research and Testing (BAM), Germany
- Karl-Franzens-Universität Graz (KFUG), Austria
- Laboratorio de Salud Pública de Alicante (LSPA), Spain
- University of Barcelona, Faculty of Chemistry (UBFC), Spain
- Instituto de Agroquímica y Tecnología de los Alimentos, Consejo Superior de Investigaciones Científicas (CSIC), Spain

Expert laboratories were asked to use the method of their choice and no further requirements were imposed regarding methodology. Expert laboratories were also asked to report their results together with the measurement uncertainty and with a clear and detailed description on how uncertainty was estimated.

The mean of the independent means provided by the certifiers was used to derive the assigned value (X_{ref}) for this PT according to ISO Guide 35:2006 [11].

Table 1 summarises the sample preparation and digestion procedures and details related to the analytical method used by the certifiers.

Table 1 *– Sample treatment, digestion procedures and analytical methods used by the certifiers*

Certifier	Sample treatment / digestion / analytical method	Technique
BAM	**Total As, Cd and Pb**: 0.25 g of sample. Microwave-assisted digestion. 6 mL of HNO_3 (sub-boiling) in an Ultra Clave III. Power 1000 W, ramp 20 min. hold 30 min. Digestion temperature 250 °C at 100 bar. ICP equipped with a collision cell. Argon + helium as collision gas. Multi-point calibration from 0 - 10 µg L^{-1} (5 points) for total As and Pb, 0 – 25 µg L^{-1} for Cd.	ICP-MS
BAM	**Total Hg (method 1)**: 0.25 g o f sample. Microwave-assisted digestion. 6 mL of HNO_3 (sub-boiling) in an Ultra Clave III. Power 1000 W, ramp 20 min. hold 30 min. Digestion temperature: 250 °C at 100 bar. CV-AFS, amalgamation mode (gold trap). Argon as gas. Multi-point calibration from 0-125 µg L^{-1} (5 points).	CV-AFS
BAM	**Total Hg (method 2)**: 0.12 g of sample. Solid sampling cold-vapour AAS, combustion + amalgamation (gold trap). Advanced elementar mercury analyser (AMA-254) at the wavelength of 253.7 nm. Oxygen as gas mode. Multi-point calibration from 0.5 – 36 ng (9 points) and from 40 to 500 ng (9 points).	Elemental Hg analyser
LSPA	**Total As, Cd, Pb**: The digestion of samples was carried out using a microwave digestion system, Ethos one (Milestone Inc., Shelton, USA), equipped with the Q-20 Quartz Rotor Ultratrace Analysis (20 mL quartz tubes, 250 ºC and 40 bars as operating parameters). A unique sample digestion procedure was applied to all samples and analytes. 0.25 g of sample was weighted in quartz digestion vessels and 5 mL of HNO_3:H_2O 1:1 were added in a fume hood. The mixture was leaved to react over an hour approximately until finishing the gas generation process. Samples were placed in the microwave digestion system and a digestion programme was followed using a power of 1200 W and temperature ranging from 95 to 190 °C in three steps taking a total of 38 minutes. Analysis were performed on an ELAN DRC II ICP-MS (PerkinElmer, Inc., Shelton, USA) equipped with a PFA standard nebulizer and a peltier cooled baffled glass cyclonic spray chamber (both from Elemental Scientific, Omaha, USA). Multi-element standard solutions were used for external calibration. Six standards in 2 % (w/w) HNO_3 matrix for As, Cd and Pb were prepared at levels ranging from 0.1 to 50 µg L^{-1}. The calibration curve was drawn from six points, including the calibration blank and there was applied a weighted linear regression approach with internal standardization.	ICP-MS
LSPA	**Total Hg**: 40 mg of sample was weighted directly in quartz samples boats and placed in the mercury analizer. To prevent explosions inside the catalizer, 500 µL of ultra-pure water were added in the quartz boats together with the samples. At least 2 quality control samples (CRM) were analysed in each sequence.	Elemental Hg analyser
KFUG	**Total As**: A portion of the powdered samples (about 250 mg weighed with a precision of 0.1 mg) was weighed directly into 12 mL quartz tubes, and concentrated nitric acid (2 mL) and H_2O (2 mL) were added. The tubes were transferred to a Teflon® rack of the Ultraclave microwave system (MLS GmbH, Leutkirch, Germany) and covered with Teflon® caps. After closing the system, an argon pressure of 4 x 106 Pa was applied and the mixture was heated to 250 °C for 30 minutes before being allowed to cool to room temperature. After mineralization, the samples were transferred to 15 mL polypropylene tubes (Greiner, Bio-one, Frickenhausen, Germany) and diluted with water to 9 mL (based on mass). Finally 1 mL of a solution containing 50 % methanol (to enhance the arsenic response) and 100 µg·L^{-1} each of Ge and In as internal standards were added to all digested samples giving a final concentration of 5 % methanol and 10 µg·L^{-1} of Ge and In. All standards for total arsenic determinations were prepared with 20% (v/v) of concentrated nitric acid and also 5% methanol for matrix matching with the digested samples. The arsenic concentrations in the digests were determined by ICP-MS using helium as collision cell gas.	ICP-MS

Certifier	Sample treatment / digestion / analytical method	Technique
KFUG	**Inorganic As**: About 0.5 g of powder was weighed with a precision of 0.1 mg into 50 mL polypropylene tubes, and a solution (10 mL) of 20 mmol·L^{-1} trifluoracetic acid containing 50 µL of a 30 % H_2O_2 solution was added. Samples were extracted with a GFL-1083 shaking water bath (Gesellschaft für Labortechnik, Burkwedel, Germany) 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 8900 g. The supernatant was used directly for HPLC-ICP-MS analysis.	HPLC-ICP-MS
CSIC	**Inorganic As**: 0.5-1 g of sample. Concentrated HCL is added and water. Reducing agent (2 mL of HBr and 1 mL of hydrazine sulphate) is added. 10 mL of $CHCl_3$. Agitate and separate the phases. Repeat the extraction 3 times. iAs is back-extracted with 10 mL of HCl. 2.5 mL of ashing aid suspension (20 % w/v $Mg(NO_3).6H_2O$ and 2 % w/v MgO) and 10 mL HNO_3 is added. Evaporated to dryness in a sand bath and place at a muffle at 150 °C. Increase the temperature to 425 ± 25 °C for 12 H. The white ash is dissolved in 6 mol L^{-1} HCl and reduced with pre-reducing solution (5 % w/v KI and 5 % w/v ascorbic acid). After 30 min, filter through Whatman N° 1 and dilute with 6 mol L^{-1} HCl. Samples are analysed by flow injection-hydride generation AAS.	FI-HG-AAS
UBFC	**Inorganic As**: A microwave digestion system, Ethos Touch Control (Milestone, Gomensoro, Barcelona, Spain), with a microwave power of 1000 W and temperature control, was used for extraction procedure. An Agilent 7500ce ICPMS was coupled to an Agilent 1200 LC quaternary pump to determine inorganic arsenic content. The analytical columns Hamilton PRP-X100 (250x4.1 mm, 10 µm, Hamilton, USA) and Zorbax-SCX300 (250x 4.6 mm, 5 µm, Agilent) were protected by guard columns filled with the corresponding stationary phases. The outlet of the LC column was connected via PEEK capillary tubing to the nebuliser (BURGENER Ari Mist HP type) of the ICP-MS system, which was the arsenic-selective detector. 0.25-g aliquots of the test material and the CRMs were weighed in PTFE vessels and then extracted by adding 10 mL of 0.2 % (w/v) HNO_3 and 1 % (w/v) H_2O_2 solution in a microwave digestion system. The temperature was raised first to 55 °C (and held for 10 min) then to 75 °C (and held for 10 min) and finally the digest was taken up to 95 °C and maintained for 30 min. Samples were cooled to room temperature and centrifuged at 3500 rpm for 12 min. The supernatant was filtered through PET filters (pore size 0.45 µm).	HPLC-ICP-MS

6.2 Uncertainty of assigned value, u_{ref}

The standard uncertainties associated to the assigned values (u_{ref}) were calculated according to ISO/IEC Guide 98:2008 (GUM) [12] by combining the uncertainty of the characterisation (u_{char}) with a contribution for homogeneity (u_{bb}) and for stability (u_{st}), according to equation 1:

$$u_{ref} = \sqrt{u_{char}^2 + u_{bb}^2 + u_{st}^2} \qquad \text{Eq. 1}$$

u_{char} was calculated combining the standard uncertainties reported by the expert laboratories (u_i) according to ISO 13528:2005 [7] (equation 2):

$$u_{char} = \frac{1.25}{p}\sqrt{\sum_1^p u_i^2} \qquad \text{Eq. 2}$$

Where *p* refers to the number of expert laboratories used to assign the reference value.

Table 2 presents the results reported by the expert laboratories, standard uncertainty contributions, the reference values (X_{ref}, u_{ref} and U_{ref}) and the standard deviation for the proficiency assessment, σ_p.

Table 2 *– Reported values by the expert laboratories (X_n), their uncertainty contributions (U_n, k=2), assigned value, standard and combined uncertainties (u_{ref}) (in mg kg^{-1})*

	Certifier	Total Cd	Total Pb	Total As	Total Hg	iAs
$X_n \pm U_n$	*BAM*	4.42 ± 0.19	0.274 ± 0.019	0.638 ± 0.026	0.0782 ± 0.0032 [a] 0.0781 ± 0.007 [b]	
	LSPA	3.99 ± 0.44	0.260 ± 0.016	0.61 ± 0.06	0.072 ± 0.007	
	KFUG			0.69 ± 0.05		0.330 ± 0.014
	CSIC					0.286 ± 0.037
	UBFC					0.348 ± 0.026
X_{ref}		**4.21**	**0.267**	**0.646**	**0.076**	**0.321**
u_{char}		0.15	0.008	0.017	0.002	0.010
u_{bb}		0.04	0.009	0.007	0.002	0.004
u_{st}		0.06	0.010	0.015	0.002	0.007
u_{ref}		0.17	0.016	0.024	0.004	0.013
U_{ref} (k=2)		**0.33**	**0.031**	**0.048**	**0.007**	**0.026**
σ_p		0.42	0.05	0.10	0.011	0.06
σ_p (%)		**10%**	**20%**	**15%**	**15%**	**19%**

Where: [a] method 1; [b] method 2

6.3 Standard deviation for the proficiency assessment, σ_p

The standard deviation for proficiency assessment (σ_p) for total Pb (20 %) and inorganic arsenic (19 %) were calculated using the Horwitz equation as modified by Thompson [13]. For the rest of the measurands σ_p was set by the advisory board of this PT to 15 % for total As and Hg and to 10 % for total Cd, on the basis of previous experience on similar measurands. For all measurands, the value (in %), refers to a percentage of the respective assigned value (X_{ref}).

7 Results and evaluation

7.1 Scores and evaluation criteria

Individual laboratory performance was expressed in terms of *z*- and *ζ-scores* in accordance with ISO 13528:2005 [7]:

$$z = \frac{x_{lab} - X_{ref}}{\sigma_p} \qquad \text{Eq. 3}$$

$$\zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}} \qquad \text{Eq. 4}$$

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

The interpretation of the *z*- and *ζ-score* is done as follows (according to ISO/IEC 17043:2010 [5]):

Satisfactory performance,	|score| ≤ 2
Questionable performance,	2 < |score| < 3
Unsatisfactory performance,	|score| ≥ 3

The z-score compares the participant's deviation from the reference value with the standard deviation for proficiency assessment (σ_p) used as common quality criterion. σ_p is defined by the PT organiser as the maximum acceptable standard uncertainty.

The ζ-score states if the laboratory result agrees with the assigned value within the respective uncertainty. The denominator is the combined uncertainty of the assigned value and the measurement uncertainty as stated by the laboratory. The ζ-score is therefore the most relevant evaluation parameter, as it includes all parts of a measurement result, namely the expected value (assigned value), its uncertainty and 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 uncertainty or both.

The standard uncertainty of the laboratory (u_{lab}) was estimated by dividing the reported expanded uncertainty by the reported coverage factor, *k*. When no uncertainty was reported, it was set to zero (u_{lab} = 0). When *k* was not specified, the reported expanded uncertainty was considered as the half-width of a rectangular distribution; u_{lab} was then calculated by dividing this half-width by √3, as recommended by Eurachem and CITAC [14].

Uncertainty estimation is not trivial; therefore an additional assessment was provided to each laboratory reporting uncertainty, indicating how reasonable their uncertainty estimate is. The standard uncertainty from the laboratory (u_{lab}) is most likely to fall in a range between a minimum uncertainty (u_{min}), and a maximum allowed (u_{max}, case "*a*"). u_{min} is set to the standard uncertainty of the reference value (u_{ref}). It is unlikely that a laboratory carrying out the analysis on a routine basis would measure the measurand with a smaller uncertainty than the expert laboratories chosen to establish the assigned value. u_{max} is set to the standard deviation (σ_p) accepted for the PT assessment.

If u_{lab} is smaller than u_{min} (case "*b*") the laboratory may have underestimated its uncertainty. However, such a statement has to be taken with care as each laboratory reported only measurement uncertainty, whereas the uncertainty of the reference value also includes contributions of homogeneity and stability. If those are large, measurement uncertainties smaller than u_{min} (u_{ref}) are possible and plausible.

If u_{lab} is larger than u_{max}, (case "*c*") the laboratory may have overestimated the uncertainty. An evaluation of this statement can be made when looking at the difference of the reported value and the assigned value: if the difference is small and the uncertainty is large, then overestimation is likely. If, however, the deviation is large but is covered by the uncertainty, then the uncertainty is properly assessed, but large. It should be pointed out that u_{max} is only a normative criterion if set down by legislation.

7.2 General observations

Results were received from 62 of the 71 registered laboratories.

Those reporting "less than X" values were not evaluated. However, reported "less than X" values were compared with the corresponding $X_{ref} - U_{ref}$. If the reported limit value "X" was lower than the corresponding $X_{ref} - U_{ref}$, this statement should be considered incorrect, since the laboratory should have detected the respective element. Those laboratories are marked in red in Annexes 9-13. For the majority of laboratories in which "lower than X" was reported, X equals the reported limit of detection (LoD).

7.3 Laboratory results and scorings

Annexes 9-13 present the reported results as a table and as a graph. Furthermore, it includes the corresponding Kernel density plot, obtained using the software available from the Statistical Subcommittee of the Analytical Methods Committee of the UK Royal Society of Chemistry [15].

Figure 1 presents an overview of the z- and ζ-scores. Up to 84 % of the participants obtained a satisfactory performance ($|z\text{-score}| \leq 2$) for the determination of the total Cd mass fraction. For total Pb, As, Hg and iAs the percentages of satisfactory performance (z-scores) were 68, 65, 72 and 64 %, respectively.

Concerning the ζ-scores a lower percentage of the population performed

satisfactorily (ranging from 44 to 66 %, for total As and Cd mass fractions, respectively) and 46, 52 and 55 % for total Pb, Hg and iAs, respectively. Thus, laboratories should enhance their effort in the estimation of the uncertainty associated with their measurements.

Annex 14 summarises all scores per participant.

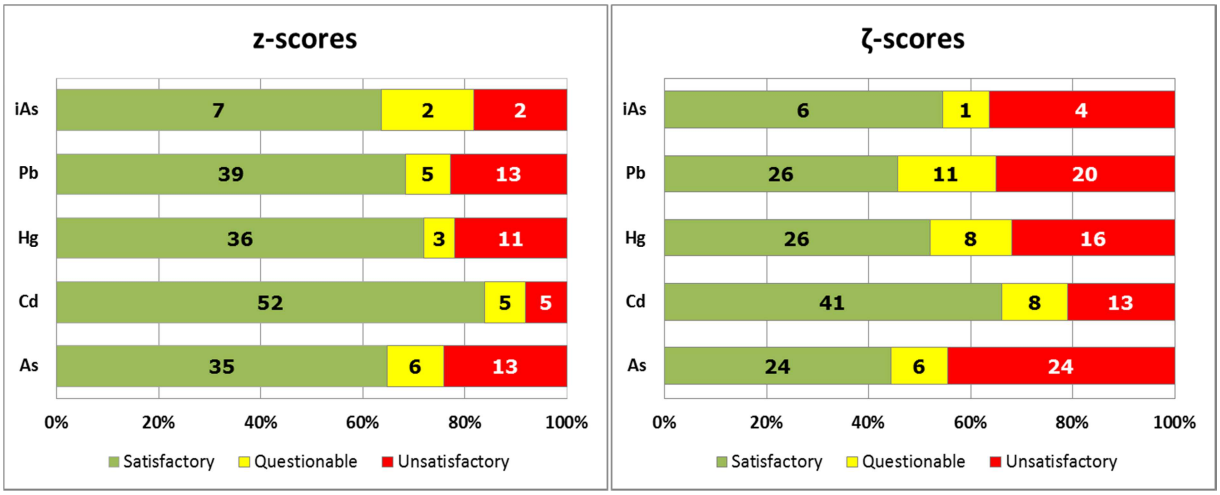

Figure 1 *- Overview of scores (in % and in the number of laboratories having satisfactory, questionable and unsatisfactory performance)*

The assessment of reported uncertainties, presented in Table 3, is based on the three uncertainty estimation categories defined in chapter 7.1: "a" (realistic), "b" (possibly underestimated) and "c" (possibly overestimated). Most of the laboratories having reported underestimated uncertainties obtained unsatisfactory ζ-scores (Annexes 9-13).

Table 3 *– Uncertainty assessment (in %).*

	Case "a"	***Case "b"***	***Case "c"***
Total Cd	*34*	*47*	*19*
Total Pb	*53*	*39*	*9*
Total As	*57*	*37*	*6*
Total Hg	*44*	*36*	*20*
iAs	*55*	*27*	*18*

Where "a": u_{min} (u_{ref}) ≤ u_{lab} ≤ u_{max} (σ_p); "b": $u_{lab} < u_{min}$; "c": $u_{lab} > u_{max}$

It is worth mentioning that more than half of the participants estimated correctly their measurement uncertainty for the total mass fractions of As and Pb and for the inorganic arsenic. However, a relatively high percentage of participants underestimated

their uncertainty (case "b"). This fact is in disagreement with what was observed in IMEP-116 (only NRLs) where the percentage of participants having overestimated their uncertainties (case "c") was higher than that having underestimated it (case "b"). Underestimation of measurement uncertainty may occur when only repeatability data is used as the way to estimate the standard uncertainty. Indeed, among the 44 participants who filled in the questionnaire, 19 (43 %) stated to have used the observed variability from replicates (precision) as the method for the estimation of their measurement uncertainty.

Among those laboratories which overestimated their uncertainties, two (L06 and L23, identified in Annexes 9-13) reported their uncertainties as a percentage of their reported value instead of in mg kg^{-1}.

7.4 Further information extracted from the questionnaire

7.4.1 Multivariate models

In addition to the submission of results, participants were asked to answer a number of questions related to:

i) The analytical method used,

ii) The quality assurance of their results.

In order to allow the identification of all major potential sources of variability among the reported results we investigated the relation between each reported value (for each measurand) and the set of responses provided in the questionnaire. The statistical data treatment was performed using The Unscrambler X 10.1 (CAMO Software AS, Norway). Answers were first transformed into numerical variables (1 if positive, 0 if negative), before applying partial least square regression modelling (PLS-R).

Multivariate models succeeded to "explain" a reasonable percentage of the total covariance relating the reported results and the set of responses. Furthermore, the model errors were generally lower than the observed variability for each corresponding set of reported values (expressed as the respective standard deviation). Therefore the multivariate models allowed reliable interpretations.

The set of questions from the questionnaire that showed the strongest correlation with satisfactory performances are presented in Table 4. Participants who answered with "yes" to those questions, generally, performed well. Table 4 lists the variables strongest correlated to satisfactory performances. Not all participants filled in their questionnaire (approximately 20 % of the participants).

***Table 4** – Questions in Annex 7 correlated with satisfactory performance (|z-score|≤2)*

Annex 7	***Question***
Q4c	Uncertainty by in-house validation?
Q6	Correct for moisture?
Q7	Follow an official method?
Q8	Use microwave?
Q9	Use HNO_3 + H_2O_2?
Q12	Carry this type of analyses regularly?
Q13	Have a quality system?
Q14	Accredited for this type of analysis?
Q15	Take part in appropriate ILCs?
Q16	Use CRMs for this type of analysis?

Participants who did not succeed to have satisfactory performance for a particular measurand are encouraged to check their response for the selected set of questions presented in Table 4.

7.4.2 Learning points about analytical methods

When looking at the results reported in IMEP-39 two clear tendencies were observed:

1) *Tendency to under-quantify the total As mass fraction*

At first glance this under-quantification was directly related to the technique used, as illustrated in Figure 2. In general, participants using AAS-based techniques reported lower values than the participants which used ICP-based techniques (ICP-MS and ICP-AES). The lower values reported by participants using AAS-based techniques resulted in a significantly lower percentage of satisfactory z-scores (30 %) when compared with those obtained by laboratories using ICP-based techniques (88 %). However, this clustering of results, based on the technique used, could only be a secondary effect of a different primary cause, namely a non-quantitative digestion of the matrix. Some organic species of arsenic are difficult to digest and require digestion temperatures of around 280 °C when microwave digestion is used (most of the participants in IMEP-39 used microwave digestion, Annex 15). Most of the laboratories which clearly under-quantified the total As mass fraction used temperatures in the range 190-200 °C with further hydride generation-AAS (HG-AAS).

The high temperatures reached in the plasma would eliminate that problem when ICP-based techniques are used. The same would apply to methods which involve a final determination of total As using electrothermal atomic absorption spectrometry (ET-AAS),

since atomisation temperatures in the graphite furnace are also high. The problem of non-quantitative digestion would mostly affect the results obtained with hydride generation because only inorganic arsenic species and, to a lesser extent, methylated arsenic species can generate the hydride. This would also explain the under-quantification of the total As mass fraction in the result reported by L20 which used atomic fluorescence spectrometry (AFS), a technique which also requires generation of the arsenic hydride before the final determination by AFS. Laboratories using HG-AAS must also keep in mind that after digestion of the matrix with a mixture of HNO_3 and H_2O_2 (mixture used by most of the participants in IMEP-39), if the digestion is quantitative, most arsenic will be present in the form of As(V) and needs to be reduced to As(III) which is the arsenic species generating the hydride form with higher yield. This means that a reduction step must be included and optimised prior to hydride generation to ensure quantitative reduction of As (V) to As(III).

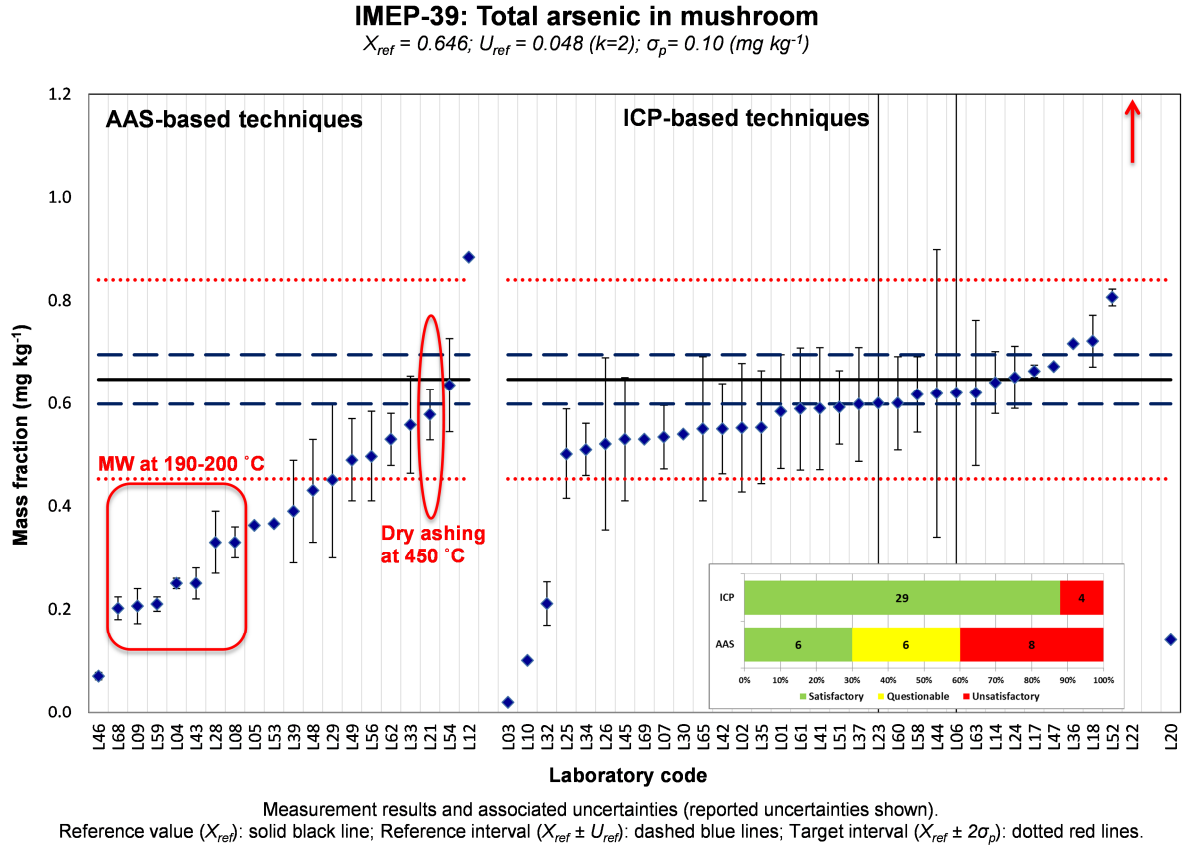

Figure 2 *– Effect of the technique used for the determination of the total mass fraction of As.*

For inorganic arsenic determination, five out of the seven laboratories that obtained satisfactory z-scores, used AAS-based techniques. If proper method validation is carried out AAS-based methods are cheap and easy-to-use methods which can provide sound results.

The influence of the technique used was not so significant for the total Cd, Pb and Hg mass fractions. However, it should be noted that the four lowest values reported for total Cd (L38, L43, L48 and L50, Annex 10) used AAS or ET-AAS. A similar observation was made for the total Pb mass fraction for which the three laboratories obtaining an unsatisfactory z-score due to a serious under-quantification of this measurand (L05, L38 and L53, Annex 11) used AAS and ET-AAS. The majority of these participants used microwave assisted digestion with a mixture HNO_3 and H_2O_2 with temperatures between 190-200 °C.

It is then the opinion of the PT provider that the observed under-quantifications are not due to any effect directly related to AAS but to the use of low digestion temperatures. AAS-based techniques can be used if high temperatures are used for sample digestion (for instance dry ashing at 450 °C), as shown by L21.

2) *Tendency to over-quantify the total Pb and Hg mass fractions*

A relatively high number of laboratories reported unsatisfactory results in terms of z-scores for total Pb and Hg due to over-quantification regardless of the technique used. Over-quantification of the total Pb mass fraction could be due to contamination problems. Several of the over-quantified values for total Pb were submitted by laboratories situated in the same geographic region. General environmental contamination due to industrial activities could be at the root of the problem.

The PT organiser was not able to find a suitable explanation for the over-quantification of total Hg. Contamination in this case is not as likely to occur as in total Pb analysis.

Other issues than the influence of the technique were scrutinised. In general the use of microwave-assisted digestion with a mixture of HNO_3 and H_2O_2 appears to be an efficient sample digestion approach, if temperatures higher than 280 °C are used.

Annex 15 summarised all answers related to experimental details and scorings. Table 6 presents the feedback received from the participants.

***Table 6** – Feedback from participants (as taken from the questionnaire)*

Lab ID	*Do you have any comments? Please let us know: …*
L03	No
L09	The amount of sample to be analysed was too small (2g). According to the actual standards, the weight of samples to be analysed should be between 5 and 10 g.
L11	The validated method of analysis in our lab. is according SR EN 14082; we use 10 grams sample
L13	No comments
L24	The mass of the sample was very low (total of 2.5 g and 0.5g for moisture determination)
L43	No
L45	We don't analayse the inorganic As
L58	We've been accredited since a month for this method. Inorganic arsenic has not been tested.
L59	Sample quantity was very small for the required parameters
L63	No
L65	No

8 Conclusion

The performance of food control laboratories for the determination of all investigated trace elements in freeze dried mushrooms was found to be ranging from 64 to 84 % (expressed as z-scores).

Thus, the present proficiency test demonstrates that the analytical capabilities of food control laboratories, for the determination of the investigated food contaminants, at the investigated levels of concentration, can be improved.

When comparing the performance in IMEP-39 with that in IMEP-116, the overall rates of satisfactory z-scores, ranged from 10 % to 26 % higher in the former than in the latter. The feedback given to NRLs in the fourteen PTs which have been so far organised by the EURL-HM, as well as the training sessions on several aspects of the analyses of heavy metals in feed and food, provided during the annual workshops organised by the EURL-HM, have seemingly an impact in the performance of the NRLs. Since most of the participants in IMEP-39 regularly take part in PTs covering this type of analyses (question 15 of the questionnaire) two things can be concluded: - that laboratories should invest in the training of their staff and – that PT providers should use their report to participants to provide feedback on general analytical issues spotted during a certain PT. ISO 17043 clearly put emphasis in the educational role that a PT should have and IMEP is looking forward to observing that accreditation bodies carefully control this during their audits to accredited PT providers.

For total As a high percentage of participants using AAS-based techniques reported lower values than participants using ICP-based techniques. The reason seems to be incomplete mineralisation of some organic species of arsenic when temperatures lower than 280 °C are used during the microwave digestion. The high temperatures reached in the plasma eliminate the impact of the incomplete mineralisation. However, AAS-based techniques can be applied if temperatures high enough are used during the digestion step. Dry ashing would then also be a suitable alternative to overcome the mentioned problem.

Attention needs also to be paid to the reduction of As(V) to As(III) when hydride generation is used.

9 Acknowledgements

The laboratories participating in this exercise, listed below, are kindly acknowledged (Non EU countries are highlighted). P. Conneely (IRMM) is acknowledged for the measurements performed to estimate the moisture of the test item. M-F. Tumba-Tshilumba (IRMM) is acknowledged for the particle size analysis measurements. W. Limberger is acknowledged for the mushroom drawing of the front page. F. Ulberth (IRMM) is acknowledged for reviewing the manuscript.

Organisation	Country
Symbio Alliance	AUSTRALIA
Seibersdorf Labor GmbH	AUSTRIA
ANALYTEC GmbH	AUSTRIA
AGES GmbH	AUSTRIA
Lebensmitteluntersuchungsanstalt Kaernten	AUSTRIA
Institut Ernest Malvoz - Laboratoire Santé et Qualité de Vie	BELGIUM
CELABOR SCRL	BELGIUM
Laboratorium ECCA NV	BELGIUM
Sofia Regional Health Inspectorate	BULGARIA
Eurobul Lovico Ltd	BULGARIA
Saskatchewan Research Council	CANADA
Shandong Entry-Extit Inspectin and Quarantine Bureau of P.R.C	CHINA
GEMANALYSIS LTD	CYPRUS
Pankemi lab	CYPRUS
Statni Veterinarni Ustav PRAHA	CZECH REPUBLIC
ZDRAVOTNI USTAV SE SIDLEM V OSTRAVE	CZECH REPUBLIC
MVDr. Sotola s.r.o.	CZECH REPUBLIC
MetropoliLab Oy	FINLAND
Eurofins Analytics France	FRANCE
INRA	FRANCE
Institute of Public Health of R.Macedonia	FYR OF MACEDONIA
Center for public health Bitola	FYR OF MACEDONIA
Eurofins WEJ Contaminants GmbH	GERMANY
Landeslabor	GERMANY
University of Athens, Laboratory of Analytical Chemistry	GREECE
General Chemical State Laboratory	GREECE
Enviro Labs Limited	HONG KONG
Food Analytica Ltd	HUNGARY
National Food Chain Safety Office	HUNGARY
Center for Agro Based Industry	INDONESIA

Organisation	Country
Milouda&Migal	ISRAEL
The Standards Institution of Israel	ISRAEL
Public Health Laboratory	ISRAEL
EPTA NORD srl	ITALY
Ltd Latvian Certification Centre	LATVIA
Analisis Tecnicos, SA DE CV (AGROLAB)	MEXICO
TLR International Laboratories	NETHERLANDS
Eurofins Food Testing Netherlands bv	NETHERLANDS
Sentrotek Corp.	PHILIPPINES
WOJEWÓDZKA STACJA SANITARNO-EPIDEMIOLOGICZNA W ŁODZI	POLAND
IBPRS Oddział Chłodnictwa i Jakości Żywnosci	POLAND
Controlvet	PORTUGAL
National Institute of Health Doutor Ricardo Jorge, I.P.	PORTUGAL
ICA Research&Development SRL	ROMANIA
Bucharets, Sanitary Veterinary and Safety Directorate	ROMANIA
DSVSA Iasi	ROMANIA
A BIO TECH LAB d.o.o.	SERBIA
Enoloska stanica Vrsac	SERBIA
ALFALAB D.O.O.	SERBIA
Zavod za zdravstveno varstvo Novo mesto	SLOVENIA
Laboratory of the Public Health Agency of Barcelona	SPAIN
Laboratorio del Centro de Salud Publica de Alicante	SPAIN
Laboratorio Salud Pública Bizkaia	SPAIN
ALS Scandinavia AB	SWEDEN
Eurofins Environment Testing Sweden AB	SWEDEN
Laboratorio Cantonale	SWITZERLAND
Labor der Urkantone	SWITZERLAND
Amt für Lebensmittelsicherheit und Tiergesundheit Graubünden	SWITZERLAND
Food Industry Research and Development Institute	TAIWAN
Central Laboratory for Analysis and Testing - LCAE	TUNISIA
Hampshire County Council	UNITED KINGDOM
MSE-TA	UNITED STATES

Abbreviations

AAS	Atomic absorption spectroscopy
APLAC	Asian Pacific Laboratory Accreditation Cooperation
CITAC	Cooperation on international traceability in analytical chemistry
CV-AFS	Cold-vapour atomic fluorescence spectrometry
EA	European Cooperation for Accreditation
ET-AAS	Electrothermal atomic absorption spectrometry
EU	European Union
EURL-HM	European Union Reference Laboratory for Heavy Metals in Feed and Food
FI-HG-AAS	Flow injection hydride-generation atomic aborption spectrometry
HPLC-ICP-MS	High performance liquid chromatography inductively-coupled plasma mass spectrometry
IAAC	InterAmerican Accreditation Cooperation
ICP-MS	Inductively-coupled plasma mass spectrometry
ICP-SFMS	Inductively-coupled plasma sector field mass spectrometry
ICP-AES	Inductively-coupled plasma atomic emission spectroscopy
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
ISO GUM	International Organisation for Standardisation – Guide to the expression of Uncertainty in Measurement
JRC	Joint Research Centre
LC-ICP-MS	Liquid chromatography inductively-coupled plasma mass spectrometry
NRL	National Reference Laboratory
PT	Proficiency testing
PLS-R	Partial least squares regression
SS-CV-AAS	Solid sampling cold-vapour atomic aborption spectrometry

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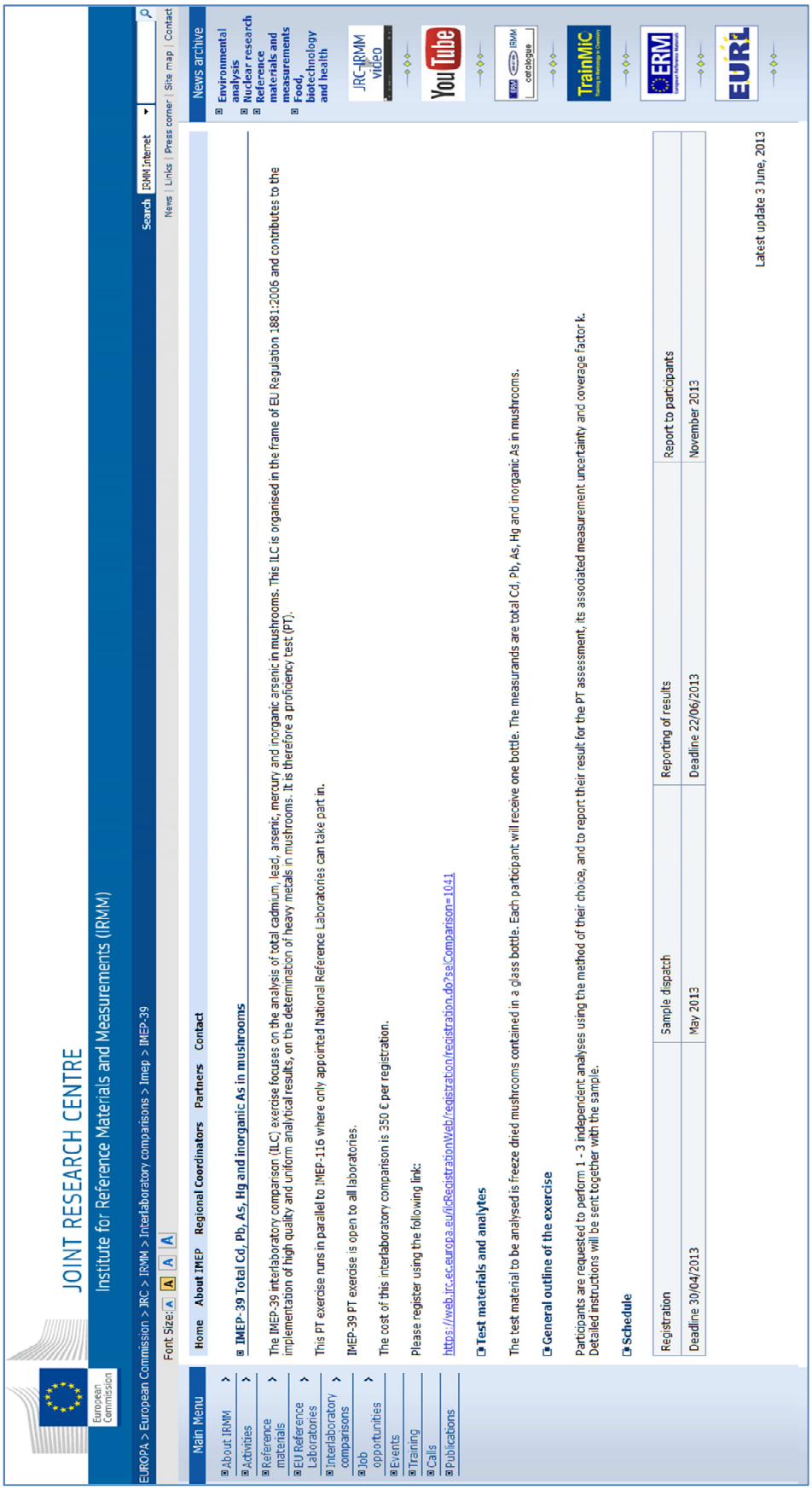
Annexes

Annex 1: IRMM/IMEP web announcement



Annex 2: Invitation to EA to nominate laboratories

Ref. Ares(2013)298405 - 06/03/2013

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
International Measurement Evaluation Program

05th March 2013

SWEDAC
Annika Norling
Box 2231
10315 Stockholm
SWEDEN

Dear Annika,

Interlaboratory comparison exercise for the determination of total Cd, Pb, As, Hg and inorganic As in mushrooms

The Institute for Reference Materials and Measurements (IRMM) organises an interlaboratory comparison named **"IMEP-39: Determination of the total Cd, Pb, As, Hg and inorganic As in mushrooms"** in support to the *EU Regulation 1881:2006 which sets maximum levels for certain contaminants in foodstuffs*.

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

I suggest that you forward this invitation to the national EA accreditation bodies for their consideration. There are a limited number of samples at your disposal and the number of nominees should not exceed 2-3 laboratories per country.

Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to you. The EA accreditation bodies may wish to inform the nominees of this disclosure.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 687, Fax: +32-(0)14-571 685.

E-mail: irc-irmm-imep@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

The registration page for laboratories appointed by EA is open until **30 April 2013**. Distribution of the samples is foreseen for the first half of May 2013. The deadline for submission of results is **15 June 2013**.

In order to register, laboratories must:

1. **Enter** their details online:

https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparison=1041

2. **Print** the completed form when the system asks to do so.

3. **Clearly indicate on the printed form that you have been appointed by the European Cooperation for Accreditation** to take part in this exercise **otherwise the laboratory will be invoiced 350 € for participation** as charged to the non-appointed laboratories.

4. **Send** the printout to both the IMEP-39 and the EA-IMEP-39 coordinators:

IMEP-39 coordinator
Dr. Fernando Cordeiro
Fax +32 14 571865
E-mail: jrc-irmm-imep@ec.europa.eu

EA-IMEP-39 coordinator
Mrs. Annika Norling
Fax +46 0 7918929
E-mail: Annika.norling@swedac.se

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

With kind regards

Fernando Cordeiro
IMEP-39 Coordinator

Annex 3: Invitation to APLAC to nominate laboratories

Ref. Ares(2013)298159 - 06/03/2013

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
International Measurement Evaluation Program

Geel, 05 March 2013

To: Aparna Dhawan
APLAC PT Committee

Interlaboratory comparison exercise for the determination of the total cadmium, lead, arsenic, mercury and inorganic arsenic in mushrooms

Dear Aparna,

The Institute for Reference Materials and Measurements (IRMM) organises an interlaboratory comparison named "**IMEP-39: Determination of the total Cd, Pb, As, Hg and inorganic As in mushrooms**".

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

In addition to the 10 laboratories above mentioned, other laboratories may take part in IMEP-39 paying a registration fee of 350 €.

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

Registration of participants is open until **30 April 2013**. Distribution of the samples is foreseen for the first week of May 2013, and the deadline for submission of results is **15 June 2013**.

In order to register, laboratories must:

1. **Enter** their details online:

https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparison=1041

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 687, Fax: +32-(0)14-571 685.

E-mail: jrc-irmm-imep@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

2. **Print** the completed form when the system asks to do so.

3. **Clearly indicate on the printed form that they have been appointed by APLAC** to take part in this exercise **otherwise the laboratory will be invoiced 350 € for participation** normally applied for non-appointed laboratories.

4. **Send** the printout to both the IMEP-39 and the APLAC coordinators:

IMEP-39 coordinator	**APLAC coordinator**
Fernando Cordeiro	Aparna Dhawan
Fax +32 14 571 865	
E-mail: jrc-irmm-imep@ec.europa.eu	E-mail: aparna@nabl-india.org

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

With kind regards

Fernando Cordeiro

Dr. Fernando Cordeiro
IMEP-39 Coordinator

Annex 4: Invitation to IAAC to nominate laboratories

Ref. Ares(2013)298148 - 06/03/2013

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
International Measurement Evaluation Program

Geel, 04 March 2013

To: Barbara Belzer
IAAC Lab Committee

Interlaboratory comparison exercise for the determination of the total cadmium, lead, arsenic, mercury and inorganic arsenic in mushrooms

Dear Mrs. Belzer,

The Institute for Reference Materials and Measurements (IRMM) organises an interlaboratory comparison named "**IMEP-39: Determination of the total Cd, Pb, As, Hg and inorganic As in mushrooms**".

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

In addition to the 10 laboratories above mentioned, other laboratories may take part in IMEP-39 paying a registration fee of 350 €.

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

Registration of participants is open until **30 April 2013**. Distribution of the samples is foreseen for the first week of May 2013, and the deadline for submission of results is **15 June 2013**.

In order to register, laboratories must:

1. **Enter** their details online:

https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparison=1041

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 687, Fax: +32-(0)14-571 685.

E-mail: jrc-lrmm-lmep@ec.europa.eu
Web site: http://lrmm.jrc.ec.europa.eu

2. **Print** the completed form when the system asks to do so.

3. **Clearly indicate on the printed form that they have been appointed by IAAC** to take part in this exercise **otherwise the laboratory will be invoiced 350 € for participation** normally applied for non-appointed laboratories.

4. **Send** the printout to both the IMEP-39 and the IAAC coordinators:

IMEP-39 coordinator	**IAAC coordinator**
Fernando Cordeiro	Barbara Belzer
Fax +32 14 571 865	
E-mail: jrc-irmm-imep@ec.europa.eu	E-mail: barbara.belzer@nist.gov

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

With kind regards

Fernando Cordeiro

Dr. Fernando Cordeiro
IMEP-39 Coordinator

Annex 5: Sample accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
International Measurement Evaluation Program

Geel, 14 May 2013
JRC.D5/FCR/acs/

Participation in IMEP-39, a proficiency test exercise for the determination of total cadmium (Cd), lead (Pb), arsenic (As), mercury (Hg) and inorganic arsenic (iAs) in mushrooms

Dear,

Thank you for participating in the IMEP-39 proficiency test for the determination of the total Cd, Pb, Ar, Hg and iAs in mushrooms. This proficiency test (PT) exercise is organised in support to the EU Regulation 1881:2006 which sets maximum levels for certain contaminants in foodstuffs.

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

This parcel contains:

(a) One bottle containing approximately 2.5 g of the test material

(b) A "Confirmation of Receipt" form

(c) This accompanying letter.

Please check whether the bottle containing the test material remained undamaged during transport. Then, please send the "Confirmation of receipt" form back (fax: +32-14-571865, e-mail: jrc-irmm-imep@ec.europa.eu). You should store the sample in a dark place at ≤4 ºC until analysis.

The measurand is total Cd, Pb, Ar, Hg and iAs in mushroom. The sample matrix is a mixture of commercially available mushroom (freeze dried).

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

The results are to be reported with correction for moisture (in dry mass).

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 687, Fax: (32-14) 571 865

E-mail: jrc-irmm-imep@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

To calculate the **water content** in the test material, please apply the following procedure:

1) Weigh approximately 500 mg of test material in a petri-dish of 3.5 cm diameter, preferably with a lid. The thickness of the powder-layer should be about 3-4 mm covering the bottom of the dish.
2) Place it in a checked and calibrated drying oven at 90 ± 2 °C for 60 ± 2 minutes. Allow the glass container (covered with the lid) to cool down for about 30 minutes in a desiccator before weighing.
3) Calculate the average mass loss from the dried material in percentage of the initial mass.

Please note that this drying method is devised to result in a mass loss that corresponds to the water content in % (m/m) as measured by Karl Fischer titration which is specific for water. Therefore it is not necessary to dry and continue weighing until constant mass. Keeping the material longer than one hour in the oven will result in an excessive mass loss and an erroneous dry-mass correction.

Note : do not use for the heavy metal determinations the aliquots of test material that you have used for the water content determination!

Reporting of results

Please perform two or three independent measurements, correct the measurements results for recovery and for the moisture content and report on the reporting website:

- the **mean** of your two or three measurement results (mg kg^{-1}, as dry mass)
- the associated expanded **uncertainty** (mg kg^{-1}),
- the **coverage factor** and
- the **technique** you used.

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

The reporting website is https://irmm.jrc.ec.europa.eu/ilc/ilcReporting.do

To access the webpage you need a personal password key, which is: xxxxxxxx. The system will guide you through the reporting procedure. After entering your results, please complete also the relating questionnaire.

Do not forget to submit and confirm always when required.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 687, Fax: (32-14) 571 865

E-mail: jrc-irmm-imep@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

Directly after submitting your results and the questionnaire information online, you will be prompted to print the completed report form. Please do so, **sign the paper version and return it to IRMM by fax (at +32-14-571-865) or by e-mail**. Check your results carefully for any errors before submission, since this is your last definitive confirmation.

The **deadline** for submission of results is **22/06/2013**.

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

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

With kind regards

Dr. Fernando Cordeiro
IMEP-39 Co-ordinator

Enclosures (3):

4) One bottle containing the test material;
5) Confirmation of receipt form;
6) Accompanying letter.

Cc: F. Ulberth

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 687, Fax: (32-14) 571 865

E-mail: jrc-irmm-imep@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

Annex 6: "Confirmation of receipt" form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
International Measurement Evaluation Program

Annex to
JRC.D5/FCR/acs/ARES(2013)

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

IMEP-39

Total cadmium (Cd), lead (Pb), arsenic (As), mercury (Hg) and inorganic arsenic (iAs) in mushrooms

Confirmation of receipt of the samples

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

ANY REMARKS .....
.....

Date of package arrival .....

Signature .....

Please return this form to:

Fernando Cordeiro Raposo

IMEP-39 Coordinator
EC-JRC-IRMM
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B-2440 GEEL, Belgium

Fax : +32-14-571865

e-mail : JRC-IRMM-IMEP@ec.europa.eu

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

Annex 7: Questionnaire

Comparison for IMEP-39

Please fill the questionnaire!

Submission Form

1. **Have you been nominated by your National accreditation body to participate in this PT? Which one?** *

2. **Did you correct your measurements for the analytical recovery?**

- a) Yes
- b) No

3. **How did you determine the analytical recovery?**

- a) adding a known amount of the same analyte (spiking)
- b) using a certified reference material
- c) other

3.1. If other, please specify:

3.1.1. Please fill the table:

Analytical recovery (in %) and limit of detection (LoD in mg/kg)

Questions/Response table	Total Cd	Total Pb	Total As	Total Hg	Inorganic As
Recovery (in %)					
LoD (in mg/kg)					

4. **What is the basis of your uncertainty estimate (multiple answers are possible)?**

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

4.1. If other, please specify

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

- a) Yes
- b) No

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

- a) Yes
- b) No

6.1. If Yes, what is the moisture content (in % of the sample mass)?

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

7. **Did you analyse the sample according to an official method?**

- a) Yes
- b) No

7.1. If Yes, which one?

Questions/Response table	Which official method?
Total Cd	
Total Pb	
Total As	
Total Hg	
Inorganic As	

8. **Did you use microwave digestion techniques?**

- a) Yes
- b) No

8.1. Any comment regarding this question?

9. **Did you use HNO3 and H2O2 for sample digestion?**

- a) Yes
- b) No

9.1. Any comments regarding this question?

10. **Did you use an internal standard?**

- a) Yes
- b) No

11. **Other experimental details**

Experimantal details

Questions/Response table	Sample pre-treatment	Digestion	Extraction/separation	Instrumental calibration
Total Cd				
Total pb				
Total As				
Total Hg				
Inorganic As				

12. **Does your laboratory carry out this type of analysis (as regards the analytes, matrix and methods) on a regular basis?**

- a) Yes
- b) No

12.1. If Yes, please fill the corresponding table (samples per year)

Questions/Response table	**b) 0-50**	**c) 50-250**	**d) > 1000**	**e) more than 1000**	*Info*
Total Cd					
Total Pb					
Total Hg					
Total As					
Inorganic As					

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

- a) Yes
- b) No

13.1. If Yes, which one?

- a) ISO 17025
- b) ISO 9000 series
- c) Other

13.1.1. If other, please specify

14. **Is your laboratory accredited for this type of analysis?**

Questions/Response table	**Accredited**	**Not accredited**	*Info*
Total Cd			
Total Pb			
Total Hg			
Total As			
Inorganic As			

15. **Does your laboratory take part in interlaboratory comparisons scheme for this type of analysis?**

- a) Yes
- b) No

15.1. If yes, which one?

Interlaboratory comparison (ILC) for:

Questions/Response table	ILC (please identify it)
Total Cd	
Total Pb	
Total As	
Total Hg	
Inorganic As	

16. **Does your laboratory use a certified reference material (CRM) for this type of analysis?**

Questions/Response table	CRM used	Validation of procedures	Instrument calibration
Total Cd			
Total Pb			
Total As			
Total Hg			
inorganic As			

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

Annex 8: Homogeneity and stability studies

8.1 Homogeneity study

Homogeneity	Total As		Total Cd		Total Hg		Total Pb	
Bottle ID	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2
3	0.539	0.558	3.88	3.95	0.0798	0.0808	0.246	0.244
37	0.531	0.524	3.83	3.95	0.0846	0.0846	0.234	0.296
52	0.568	0.532	3.99	3.89	0.0846	0.0842	0.232	0.236
60	0.558	0.536	3.84	3.94	0.0842	0.0835	0.237	0.244
97	0.523	0.555	3.88	3.91	0.0842	0.0819	0.242	0.260
113	0.528	0.562	4.07	3.92	0.0852	0.0822	0.250	0.259
138	0.535	0.554	3.87	4.06	0.0832	0.0877	0.241	0.258
141	0.558	0.552	3.93	3.98	0.0819	0.0828	0.239	0.247
174	0.554	0.548	3.91	3.96	0.0863	0.0817	0.237	0.238
194	0.554	0.562	3.96	3.84	0.0783	0.0785	0.235	0.292
Homogeneity assessment according to ISO 13528 [7]								
Mean	0.546		3.93		0.0830		0.248	
σ_p	0.082		0.393		0.0125		0.050	
0.3* σ_p	0.025		0.118		0.0037		0.015	
s_x	0.009		0.036		0.0021		0.010	
s_w	0.016		0.077		0.0017		0.020	
s_s	0.000		0.000		0.0018		0.000	
$s_s \leq 0.3 * \sigma_p$	Pass		Pass		Pass		Pass	

Where σ_p 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,

8.2 Stability study

	Time in Weeks						
	0	3	5	8			
As	0.576	0.57	0.571	0.547	Slope of linear regression significantly <> 0 (95%) : No		
	0.542	0.534	0.565	0.564	Standard error of the slope =	0.002	
					Uncertainty contribution	**u_{st} =**	**0.015**
Cd	3.94	4.03	3.86	3.99	Slope of linear regression significantly <> 0 (95%) : No		
	3.92	3.92	4.03	3.9	Standard error of the slope =	0.008	
					Uncertainty contribution	**u_{st} =**	**0.060**
Hg	0.0849	0.0814	0.0833	0.0861	Slope of linear regression significantly <> 0 (95%) : No		
	0.0807	0.0833	0.0845	0.0839	Standard error of the slope =	0.000	
					Uncertainty contribution	**u_{st} =**	**0.002**
Pb	0.243	0.267	0.262	0.244	Slope of linear regression significantly <> 0 (95%) : No		
	0.242	0.262	0.252	0.245	Standard error of the slope =	0.001	
					Uncertainty contribution	**u_{st} =**	**0.010**

Annex 9: Results for total Cd

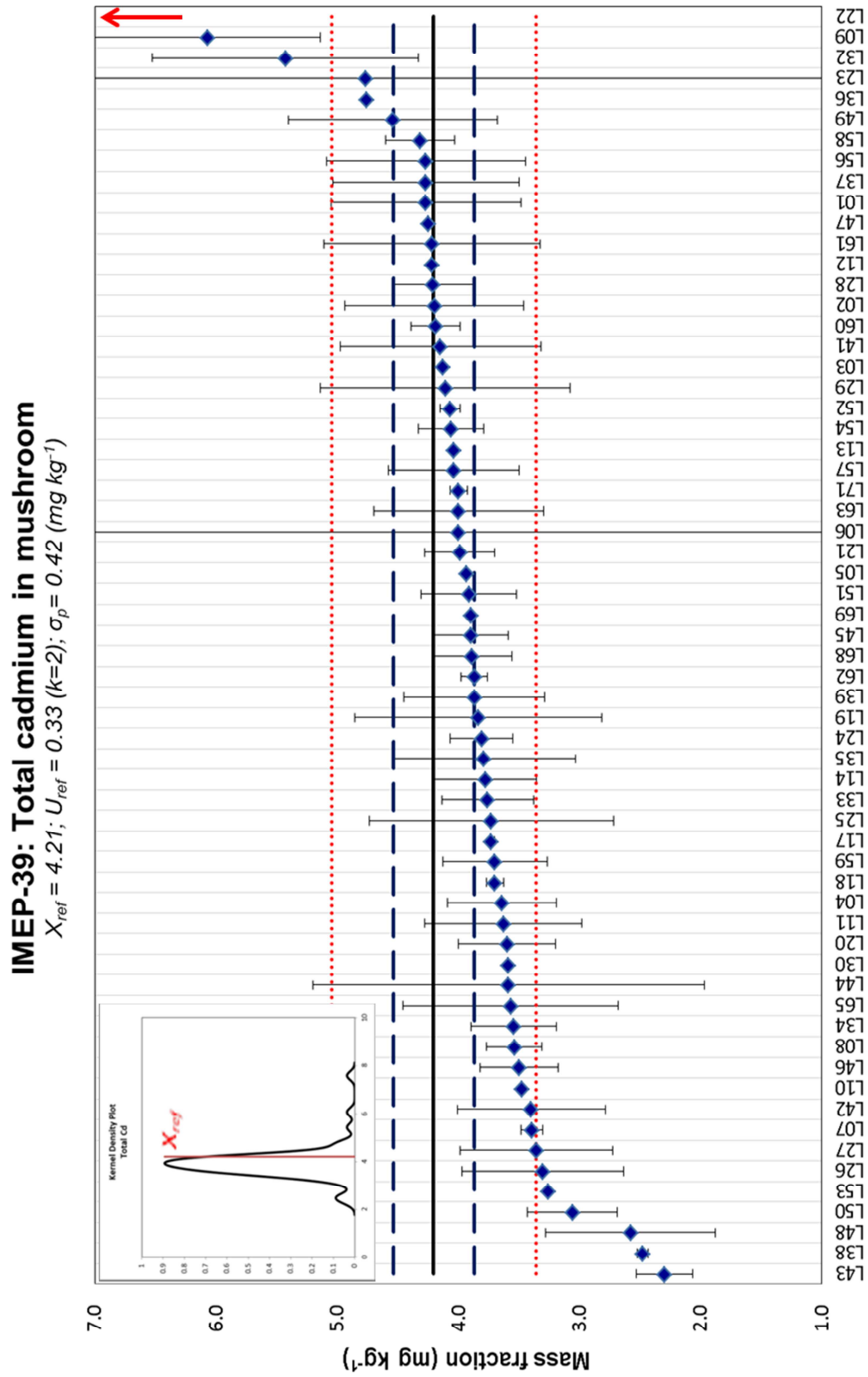
Assigned range: X_{ref} = 4.21; U_{ref} = 0.33 (*k=2);* σ_p = 0.42 (all values in mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k [a]	Technique	u_{lab}	z-score [b]	ζ-score [b]	u_{lab} [c]
L01	**4.27**	0.785	2	ICP	0.3925	**0.2**	**0.2**	a
L02	**4.2**	0.74	2	ICP-MS	0.37	**0.0**	**0.0**	a
L03	**4.1263**	0.00362	2	ICP-AES	0.00181	**-0.2**	**-0.5**	b
L04	**3.64**	0.45	2	AAS	0.225	**-1.3**	**-2.0**	a
L05	**3.935**			AAS	0	**-0.6**	**-1.6**	b
L06	**4**	20	2	ETV-ICPMS	10	**-0.5**	**0.0**	c
L07	**3.394**	0.088	2	ICP-MS DRC	0.044	**-1.9**	**-4.7**	b
L08	**3.54**	0.23	2	AAS	0.115	**-1.6**	**-3.3**	b
L09	**6.074**	0.929	2	AAS	0.4645	**4.4**	**3.8**	c
L10	**3.48**			ICP	0	**-1.7**	**-4.4**	b
L11	**3.63**	0.65	2	AAS	0.325	**-1.4**	**-1.6**	a
L12	**4.22**			AAS	0	**0.0**	**0.1**	b
L13	**4.041**		1	AAS	0	**-0.4**	**-1.0**	b
L14	**3.78**	0.42	2	ICP-MS	0.21	**-1.0**	**-1.6**	a
L17	**3.729**	0.029	2	ICP-AES	0.0145	**-1.1**	**-2.9**	b
L18	**3.7**	0.07	2	ICP	0.035	**-1.2**	**-3.0**	b
L19	**3.84**	1.02	2	ICP-AES	0.51	**-0.9**	**-0.7**	c
L20	**3.6**	0.4	2	AAS	0.2	**-1.4**	**-2.3**	a
L21	**3.99**	0.29	2	AAS	0.145	**-0.5**	**-1.0**	b
L22	**7.58**			ICP-AES	0	**8.0**	**20.4**	b
L23	**4.77**	20	2	ICP	10	**1.3**	**0.1**	c
L24	**3.81**	0.26	2	ICP	0.13	**-0.9**	**-1.9**	b
L25	**3.732**	1.008	2	ICP-MS	0.504	**-1.1**	**-0.9**	c
L26	**3.303**	0.667	2	ICP-AES	0.3335	**-2.1**	**-2.4**	a
L27	**3.36**	0.63	2	AAS	0.315	**-2.0**	**-2.4**	a
L28	**4.21**	0.33	2	ETAAS	0.165	**0.0**	**0.0**	b
L29	**4.11**	1.03	√3	AAS	0.594671	**-0.2**	**-0.2**	c
L30	**3.59**			ICP-AES	0	**-1.5**	**-3.7**	b
L32	**5.43**	1.1	√3	ICP-MS	0.635085	**2.9**	**1.9**	c
L33	**3.759**	0.376	2	ICP-AES	0.188	**-1.1**	**-1.8**	a
L34	**3.543**	0.354	√3	ICP	0.204382	**-1.6**	**-2.5**	a
L35	**3.79**	0.758	√3	ICP-MS	0.437632	**-1.0**	**-0.9**	c
L36	**4.757**			ETV-ICPMS	0	**1.3**	**3.3**	b
L37	**4.27**	0.77	2	ICP	0.385	**0.2**	**0.2**	a
L38	**2.48**	0.043	√3	ETAAS	0.024826	**-4.1**	**-10.3**	b
L39	**3.87**	0.58	2	ETAAS	0.29	**-0.8**	**-1.0**	a
L41	**4.15**	0.83	2	ICP-MS	0.415	**-0.1**	**-0.1**	a
L42	**3.4**	0.61	2	ICP-MS	0.305	**-1.9**	**-2.3**	a
L43	**2.3**	0.23	√3	AAS	0.132791	**-4.5**	**-9.0**	b
L44	**3.589**	1.615	1.98	MS	0.815657	**-1.5**	**-0.7**	c
L45	**3.9**	0.31	2	ICP	0.155	**-0.7**	**-1.3**	b
L46	**3.50**	0.32	2	ETAAS	0.16	**-1.7**	**-3.1**	b
L47	**4.25**			ICP-MS	0	**0.1**	**0.3**	b
L48	**2.58**	0.7	2	AAS	0.35	**-3.9**	**-4.2**	a
L49	**4.54**	0.863	2	AAS	0.4315	**0.8**	**0.7**	c
L50	**3.060**	0.37	2	AAS	0.185	**-2.7**	**-4.6**	a
L51	**3.916**	0.392	2	ICP	0.196	**-0.7**	**-1.1**	a
L52	**4.07**	0.08	√3	ICP	0.046188	**-0.3**	**-0.8**	b
L53	**3.2632**			AAS	0	**-2.2**	**-5.7**	b
L54	**4.06**	0.27	2	AAS	0.135	**-0.3**	**-0.7**	b
L56	**4.27**	0.82	1.96	AAS	0.418367	**0.2**	**0.1**	a
L57	**4.04**	0.54	2	ETAAS	0.27	**-0.4**	**-0.5**	a
L58	**4.32**	0.285	√3	ICP-MS	0.164545	**0.3**	**0.5**	b
L59	**3.7**	0.43	2	AAS	0.215	**-1.2**	**-1.9**	a
L60	**4.2**	0.2	√3	ICP-MS	0.11547	**0.0**	**-0.1**	b
L61	**4.22**	0.89	2	ICP	0.445	**0.0**	**0.0**	c
L62	**3.87**	0.11	√3	AAS	0.063509	**-0.8**	**-1.9**	b
L63	**4**	0.7	2	ICP	0.35	**-0.5**	**-0.5**	a
L65	**3.57**	0.89	2	ICP-MS	0.445	**-1.5**	**-1.3**	c
L68	**3.89**	0.33	2	ETAAS	0.165	**-0.7**	**-1.3**	b
L69	**3.9**			ICP	0	**-0.7**	**-1.8**	b
L71	**4.00**	0.07	2	AAS	0.035	**-0.5**	**-1.2**	b

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

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

[c] ***a*** : u_{min} (u_{ref}) ≤ u_{lab} ≤ u_{max} (σ_p); **b** : u_{lab} < u_{min}; **c** : u_{lab} > u_{max} (σ_p)



Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{ref}): solid black line; Reference interval ($X_{ref} \pm U_{ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 10: Results for total Pb

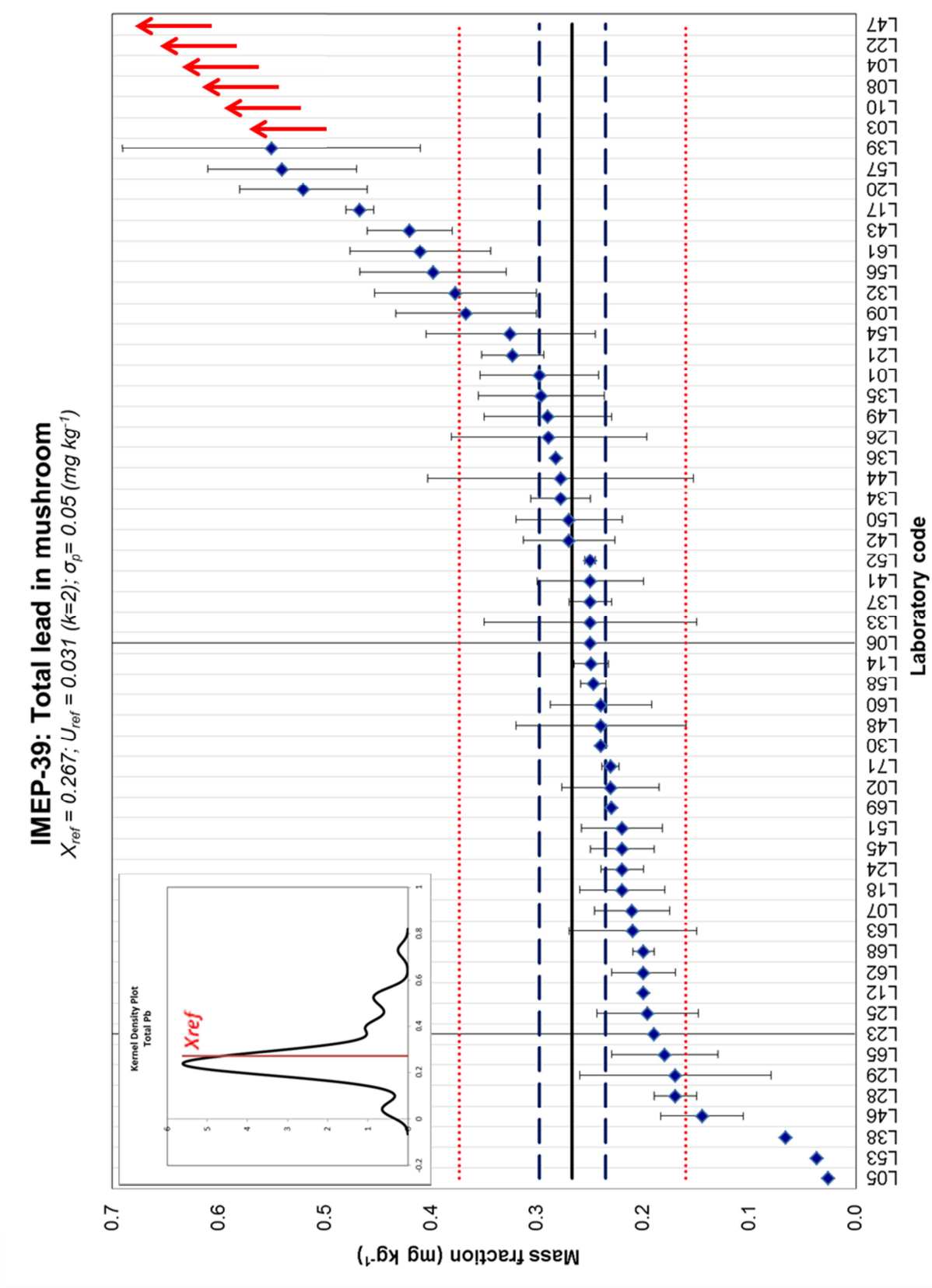
Assigned range: X_{ref} = 0.267; U_{ref} = 0.031 (k=2); σ_p = 0.05 (all values in mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k [a]	Technique	u_{lab}	z-score [b]	ζ-score [b]	u_{lab} [c]
L01	**0.298**	0.056	2	ICP	0.028	**0.6**	**1.0**	a
L02	**0.231**	0.046	2	ICP-MS	0.023	**-0.7**	**-1.3**	a
L03	**0.7285**	0.00293	2	ICP-AES	0.001465	**8.6**	**29.6**	b
L04	**1.41**	0.2	2	AAS	0.1	**21.4**	**11.3**	c
L05	**0.026**			AAS	0	**-4.5**	**-15.5**	b
L06	**0.25**	20	2	ETV-ICP-MS	10	**-0.3**	**0.0**	c
L07	**0.2109**	0.0355	2	ICP-MS DRC	0.01775	**-1.1**	**-2.4**	a
L08	**1.36**	0.08	2	AAS	0.04	**20.5**	**25.5**	a
L09	**0.367**	0.066	2	AAS	0.033	**1.9**	**2.7**	a
L10	**1.27**			ICP	0	**18.8**	**64.6**	b
L11	**< 0.2**			AAS				
L12	**0.2**			AAS	0	**-1.3**	**-4.3**	b
L13	**< 0.5**			AAS				
L14	**0.249**	0.016	2	ICP-MS	0.008	**-0.3**	**-1.0**	b
L17	**0.467**	0.013	2	ICP-AES	0.0065	**3.7**	**11.9**	b
L18	**0.22**	0.04	2	ICP	0.02	**-0.9**	**-1.9**	a
L19	**< 0.5**			ICP-AES				
L20	**0.52**	0.06	2	ICP-AES	0.03	**4.7**	**7.5**	a
L21	**0.323**	0.029	2	AAS	0.0145	**1.0**	**2.6**	b
L22	**2**			ICP-AES	0	**32.5**	**111.6**	b
L23	**0.19**	20	2	ICP	10	**-1.4**	**0.0**	c
L24	**0.22**	0.02	2	ICP	0.01	**-0.9**	**-2.5**	b
L25	**0.196**	0.048	2	ICP-MS	0.024	**-1.3**	**-2.5**	a
L26	**0.289**	0.092	2	ICP-AES	0.046	**0.4**	**0.5**	a
L27	**< 0.2**			AAS				
L28	**0.17**	0.02	√3	ET-AAS	0.011547	**-1.8**	**-5.0**	b
L29	**0.17**	0.09	√3	AAS	0.051962	**-1.8**	**-1.8**	a
L30	**0.24**			ICP-MS	0	**-0.5**	**-1.7**	b
L32	**0.377**	0.076	√3	ICP-MS	0.043879	**2.1**	**2.4**	a
L33	**0.25**	0.1	2	AAS	0.05	**-0.3**	**-0.3**	a
L34	**0.278**	0.028	√3	ICP	0.016166	**0.2**	**0.5**	a
L35	**0.296**	0.0592	√3	ICP-MS	0.034179	**0.5**	**0.8**	a
L36	**0.282**			ETV-ICPMS	0	**0.3**	**1.0**	b
L37	**0.25**	0.02	2	ICP	0.01	**-0.3**	**-0.9**	b
L38	**0.0659**	0.000712	√3	ET-AAS	0.000411	**-3.8**	**-12.9**	b
L39	**0.55**	0.14	2	ET-AAS	0.07	**5.3**	**3.9**	c
L41	**0.25**	0.05	2	ICP-MS	0.025	**-0.3**	**-0.6**	a
L42	**0.27**	0.043	2	ICP-MS	0.0215	**0.1**	**0.1**	a
L43	**0.42**	0.04	√3	AAS	0.023094	**2.9**	**5.5**	a
L44	**0.278**	0.125	1.98	HPLC-ICP-MS	0.063131	**0.2**	**0.2**	c
L45	**0.22**	0.03	2	ICP	0.015	**-0.9**	**-2.2**	b
L46	**0.1447**	0.039	2	ET-AAS	0.0195	**-2.3**	**-4.9**	a
L47	**7.38**			ICP-MS	0	**133.2**	**457.9**	b
L48	**0.24**	0.08	2	AAS	0.04	**-0.5**	**-0.6**	a
L49	**0.29**	0.06	2	AAS	0.03	**0.4**	**0.7**	a
L50	**0.27**	0.05	2	AAS	0.025	**0.1**	**0.1**	a
L51	**0.22**	0.038	2	ICP	0.019	**-0.9**	**-1.9**	a
L52	**0.25**	0.005	√3	ICP	0.002887	**-0.3**	**-1.1**	b
L53	**0.0365**			AAS	0	**-4.3**	**-14.8**	b
L54	**0.325**	0.08	2	AAS	0.04	**1.1**	**1.4**	a
L56	**0.398**	0.069	1.96	AAS	0.035204	**2.5**	**3.4**	a
L57	**0.54**	0.07	2	ET-AAS	0.035	**5.1**	**7.1**	a
L58	**0.247**	0.012	√3	ICP-MS	0.006928	**-0.4**	**-1.2**	b
L60	**0.24**	0.048	√3	ICP-MS	0.027713	**-0.5**	**-0.8**	a
L61	**0.41**	0.066	2	ICP	0.033	**2.7**	**3.9**	a
L62	**0.2**	0.03	√3	AAS	0.017321	**-1.3**	**-2.9**	a
L63	**0.21**	0.06	2	ICP	0.03	**-1.1**	**-1.7**	a
L65	**0.18**	0.05	2	ICP-MS	0.025	**-1.6**	**-3.0**	a
L68	**0.2**	0.01	2	ET-AAS	0.005	**-1.3**	**-4.1**	b
L69	**0.23**			ICP	0	**-0.7**	**-2.4**	b
L71	**0.231**	0.008	2	AAS	0.004	**-0.7**	**-2.2**	b

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

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

[c] ***a*** : u_{min} (u_{ref}) ≤ u_{lab} ≤ u_{max} (σ_p); **b** : u_{lab} < u_{min}; **c** : u_{lab} > u_{max} (σ_p)



Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{ref}): solid black line; Reference interval ($X_{ref} \pm U_{ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 11: Results for total As

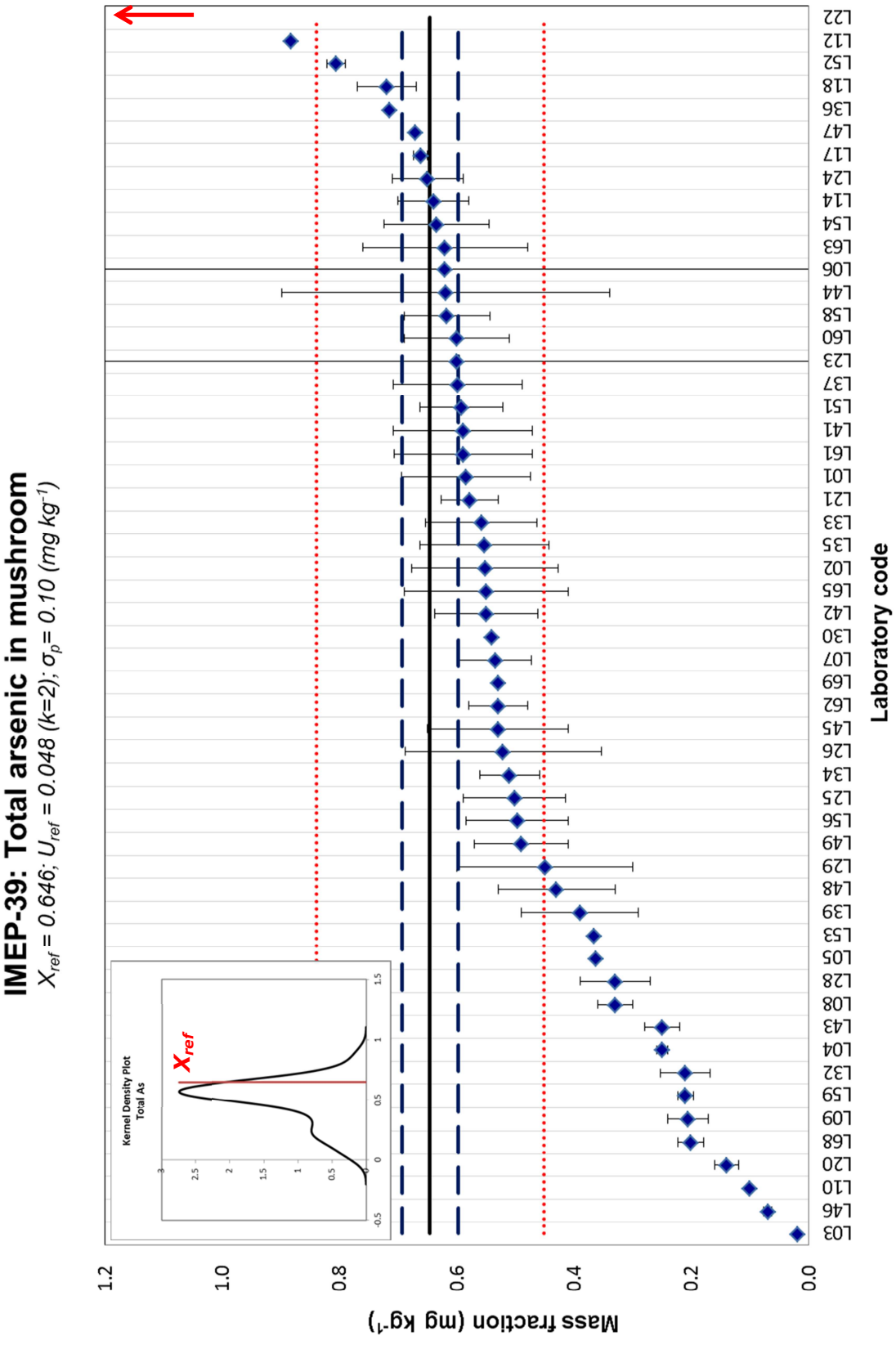
Assigned range: X_{ref} = 0.646; U_{ref} = 0.048 (k=2); σ_p = 0.10 (all values in mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k [a]	Technique	u_{lab}	z-score [b]	ζ-score [b]	u_{lab} [c]
L01	**0.58**	0.11	2	ICP	0.055	**-0.6**	**-1.0**	a
L02	**0.552**	0.125	2	ICP-MS	0.0625	**-1.0**	**-1.4**	a
L03	**0.0195**	0.00233	2	ICP-AES	0.001165	**-6.5**	**-26.1**	b
L04	**0.25**	0.01	2	AAS	0.005	**-4.1**	**-16.2**	b
L05	**0.363**			HG-AAS	0	**-2.9**	**-11.8**	b
L06	**0.62**	15	2	ETV-ICP-MS	7.5	**-0.3**	**0.0**	c
L07	**0.5344**	0.061	2	ICP-MS DRC	0.0305	**-1.2**	**-2.9**	a
L08	**0.3**	0.03	2	HG-AAS	0.015	**-3.3**	**-11.2**	b
L09	**0.206**	0.034	2	HG-AAS	0.017	**-4.5**	**-15.0**	b
L10	**0.1**			ICP	0	**-5.6**	**-22.8**	b
L12	**0.883**			AAS	0	**2.4**	**9.9**	b
L14	**0.64**	0.06	2	ICP-MS	0.03	**-0.1**	**-0.2**	a
L17	**0.662**	0.012	2	ICP-AES	0.006	**0.2**	**0.6**	b
L18	**0.72**	0.05	2	ICP	0.025	**0.8**	**2.1**	a
L19	**< 2.4**			ICP-AES				
L20	**0.14**	0.02	2	AFS	0.01	**-5.2**	**-19.5**	b
L21	**0.578**	0.049	2	AAS	0.0245	**-0.7**	**-2.0**	a
L22	**18.57**			ICP-AES	0	**185.0**	**748.2**	b
L23	**0.6**	20	2	ICP	10	**-0.5**	**0.0**	c
L24	**0.65**	0.06	2	ICP	0.03	**0.0**	**0.1**	a
L25	**0.502**	0.087	2	ICP-MS	0.0435	**-1.5**	**-2.9**	a
L26	**0.521**	0.167	2	ICP-AES	0.0835	**-1.3**	**-1.4**	a
L28	**0.33**	0.06	2	ETAAS	0.03	**-3.3**	**-8.2**	a
L29	**0.45**	0.15	√3	AAS	0.086603	**-2.0**	**-2.2**	a
L30	**0.54**			ICP-MS	0	**-1.1**	**-4.4**	b
L32	**0.211**	0.042	√3	ICP-MS	0.024249	**-4.5**	**-12.8**	a
L33	**0.558**	0.095	2	HG-AAS	0.0475	**-0.9**	**-1.7**	a
L34	**0.51**	0.051	√3	ICP	0.029445	**-1.4**	**-3.6**	a
L35	**0.553**	0.11	√3	ICP-MS	0.063509	**-1.0**	**-1.4**	a
L36	**0.715**			ETV-ICP-MS	0	**0.7**	**2.9**	b
L37	**0.598**	0.11	2	ICP	0.055	**-0.5**	**-0.8**	a
L39	**0.390**	0.1	2	HG-AAS	0.05	**-2.6**	**-4.6**	a
L41	**0.59**	0.118	2	ICP-MS	0.059	**-0.6**	**-0.9**	a
L42	**0.55**	0.088	2.00	ICP-MS	0.044	**-1.0**	**-1.9**	a
L43	**0.25**	0.03	√3	HG-AAS	0.017321	**-4.1**	**-13.4**	b
L44	**0.619**	0.279	1.98	HPLC-ICP-MS	0.140909	**-0.3**	**-0.2**	c
L45	**0.53**	0.12	2	ICP	0.06	**-1.2**	**-1.8**	a
L46	**0.07**	0.007	2	HG-AAS	0.0035	**-5.9**	**-23.8**	b
L47	**0.671**			ICP-MS	0	**0.3**	**1.0**	b
L48	**0.43**	0.1	2	HG-AAS	0.05	**-2.2**	**-3.9**	a
L49	**0.49**	0.08	2	HG-AAS	0.04	**-1.6**	**-3.3**	a
L51	**0.592**	0.071	2	ICP	0.0355	**-0.6**	**-1.3**	a
L52	**0.806**	0.016	√3	ICP	0.009238	**1.7**	**6.2**	b
L53	**0.3659**			AAS	0	**-2.9**	**-11.7**	b
L54	**0.635**	0.09	2	AAS	0.045	**-0.1**	**-0.2**	a
L56	**0.497**	0.087	1.96	AAS	0.044388	**-1.5**	**-3.0**	a
L58	**0.617**	0.073	√3	ICP-MS	0.042147	**-0.3**	**-0.6**	a
L59	**0.21**	0.014	2	AAS	0.007	**-4.5**	**-17.5**	b
L60	**0.6**	0.09	√3	ICP-MS	0.051962	**-0.5**	**-0.8**	a
L61	**0.589**	0.118	2	ICP	0.059	**-0.6**	**-0.9**	a
L62	**0.53**	0.05	√3	AAS	0.028868	**-1.2**	**-3.1**	a
L63	**0.62**	0.14	2	ICP	0.07	**-0.3**	**-0.4**	a
L65	**0.55**	0.14	2	ICP-MS	0.07	**-1.0**	**-1.3**	a
L68	**0.202**	0.022	2	HG-AAS	0.011	**-4.6**	**-16.8**	b
L69	**0.53**			ICP	0	**-1.2**	**-4.8**	b

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

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

[c] ***a*** : u_{min} (u_{ref}) ≤ u_{lab} ≤ u_{max} (σ_p); **b** : u_{lab} < u_{min}; **c** : u_{lab} > u_{max} (σ_p)



Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{ref}): solid black line; Reference interval ($X_{ref} \pm U_{ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 12: Results for total Hg

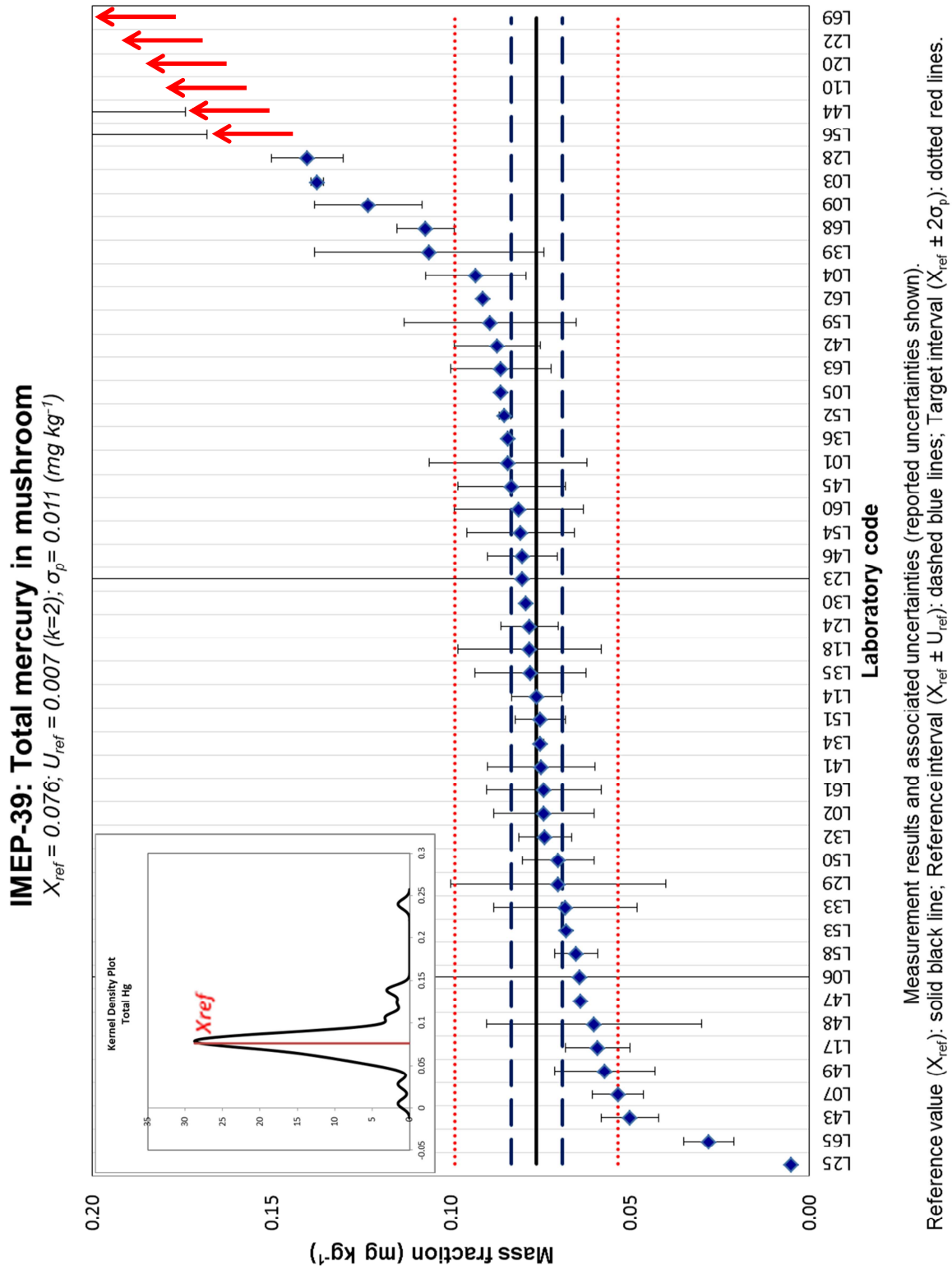
Assigned range: X_{ref} = 0.076; U_{ref} = 0.007 (k=2); σ_p = 0.011 (all values in mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k [a]	Technique	u_{lab}	z-score [b]	ζ-score [b]	u_{lab} [c]
L01	**0.084**	0.022	2	ICP	0.011	**0.7**	**0.7**	a
L02	**0.074**	0.014	2	ICP-MS	0.007	**-0.2**	**-0.3**	a
L03	**0.1373**	0.00187	2	ICP-AES	0.000935	**5.4**	**16.6**	b
L04	**0.093**	0.014	2	DMA	0.007	**1.5**	**2.2**	a
L05	**0.086**			CV-AAS	0	**0.9**	**2.8**	b
L06	**0.064**	30	2	CV-AAS	15	**-1.1**	**0.0**	c
L07	**0.0533**	0.0071	2	CV-AAS	0.00355	**-2.0**	**-4.5**	b
L09	**0.123**	0.015	2	CV-AAS	0.0075	**4.1**	**5.6**	a
L10	**0.39**			ICP	0	**27.5**	**88.1**	b
L12	**< 0.048**			CV-AAS				
L14	**0.076**	0.007	2	DMA	0.0035	**0.0**	**0.0**	b
L17	**0.059**	0.009	2	ICP-AES	0.0045	**-1.5**	**-3.0**	a
L18	**0.078**	0.02	2	ICP	0.01	**0.2**	**0.2**	a
L19	**< 2.5**			ICP-AES				
L20	**0.41**	0.04	2	CV-AAS	0.02	**29.3**	**16.4**	c
L22	**4.62**			ICP-AES	0	**398.1**	**1275.2**	b
L23	**0.08**	30	2	ICP	15	**0.3**	**0.0**	c
L24	**0.078**	0.008	2	CV-AAS	0.004	**0.2**	**0.4**	a
L25	**0.005**	0.0003	2	AAS	0.00015	**-6.2**	**-19.9**	b
L26	**< 0.1**			ICP-AES				
L28	**0.14**	0.01	2	CV-AAS	0.005	**5.6**	**10.4**	a
L29	**0.07**	0.03	√3	CV-AAS	0.017321	**-0.5**	**-0.3**	c
L30	**0.079**			CV-AAS	0	**0.3**	**0.8**	b
L32	**0.0737**	0.0074	√3	CV-AAS	0.004272	**-0.2**	**-0.4**	a
L33	**0.068**	0.02	2	CV-AAS	0.011547	**-0.7**	**-0.7**	c
L34	**0.075**	0.001	√3	ICP	0.000577	**-0.1**	**-0.3**	b
L35	**0.0777**	0.0155	√3	AAS	0.008949	**0.1**	**0.2**	a
L36	**0.084**			ETV-ICPMS	0	**0.7**	**2.2**	b
L39	**0.106**	0.032	2	CV-AAS	0.016	**2.6**	**1.8**	c
L41	**0.0747**	0.015	2	CV-AAS	0.0075	**-0.1**	**-0.2**	a
L42	**0.087**	0.012	2	CV-AAS	0.006	**1.0**	**1.6**	a
L43	**0.05**	0.008	√3	HG-AAS	0.004619	**-2.3**	**-4.5**	a
L44	**0.316**	0.142	1.98	HPLC-ICP-MS	0.071717	**21.0**	**3.3**	c
L45	**0.083**	0.015	2	AAS	0.0075	**0.6**	**0.8**	a
L46	**0.08**	0.0097	2	HG-AAS	0.00485	**0.3**	**0.6**	a
L47	**0.0638**			ICP-MS	0	**-1.1**	**-3.5**	b
L48	**0.06**	0.03	2	CV-AAS	0.015	**-1.4**	**-1.0**	c
L49	**0.057**	0.014	2	CV-AAS	0.007	**-1.7**	**-2.4**	a
L50	**0.07**	0.01	2	CV-AAS	0.005	**-0.5**	**-1.0**	a
L51	**0.075**	0.007	2	AAS	0.0035	**-0.1**	**-0.2**	b
L52	**0.0849**	0.0017	√3	AAS	0.000981	**0.8**	**2.4**	b
L53	**0.0678**			AAS	0	**-0.7**	**-2.3**	b
L54	**0.0804**	0.015	2	AAS amalgamation	0.0075	**0.4**	**0.5**	a
L56	**0.24**	0.072	1.96	CV-AAS	0.036735	**14.4**	**4.4**	c
L57	**< 0.05**			DMA				
L58	**0.065**	0.006	√3	ICP-MS	0.003464	**-1.0**	**-2.2**	b
L59	**0.089**	0.024	2	FIAS-AAS	0.012	**1.1**	**1.0**	c
L60	**0.081**	0.018	√3	ICP-MS	0.010392	**0.4**	**0.4**	a
L61	**0.074**	0.016	2	CV-AAS	0.008	**-0.2**	**-0.2**	a
L62	**0.0909**	0.0006	√3	HG-AAS	0.000346	**1.3**	**4.1**	b
L63	**0.086**	0.014	2	CV-AAS	0.007	**0.9**	**1.3**	a
L65	**0.028**	0.007	2	ICP-MS	0.0035	**-4.2**	**-9.6**	b
L68	**0.107**	0.008	2	HG-AAS	0.004	**2.7**	**5.8**	a
L69	**74**			ICP	0	**6476.0**	**20745.2**	b

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

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

[c] ***a*** : u_{min} (u_{ref}) ≤ u_{lab} ≤ u_{max} (σ_p); ***b*** : u_{lab} < u_{min}; **c** : u_{lab} > u_{max} (σ_p)


IMEP-39: Total mercury in mushroom
X_{ref} = 0.076; U_{ref} = 0.007 (k=2); σ_p = 0.011 (mg kg^{-1})
Mass fraction (mg kg^{-1})
0.20
0.15
0.10
0.05
0.00
Laboratory code
L25 L65 L43 L07 L49 L17 L48 L47 L06 L58 L53 L33 L29 L50 L32 L02 L61 L41 L34 L51 L14 L35 L18 L24 L30 L23 L46 L54 L60 L45 L01 L36 L52 L05 L63 L42 L59 L62 L04 L39 L68 L09 L03 L28 L56 L44 L10 L20 L22 L69
Kernel Density Plot
Total Hg
Xref
Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{ref}): solid black line; Reference interval ($X_{ref} \pm U_{ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 13: Results for inorganic As

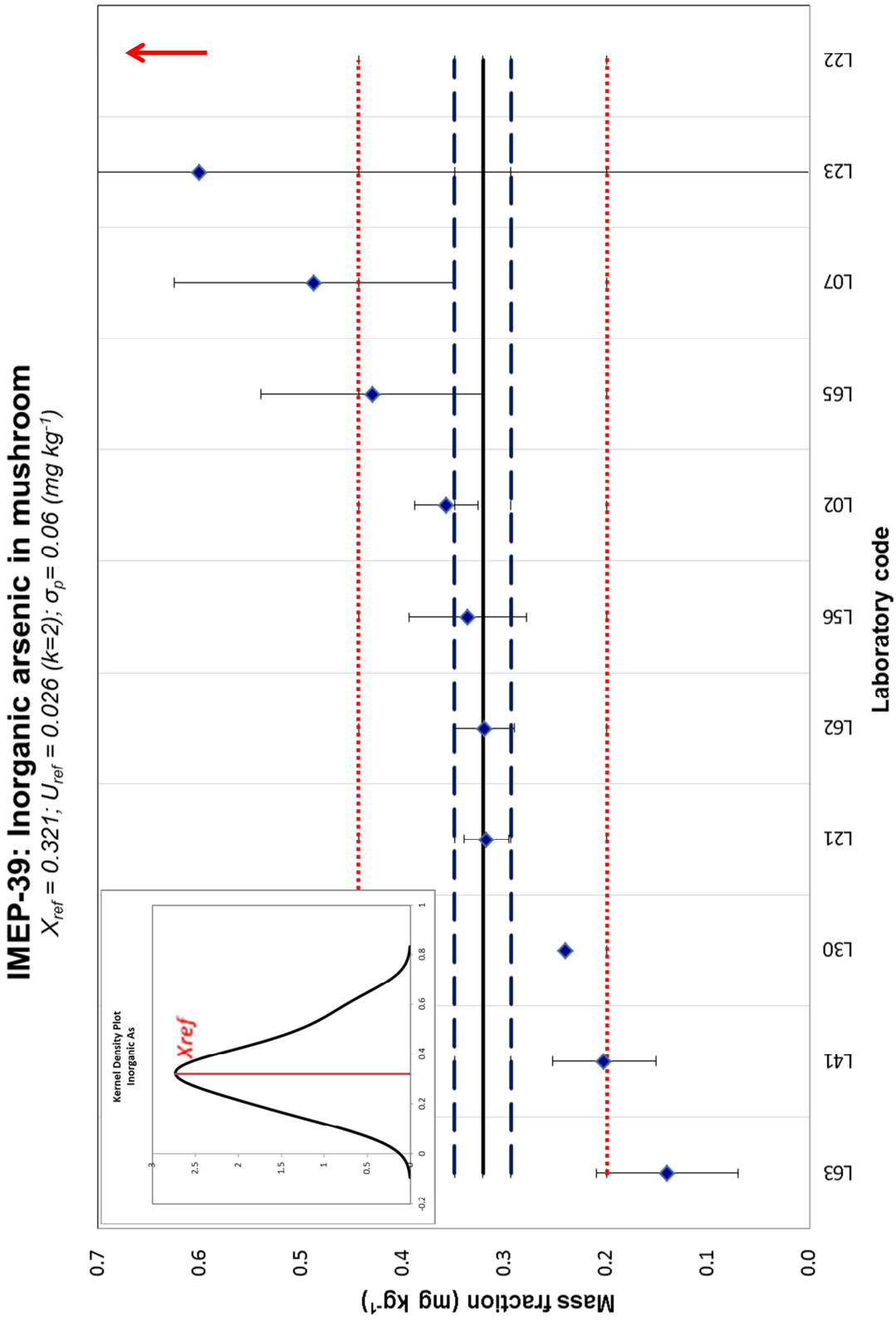
Assigned range: X_{ref} = 0.321; U_{ref} = 0.026 (k=2); σ_p = 0.06 (all values in mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k [a]	Technique	u_{lab}	z-score [b]	ζ-score [b]	u_{lab} [c]
L02	**0.357**	0.031	2	ICP-MS	0.0155	**0.6**	**1.7**	a
L07	**0.4871**	0.1374	2	ICP-MS	0.0687	**2.7**	**2.4**	c
L19	**< 3.2**			ICP-AES				
L21	**0.318**	0.022	2	AAS	0.011	**-0.1**	**-0.2**	b
L22	**9.4**			ICP-AES	0	**148.7**	**651.4**	b
L23	**0.6**	20	√3	ETV-ICPMS	11.54701	**4.6**	**0.0**	c
L30	**0.24**			HG-AAS	0	**-1.3**	**-5.8**	b
L41	**0.202**	0.051	2	HG-AAS	0.0255	**-2.0**	**-4.1**	a
L50	**< 1.5**			ICP-AES				
L56	**0.336**	0.058	1.96	AAS	0.029592	**0.2**	**0.4**	a
L62	**0.32**	0.03	√3	HG-AAS	0.017321	**0.0**	**-0.1**	a
L63	**0.14**	0.07	2	HG-AAS	0.035	**-3.0**	**-4.8**	a
L65	**0.43**	0.11	2	ICP-MS	0.055	**1.8**	**1.9**	a

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

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

[c] ***a*** : u_{min} (u_{ref}) ≤ u_{lab} ≤ u_{max} (σ_p); **b** : u_{lab} < u_{min}; **c** : u_{lab} > u_{max} (σ_p)



Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{ref}): solid black line; Reference interval ($X_{ref} \pm U_{ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 14: Summary of scorings

	Arsenic		Cadmium		Lead		Mercury		Inorganic As	
Lab Code	*z-score*	*ζ-score*	*z-score*	*ζ-score*	*z-score*	*ζ-score*	*z-score*	*ζ-score*	*z-score*	*ζ-score*
L01	-0.6	-1.0	0.2	0.2	0.6	1.0	0.7	0.7		
L02	-1.0	-1.4	0.0	0.0	-0.7	-1.3	-0.2	-0.3	0.6	1.7
L03	-6.5	-26.1	-0.2	-0.5	8.6	29.6	5.4	16.6		
L04	-4.1	-16.2	-1.3	-2.0	21.4	11.3	1.5	2.2		
L05	-2.9	-11.8	-0.6	-1.6	-4.5	-15.5	0.9	2.8		
L06	-0.3	0.0	-0.5	0.0	-0.3	0.0	-1.1	0.0		
L07	-1.2	-2.9	-1.9	-4.7	-1.1	-2.4	-2.0	-4.5	2.7	2.4
L08	-3.3	-11.2	-1.6	-3.3	20.5	25.5				
L09	-4.5	-15.0	4.4	3.8	1.9	2.7	4.1	5.6		
L10	-5.6	-22.8	-1.7	-4.4	18.8	64.6	27.5	88.1		
L11			-1.4	-1.6						
L12	2.4	9.9	0.0	0.1	-1.3	-4.3				
L13			-0.4	-1.0						
L14	-0.1	-0.2	-1.0	-1.6	-0.3	-1.0	0.0	0.0		
L17	0.2	0.6	-1.1	-2.9	3.7	11.9	-1.5	-3.0		
L18	0.8	2.1	-1.2	-3.0	-0.9	-1.9	0.2	0.2		
L19			-0.9	-0.7						
L20	-5.2	-19.5	-1.4	-2.3	4.7	7.5	29.3	16.4		
L21	-0.7	-2.0	-0.5	-1.0	1.0	2.6			-0.1	-0.2
L22	185.0	748.2	8.0	20.4	32.5	111.6	398.1	1275.2	148.7	651.4
L23	-0.5	0.0	1.3	0.1	-1.4	0.0	0.3	0.0	4.6	0.0
L24	0.0	0.1	-0.9	-1.9	-0.9	-2.5	0.2	0.4		
L25	-1.5	-2.9	-1.1	-0.9	-1.3	-2.5	-6.2	-19.9		
L26	-1.3	-1.4	-2.1	-2.4	0.4	0.5				
L27			-2.0	-2.4						
L28	-3.3	-8.2	0.0	0.0	-1.8	-5.0	5.6	10.4		
L29	-2.0	-2.2	-0.2	-0.2	-1.8	-1.8	-0.5	-0.3		
L30	-1.1	-4.4	-1.5	-3.7	-0.5	-1.7	0.3	0.8	-1.3	-5.8
L32	-4.5	-12.8	2.9	1.9	2.1	2.4	-0.2	-0.4		
L33	-0.9	-1.7	-1.1	-1.8	-0.3	-0.3	-0.7	-0.7		
L34	-1.4	-3.6	-1.6	-2.5	0.2	0.5	-0.1	-0.3		
L35	-1.0	-1.4	-1.0	-0.9	0.5	0.8	0.1	0.2		
L36	0.7	2.9	1.3	3.3	0.3	1.0	0.7	2.2		
L37	-0.5	-0.8	0.2	0.2	-0.3	-0.9				
L38			-4.1	-10.3	-3.8	-12.9				
L39	-2.6	-4.6	-0.8	-1.0	5.3	3.9	2.6	1.8		
L41	-0.6	-0.9	-0.1	-0.1	-0.3	-0.6	-0.1	-0.2	-2.0	-4.1
L42	-1.0	-1.9	-1.9	-2.3	0.1	0.1	1.0	1.6		
L43	-4.1	-13.4	-4.5	-9.0	2.9	5.5	-2.3	-4.5		
L44	-0.3	-0.2	-1.5	-0.7	0.2	0.2	21.0	3.3		
L45	-1.2	-1.8	-0.7	-1.3	-0.9	-2.2	0.6	0.8		
L46	-5.9	-23.8	-1.7	-3.1	-2.3	-4.9	0.3	0.6		
L47	0.3	1.0	0.1	0.3	133.2	457.9	-1.1	-3.5		
L48	-2.2	-3.9	-3.9	-4.2	-0.5	-0.6	-1.4	-1.0		
L49	-1.6	-3.3	0.8	0.7	0.4	0.7	-1.7	-2.4		
L50			-2.7	-4.6	0.1	0.1	-0.5	-1.0		
L51	-0.6	-1.3	-0.7	-1.1	-0.9	-1.9	-0.1	-0.2		
L52	1.7	6.2	-0.3	-0.8	-0.3	-1.1	0.8	2.4		
L53	-2.9	-11.7	-2.2	-5.7	-4.3	-14.8	-0.7	-2.3		
L54	-0.1	-0.2	-0.3	-0.7	1.1	1.4	0.4	0.5		
L56	-1.5	-3.0	0.2	0.1	2.5	3.4	14.4	4.4	0.2	0.4
L57			-0.4	-0.5	5.1	7.1				
L58	-0.3	-0.6	0.3	0.5	-0.4	-1.2	-1.0	-2.2		
L59	-4.5	-17.5	-1.2	-1.9			1.1	1.0		
L60	-0.5	-0.8	0.0	-0.1	-0.5	-0.8	0.4	0.4		
L61	-0.6	-0.9	0.0	0.0	2.7	3.9	-0.2	-0.2		
L62	-1.2	-3.1	-0.8	-1.9	-1.3	-2.9	1.3	4.1	0.0	-0.1
L63	-0.3	-0.4	-0.5	-0.5	-1.1	-1.7	0.9	1.3	-3.0	-4.8
L65	-1.0	-1.3	-1.5	-1.3	-1.6	-3.0	-4.2	-9.6	1.8	1.9
L68	-4.6	-16.8	-0.7	-1.3	-1.3	-4.1	2.7	5.8		
L69	-1.2	-4.8	-0.7	-1.8	-0.7	-2.4	6476.0	20745.2		
L71			-0.5	-1.2	-0.7	-2.2				

Annex 15: Experimental details and scoring

(Questions 3, 7, 8, 9, 11, 12.1 and Q16 of Annex 7)

Lab	Official method	CRM used	Digestion	Digestion acids	Technique	LoD (mg kg^{-1})	Analysis frequency	z-scoring
L01	EPA 200.8	NIST 1547	Microwave	HNO_3+H_2O_2+HF	ICP	0.005	50-250	Total As
					ICP	0.002	50-250	Total Cd
					ETV-ICP-MS	0.005	50-250	Total Hg
					ICP	0.01	50-250	Total Pb
								iAs
L02	No		Microwave	HNO_3 + H_2O_2	ICP-MS	0.006	> 1000	Total As
			Microwave		ICP-MS	0.003	> 1000	Total Cd
					ICP-MS	0.006	> 1000	Total Hg
			Microwave		ICP-MS	0.006	> 1000	Total Pb
					LC-ICP-MS	0.002	50-250	iAs
L03	EPA 6010c	LGC CS-M-3	Microwave	HNO_3 + H_2O_2	ICP-OES	0.001	50-250	Total As
					ICP-OES	0.001	50-250	Total Cd
					ICP-OES	0.001	50-250	Total Hg
					ICP-OES	0.001	50-250	Total Pb
								iAs
L04		LGC 162	Microwave	HNO_3 + H_2O_2	AAS	0.05	> 1000	Total As
		NIST 1573a			AAS	0.005	50-250	Total Cd
	EPA 7473	LGC 162			DMA	0.002	> 1000	Total Hg
		LGC 162			AAS	0.05	50-250	Total Pb
								iAs
L05	EN 14546		Microwave	HNO_3 + H_2O_2	HG-AAS		> 1000	Total As
	EN 14083				AAS		> 1000	Total Cd
	EN 13806				CV-AAS		50-250	Total Hg
	EN 14083				AAS		> 1000	Total Pb
								iAs
L06					ETV-ICP-MS			Total As
					ETV-ICP-MS			Total Cd
					CV-AAS			Total Hg
					ETV-ICP-MS			Total Pb
								iAs
L07				HNO_3 + H_2O_2	ICP-MS	0.01		Total As
					ICP-MS	0.0016		Total Cd
	245.5				CV-AAS	0.003		Total Hg
					ICP-MS	0.0014		Total Pb
					ICP-MS	0.08		iAs
L08				HNO_3 + H_2O_2	HG-AAS	0.001	> 1000	Total As
	ISO 5515/5516			HNO_3 + H_2O_2	AAS	0.01	> 1000	Total Cd
								Total Hg
	ISO 5515/5516			HNO_3 + H_2O_2	AAS	0.1	> 1000	Total Pb
								iAs
L09	EN 14546	BCR-679	Dry ashing	HNO_3 + H_2O_2	HG-AAS	0,000036	50-250	Total As
	EN 14082	BCR-679	Dry ashing		AAS	0,000018	> 1000	Total Cd
	EN 13806	BCR-679	Microwave		CV-AAS	0,000029	50-250	Total Hg
	EN 14082	BCR-063R	Dry ashing		AAS	0,00028	> 1000	Total Pb
								iAs
L10	No	LPCS-01-1		HNO_3 + H_2O_2	ICP	0.1	50-250	Total As
					ICP	0.05	50-250	Total Cd
					ICP	0.02	50-250	Total Hg
					ICP	0.01	50-250	Total Pb
								iAs
L11								Total As
		GBW 10014	Microwave	HNO_3 + H_2O_2 + HCL	AAS	0.1	50-250	Total Cd
								Total Hg
		GBW 10014	Microwave	HNO_3 + H_2O_2 + HCL	AAS	0.2	50-250	Total Pb
								iAs
L12	Yes		Microwave	HNO_3 + H_2O_2	AAS	LOQ=0.400	> 1000	Total As
					AAS	LOQ=0.008	> 1000	Total Cd
					CV-AAS	LOQ=0.048	> 1000	Total Hg
					AAS	LOQ=0.060	> 1000	Total Pb
								iAs
L13						no		Total As
	AOAC	No	Microwave	HNO_3	AAS	LESS 80	> 1000	Total Cd
						no		Total Hg
	AOAC	No	Microwave	HNO_3	AAS	LESS 500	> 1000	Total Pb
						no		iAs
L14	IRMM 804		Microwave	HNO_3 + H_2O_2	ICP-MS	0.003	50-250	Total As
	IRMM 804		Microwave		ICP-MS	0.003	50-250	Total Cd
	LGC 7162				DMA	0.003	50-250	Total Hg
	IRMM 804		Microwave		ICP-MS	0.006	50-250	Total Pb
								iAs

Lab	Official method	CRM used	Digestion	Digestion acids	Technique	LoD (mg kg^{-1})	Analysis frequency	z-scoring
L17	No	Food	Microwave	HNO_3 + H_2O_2	ICP-OES	0.01	> 1000	Total As
					ICP-OES	0.01	> 1000	Total Cd
					ICP-OES	0.01	> 1000	Total Hg
					ICP-OES	0.01	> 1000	Total Pb
								iAs
L18	SM 3125	Aquatic plant	Microwave	HNO_3 + H_2O_2	ICP	0.05	50-250	Total As
					ICP	0.01	50-250	Total Cd
					ICP	0.005	50-250	Total Hg
					ICP	0.01	50-250	Total Pb
								iAs
L19	No		Microwave	HNO_3 + H_2O_2	ICP-OES	2.5		Total As
					ICP-OES	0.05		Total Cd
					ICP-OES	1		Total Hg
					ICP-OES	0.5		Total Pb
					ICP-OES	3.2		iAs
L20	No		Microwave	HNO_3 + H_2O_2	AFS	0.005	50-250	Total As
					AAS	0.5	50-250	Total Cd
					CV-AAS	2.5	50-250	Total Hg
					ICP-AES	1.0		Total Pb
								iAs
L21	No	CRM 1568a	Ashing at 450ºC		AAS	0.005	0-50	Total As
		BCR 191	Ashing at 450ºC		AAS	0.001	50-250	Total Cd
								Total Hg
		BCR 191	Ashing at 450ºC		AAS	0.005	50-250	Total Pb
		FAPAS 169	Ashing at 450ºC		AAS	0.015	0-50	iAs
L22					ICP-OES			Total As
					ICP-OES			Total Cd
					ICP-OES			Total Hg
					ICP-OES			Total Pb
					ICP-OES			iAs
L23	ISO 17294-2	DOLT-4	Microwave	7ml HNO_3+1ml H_2O_2	ICP	0.5	0-50	Total As
		Mussels powder T-8			ICP	0.05	0-50	Total Cd
		DOLT-4			ICP	0.1	0-50	Total Hg
		Mussels powder T-8			ICP	0.05	0-50	Total Pb
					ETV-ICP-MS			iAs
L24	ISO 17294	CRM TMDW	UV digestion	HNO_3 + H_2O_2	ICP			Total As
	ISO 17294	CRM TMDW	UV digestion		ICP		0-50	Total Cd
	EN 1483		UV digestion with flux		CV-AAS		0-50	Total Hg
	ISO 17294	CRM TMDW	UV digestion		ICP		0-50	Total Pb
	ISO 17294							iAs
L25					ICP-MS			Total As
					ICP-MS			Total Cd
	EPA 7473	NIST 1566b			AAS	0.0095	0-50	Total Hg
					ICP-MS			Total Pb
								iAs
L26	EN 15510	IMEP/FAPAS	Microwave	HNO_3 + H_2O_2	ICP-OES	0.141	50-250	Total As
					ICP-OES	0.01	50-250	Total Cd
					ICP-OES		50-250	Total Hg
					ICP-OES	0.048	50-250	Total Pb
								iAs
L27	No					0		Total As
			Microwave	HNO_3 + H_2O_2	AAS	0.1	0-50	Total Cd
						0		Total Hg
			Microwave	HNO_3 + H_2O_2	AAS	0.2	0-50	Total Pb
						0		iAs
L28	TFDA 1001903783	SRM 1566b	Microwave	HNO_3 + H_2O_2	GF-AAS	0.025	> 1000	Total As
	AOAC 999.10	SRM 1566b			GF-AAS	0.003	> 1000	Total Cd
	TFDA 1001903783				CV-AAS	0.05	> 1000	Total Hg
	AOAC 999.10	SRM 1566b			GF-AAS	0.025	> 1000	Total Pb
								iAs
L29	No		Microwave		AAS		> 1000	Total As
					AAS		> 1000	Total Cd
					CV-AAS		> 1000	Total Hg
					AAS		> 1000	Total Pb
								iAs
L30					ICP-MS			Total As
					ICP-OES			Total Cd
					CV-AAS			Total Hg
					ICP-MS			Total Pb
					HG-AAS			iAs
L32	No	NIST 1547		HNO_3	ICP-MS		> 1000	Total As
		V 463		HNO_3	ICP-MS		> 1000	Total Cd
		NIST 1568a			CV-AAS		50-250	Total Hg
		NIST 1547		HNO_3	ICP-MS		> 1000	Total Pb
								iAs
L33	No	DORM 3	Microwave	HNO_3 + H_2O_2	HG-AAS		0-50	Total As
					ICP-AES		50-250	Total Cd
					CV-AAS		0-50	Total Hg
					AAS		50-250	Total Pb
								iAs

Lab	Official method	CRM used	Digestion	Digestion acids	Technique	LoD (mg kg^{-1})	Analysis frequency	z-scoring
L34	No	Merck 1.70333.0100	Microwave	HNO_3 + H_2O_2	ICP	0.0003	0-50	Total As
					ICP	0.0003	0-50	Total Cd
					ICP	0.0003	0-50	Total Hg
					ICP	0.0002	0-50	Total Pb
								iAs
L35	No	No	Microwave	HNO_3	ICP-MS	0.02	0-50	Total As
					ICP-MS	0.002	0-50	Total Cd
					AAS	0.000005	0-50	Total Hg
			Microwave	HNO_3	ICP-MS	0.01	0-50	Total Pb
								iAs
L36					ETV-ICP-MS		50-250	Total As
					ETV-ICP-MS		50-250	Total Cd
					ETV-ICP-MS		50-250	Total Hg
					ETV-ICP-MS		50-250	Total Pb
								iAs
L37					ICP			Total As
					ICP			Total Cd
								Total Hg
					ICP			Total Pb
								iAs
L38								Total As
	GFAAS	Cd Std for AAS		HNO_3	GF-AAS	0.065		Total Cd
								Total Hg
	GFAAS	Pb Std for AAS		HNO_3	GF-AAS	0.00083		Total Pb
								iAs
L39	EN 14627		Microwave	HNO_3 + H_2O_2	HG-AAS	0.001	0-50	Total As
	EN 14084				ET-AAS	0.005	0-50	Total Cd
	EN 13806				CV-AAS	0.001	0-50	Total Hg
	EN 14084				ET-AAS	0.01	0-50	Total Pb
								iAs
L41	EN 15763	NIST 1547	Microwave	HNO_3	ICP-MS	0.025	> 1000	Total As
	EN 15763				ICP-MS	0.006	> 1000	Total Cd
	EN 13806				CV-AAS	0.0025	> 1000	Total Hg
	EN 15763				ICP-MS	0.02	> 1000	Total Pb
	EN 16278				HG-AAS		0-50	iAs
L42					ICP-MS			Total As
					ICP-MS			Total Cd
					CV-AAS			Total Hg
					ICP-MS			Total Pb
								iAs
L43	EN 14627	FAPAS	Microwave	HNO_3 + H_2O_2	HG-AAS	0.02	50-250	Total As
	EN 14084				AAS	0.01	50-250	Total Cd
	EN 14627				HG-AAS	0.02	50-250	Total Hg
	EN 14084				AAS	0.02	50-250	Total Pb
								iAs
L44	FDA	Perkin Lot:1-266YP	Microwave	HNO_3	HPLC-ICP-MS	0.001	0-50	Total As
		Perkin Lot:1-266YP			MS	0.0026	0-50	Total Cd
		Perkin Lot:17-08HG			HPLC-ICP-MS	0.0005	0-50	Total Hg
		Perkin Lot:1-266YP			HPLC-ICP-MS	0.001	0-50	Total Pb
								iAs
L45	Yes	NIST 1570a	Microwave	HNO_3 + H_2O_2	ICP	0.001	0-50	Total As
					ICP	0.0004	50-250	Total Cd
					AAS	0.001	0-50	Total Hg
					ICP	0.01	50-250	Total Pb
								iAs
L46			Microwave	HNO_3	HG-AAS			Total As
					GF-AAS			Total Cd
					HG-AAS			Total Hg
					GF-AAS			Total Pb
								iAs
L47					ICP-MS			Total As
					ICP-MS			Total Cd
					ICP-MS			Total Hg
					ICP-MS			Total Pb
								iAs
L48	EN 14627	PT material	Microwave	HNO_3 + H_2O_2	HG-AAS	0.005	50-250	Total As
	EN 14084				AAS	0.001	50-250	Total Cd
	EN 13806				CV-AAS	0.008	50-250	Total Hg
	EN 14084				AAS	0.003	50-250	Total Pb
								iAs
L49					HG-AAS			Total As
					AAS			Total Cd
					CV-AAS			Total Hg
					AAS			Total Pb
								iAs
L50								Total As
					AAS			Total Cd
					CV-AAS			Total Hg
					AAS			Total Pb
					ICP-AES			iAs

Lab	Official method	CRM used	Digestion	Digestion acids	Technique	LoD (mg kg^{-1})	Analysis frequency	z-scoring
L51	No	SRM 1566b	Microwave	HNO_3 + H_2O_2	ICP	0.005	0-50	Total As
					ICP	0.0025	0-50	Total Cd
					AAS	0.0005	50-250	Total Hg
					ICP	0.025	0-50	Total Pb
								iAs
L52	ISO 17294-1				ICP			Total As
	ISO 17294-1				ICP			Total Cd
	CSN 75 7440				AAS			Total Hg
	ISO 17294-1				ICP			Total Pb
								iAs
L53	No			HNO_3 + H_2O_2	AAS		50-250	Total As
					AAS		> 1000	Total Cd
					AAS		> 1000	Total Hg
					AAS		> 1000	Total Pb
								iAs
L54				HNO_3 + H_2O_2	AAS	0.004	0-50	Total As
	EN 14085				AAS	0.005	> 1000	Total Cd
					AAS	0.0002	0-50	Total Hg
	EN 14082				AAS	0.006	> 1000	Total Pb
								iAs
L56	No	BCR 281, NIST 1573a	Microwave	5mL HNO_3 + 1mL H_2O_2	AAS	0.03	0-50	Total As
					AAS	0.0005	0-50	Total Cd
					CV-AAS	0.06	0-50	Total Hg
					AAS	0.018	0-50	Total Pb
					AAS	0.06	0-50	iAs
L57								Total As
			Microwave	HNO_3 + H_2O_2	GF-AAS	0.01	> 1000	Total Cd
	EPA 7473				DMA	0.05	> 1000	Total Hg
					GF-AAS	0.08	> 1000	Total Pb
								iAs
L58	EN 13805/EN 1576	FAPAS	Microwave digestion	HNO_3 + H_2O_2	ICP-MS	0.001		Total As
					ICP-MS	0.00025		Total Cd
					ICP-MS	0.0001		Total Hg
					ICP-MS	0.0005		Total Pb
								iAs
L59	No	FAPAS	Microwave	HNO_3 + H_2O_2	AAS		0-50	Total As
					AAS		50-250	Total Cd
					FIAS-AAS		0-50	Total Hg
								Total Pb
								iAs
L60	EN 15763	SRM 1643e/TORT-2	Microwave	HNO_3	ICP-MS	0.041	> 1000	Total As
					ICP-MS	0.015	50-250	Total Cd
		NCR TORT-2			ICP-MS	0.006	0-50	Total Hg
		SRM 1643e/TORT-2			ICP-MS	0.016	50-250	Total Pb
								iAs
L61	No			HNO_3 + H_2O_2	ICP	0.05	> 1000	Total As
					ICP	0.05	> 1000	Total Cd
					CV-AAS	0.05	> 1000	Total Hg
					ICP	0.05	> 1000	Total Pb
								iAs
L62	L 12.00 6		Microwave	HNO_3	AAS	0.02	> 1000	Total As
	L 00.00 1913				AAS	0.002	> 1000	Total Cd
	L 00.00 1914				HG-AAS	0.005	> 1000	Total Hg
	L 00.00 1913				AAS	0.02	> 1000	Total Pb
	L 25.06 1				HG-AAS	0.02	0-50	iAs
L63	EN 13905	NIST 1549	Microwave	HNO_3	ICP	0.04	> 1000	Total As
	EN 13905	DORM-3			ICP	0.001	> 1000	Total Cd
	EN 16277	NIST 1568a		Pyrolysis	CV-AAS	0.005	> 1000	Total Hg
	EN 13905	TORT-2		HNO_3	ICP	0.05	> 1000	Total Pb
	EN 15517	BCR 279		HCL	HG-AAS	0.10	50-250	iAs
L65	No			HNO_3	ICP-MS	0.005	> 1000	Total As
					ICP-MS	0.001	> 1000	Total Cd
					ICP-MS	0.001	> 1000	Total Hg
					ICP-MS	0.001	> 1000	Total Pb
				Enzyme	ICP-MS	0.01	50-250	iAs
L68	EN 14627		Microwave	HNO_3 + H_2O_2	HG-AAS		0-50	Total As
	EN 14084				GF-AAS		50-250	Total Cd
	EN 13806				HG-AAS		0-50	Total Hg
	EN 14084				GF-AAS		50-250	Total Pb
								iAs
L69	No		Microwave		ICP		> 1000	Total As
					ICP		> 1000	Total Cd
					ICP		> 1000	Total Hg
					ICP		> 1000	Total Pb
							0-50	iAs
L71								Total As
					AAS			Total Cd
								Total Hg
					AAS			Total Pb
								iAs

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Abstract

This report presents the results of a proficiency test exercise (PT) focussed on the determination of total cadmium, lead, arsenic, mercury and inorganic arsenic in mushrooms. The exercise is organised in support of the European Union Regulation 1881:2006 which sets the maximum levels for certain contaminants in foodstuffs.
Seventy one participants from thirty six countries registered to the exercise, of which sixty two reported results.
The test item used was a blend of mushrooms (of the variety *Lentinula edodes*). The assigned value was obtained as the average of results reported by five expert laboratories having demonstrated experience in the analysis of trace elements in different matrices. The associated uncertainties of the assigned values were computed according to the ISO/IEC Guide 98:2008 (GUM) and following ISO 13528:2005.
Participants were invited to report their measurement uncertainties. This was done by the majority of laboratories having submitted results in this exercise.
Laboratory results were rated with z- and zeta (ζ-) scores in accordance with ISO 13528:2005. The standard deviation for the proficiency assessment was based on the use of the modified Horwitz equation (for inorganic arsenic (19 % of X_{ref}) and for the total mass fraction of lead, 20 % of X_{ref}) while slightly lower percentages were decided, upon expert judgment of the advisory board of this PT exercise and based on previous participants' performance on similar measurands, for the total mass fractions of arsenic and mercury (15 % of X_{ref}) and for the total mass fraction of cadmium (10 % of X_{ref}).
The percentage of satisfactory z-scores ranged from 64 % (inorganic arsenic) to 84 % (total cadmium). Thus, the outcome of the present proficiency test demonstrates that the analytical capability of food control laboratories on the determination of the investigated food contaminants, at the investigated levels of concentration, deserves further improvements.

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