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Determination of total and inorganic arsenic in rice

IRMM-PT-43
Proficiency Test Report

Fernando Cordeiro, Aneta Cizek-Stroh and Beatriz de la Calle

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Executive summary

The Joint Research Centre (JRC), a Directorate General of the European Commission (EC), organised a proficiency test (IRMM-PT-43) for the determination of the mass fractions of total arsenic (As) and inorganic arsenic (iAs) in rice in support to the implementation of provisions of Commission Regulation (EU) 2015/1006 which amends Regulation (EC) 1881/2006 as regards maximum levels of inorganic arsenic in foodstuffs.

The present proficiency test (PT) was open to National Reference Laboratories (NRLs) and official control laboratories (OCLs). Fifty three participants from twenty countries registered to the exercise. Seven participants did not report results.

The material used as test item was a certified rice flour reference material (SRM 1568b), which, after appropriate processing, was bottled, labelled and dispatched to the participants during the first half of March 2016.

Laboratory results were rated using z and ζ scores in accordance with the international standard ISO 13528:2015. The relative standard deviation for proficiency assessment was set to 15 % of the assigned value for both measurands.

Most of the laboratories (91 %) reported realistic measurement uncertainties and performed satisfactorily (with $|z| \leq 2$) for the determination of the total As mass fraction. For the determination of iAs mass fraction 55 % of the participating laboratories performed satisfactorily.

Acknowledgements

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The laboratories listed below are kindly acknowledged for their participation in this PT exercise.

Organisation	Country
Seibersdorf Labor GmbH	Austria
AGES GmbH	Austria
CODA-CERVA	Belgium
Croatian National Institute for Public Health	Croatia
Public Health for Osijek - baranya County	Croatia
CISTA (ÚKZÚZ)	Czech Republic
State Veterinary Institute Olomouc	Czech Republic
Danish Veterianry and Food Administration	Denmark
DTU Food	Denmark
Laboratoire SCL de Bordeaux	France
ANSES-French Agency for Food, Environmental and Occupational Health and Safety	France
CAMP66	France
INOVALYS	France
La Drôme Laboratoire	France
Laboratoire Départemental du Morbihan	France
Landesbetrieb Hessisches Landeslabor	Germany
LAVES, Lebensmittel- und Veterinärinstitut Oldenburg	Germany
Landeslabor Schleswig-Holstein	Germany
Thüringer Landesamt für Verbraucherschutz (TLV)	Germany
Landeslabor Berlin-Brandenburg	Germany
Landesuntersuchungsamt, Institut für Lebensmittelchemie	Germany
Chemisches und Verterinäruntersuchungsamt	Germany
Kreis Mettmann - Amt für Verbraucherschutz	Germany
Bayerisches Landesamt fuer Gesundheit und Lebensmittelsicherheit (LGL)	Germany
Landesamt für Verbraucherschutz Sachsen-Anhalt	Germany
General Country State Laboratory	Greece
Regional Center of Plant Protection and Quality Control of Magnissia	Greece
National Food Chain Office Food and Feed Safety	Hungary
ISS	Italy
Istituto Zooprofilattico Sperimentale del Piemonte, Liguria e Valle D'aosta	Italy
National Food and Veterinary Risk Assessment Institute	Lithuania
Public Health Laboratory	Malta
RIKILT	Netherlands
Aris Industrial S.A.	Peru
Powiatowa Stacja Sanitarno-Epidemiologiczna w Siedlcach	Poland
Wojewódzka Stacja Sanitarno-Epidemiologiczna w Łodzi	Poland
National Institute of Public Health – National Institute of Hygiene (NIPH – NIH)	Poland
WSSE Gorzow Wielkopolski	Poland
Wojewódzka Stacja Saniatrno-Epidemiologiczna	Poland
WSSE Lublin	Poland
State veterinary and food institute Dolný Kubín, Veterinary and food institute Košice	Slovakia
National Laboratory of Health, Environment and Food	Slovenia
Laboratorio Salud Pública Bizkaia	Spain
Laboratory of the Public Health Agency of Barcelona	Spain
Laboratorio de Salud Pública de Gran Canaria	Spain
Laboratorio Arbitral Agroalimentario (MAGRAMA)	Spain
Laboratorio de Salud Publica de Alicante	Spain
National Food Agency	Sweden
Kent County Council	United Kingdom
Glasgow Scientific Services	United Kingdom
Staffordshire County Council	United Kingdom

1. Introduction

The present proficiency test (PT) named IRMM-PT-43, was organised by the European Commission's Joint Research Centre - Institute for Reference Materials and Measurements (JRC - IRMM) to assess the performance of National Reference Laboratories (NRLs) and official food control laboratories (OCLs) in the determination of total arsenic (As) and inorganic arsenic (iAs) mass fractions in rice.

The Scientific Panel on Contaminants in the Food Chain (CONTAM Panel) of the European Food Safety Authority (EFSA) identified that inorganic arsenic causes cancer of the lung and urinary bladder, in addition to skin and that the dietary exposure to inorganic arsenic for average and high level consumers of rice, such as some ethnic groups and particularly children under three years of age, results in a high exposure and high risk for the above mentioned disease [1].
The reliability of the analysis of total and iAs in rice was demonstrated by the performance of participating laboratories in an interlaboratory comparison (ILC) round organised by the European Union Laboratory for Heavy Metals in Feed and Food (EURL-HM) [2]. As a result an amendment was considered appropriate for Commission Regulation (EC) 1881/2006 [3] as regards the introduction of maximum levels (MLs) for inorganic arsenic in rice and rice-derived products, which entered into force in January 2016 [4].

Several validated methods are available for the determination of iAs in foodstuffs. In 2012 the European Committee for Standardization (CEN) standardised a method for the determination of iAs in animal feeding stuffs by hydride generation atomic absorption spectroscopy (HG-AAS) after microwave extraction and off-line separation of iAs by solid phase extraction (SPE, EN 16278:2012 [5]). This method was validated in a collaborative trial in the frame of the IMEP-32 project [6] and has furthermore been used in studies on iAs content in seafood and rice. Currently, CEN is validating a method for the selective determination of iAs in food based on high performance liquid chromatography hyphenated with inductively coupled plasma mass spectrometry (HPLC-ICP-MS). Two other standard methods have been published, GB/T 5009.11-2003 (China) [7] and EN 15517:2008 [8] for the determination of abio-arsenic in food and of iAs in seaweed, respectively. Both methods are based on the selective determination of arsine from iAs under specific conditions without any previous separation of species and with final determination by atomic fluorescence [7] or by HG-AAS [8], respectively. Recently, the JRC organised a collaborative trial (IMEP-41 [6]) for the validation of a method to determine iAs in several foodstuffs. This method, which is based on the selective extraction of iAs into chloroform and further determination by HG-AAS, should serve as an inexpensive complement to the method being validated by CEN based on HPLC-ICP-MS.

This report evaluates and summarises the performance of NRLs and OCLs in the determination of total and inorganic arsenic mass fractions in rice, in the frame of the IRMM-PT-43 round. Additionally, it evaluates the ability of laboratories in assessing the compliance of the test item against the maximum levels set in the European legislation for contaminants in food.

2. Scope and aim

The present PT aims to assess the performance of NRLs and OCLs in the determination of total As and iAs mass fractions in rice. In addition, participants were requested to evaluate the conformity of the analysed test item according to the maximum levels (MLs) set in the European legislation for contaminants in food.

The assessment of measurement results follows the administrative and logistic procedures of the EC-JRC-IRMM for the organisation of PTs, which is accredited according to ISO/IEC 17043:2010 [9].

The name of this proficiency testing round is IRMM-PT-43.

3. Set up of the exercise

3.1 Time frame

The web announcement (Annex 1) for the exercise was made on January 19, 2016 on the JRC webpage [6]. Invitation letters were sent to the NRLs on the same day (Annex 2). The registration deadline was set to February 28, 2016. The test item was dispatched to participants the first half of March 2016. The reporting deadline was set to April 15, 2016. Dispatch was followed by the PT coordinator using the messenger's parcel tracking system on the internet.

3.2 Confidentiality

According to the IRMM quality system for the organisation of PTs the confidentiality of participants is guaranteed.

3.3 Distribution

The test item was dispatched to participants on March 7 and 8, 2016. Each participant received:

- One glass bottle containing approximately 6 g of test item;
- A "Sample accompanying letter" (Annex 3); and
- A "Confirmation of receipt form" to be sent back to IRMM after receipt of the test item (Annex 4).

3.4 Instructions to participants

Detailed instructions were given to participants in the "Sample accompanying letter" mentioned above. Measurands were defined as "Total and inorganic As mass fractions in rice".

Participants were asked to perform two or three independent measurements, to correct their measurements for recovery and for moisture content and to report their calculated mean (x_{lab}), the associated expanded measurement uncertainty (U_{lab}) together with the corresponding coverage factor and the technique used.

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

Participants were informed that the procedure used for the analysis should resemble as closely as possible the one they use for routine analysis.

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

4. Test item

4.1 Preparation

The test item used was a certified reference material (SRM 1568b) purchased from the National Institute of Standards & Technology (NIST, USA). The material was rebottled

(portions of 6 g were filled into 30 ml acid-washed amber glass bottles) and relabelled. The bottles were manually filled using acid washed plastic spoons under an air extraction point. The bottles were closed with acid washed inserts and screw caps.

Each vial was identified / labelled with a unique number and with the name of the PT round, following the EC-JRC-IRMM procedures.

4.2 Homogeneity and stability

The certified reference material (CRM) used in the present PT exercise was considered to be adequately homogeneous and stable for the purpose of the exercise on the basis of the information provided by the CRM producer. Therefore, no additional homogeneity and stability studies were carried out for the material used.

5. Assigned values and their uncertainties

5.1 Assigned value, X_{pt}

The certified values and their corresponding expanded uncertainties, used as assigned values for the present PT exercise, were derived from the SRM 1568b certificate [10], and are presented in Table 1.

5.2 Associated uncertainty, u_{pt}

The standard uncertainties (u_{pt}) associated to the assigned values were calculated as the ratio between the expanded uncertainties listed in the CRM certificate and the respective coverage factor.

Table 1 presents the assigned values (X_{pt}), their associated expanded uncertainties (U_{pt}, k = 2 which corresponds to a confidence interval of 95 % around the assigned value) and the standard deviation for PT assessment (σ_{pt}).

Table 1 – *Assigned values (X_{pt}, and U_{pt} (k=2)) and the standard deviation for PT assessment (σ_{pt}). All values in mg kg^{-1} [10].*

	X_{pt}	U_{pt} (k=2)	σ_{pt}	σ_{pt} (%)
As	0.285	0.014	0.043	15
iAs	0.092	0.010	0.014	15

5.3 Standard deviation for proficiency assessment, σ_{pt}

The relative standard deviation for proficiency assessment (σ_{pt}, in % of the respective X_{pt}) was set to 15 % of the assigned value for both measurands considering the performance of participants in a previous PT round with similar measurands [2], Table 1.

6. Evaluation of results

6.1 Scores and evaluation criteria

Individual laboratory performance was expressed in terms of z and ζ scores in accordance with ISO 13528:2015 [11]:

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

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

Where: x_{lab} is the measurement result reported by a participant;
X_{pt} is the assigned value;
σ_{pt} is the standard deviation for proficiency assessment;
u_{pt} is the standard measurement uncertainty of the assigned value;
u_{lab} is the standard measurement uncertainty reported by a participant.

The interpretation of the z and ζ scores is done according to ISO 17043:2010 [9]:

|score| ≤ 2	satisfactory performance	(green in Annexes 6 - 9)
2 < |score| < 3	questionable performance	(yellow in Annexes 6 - 9)
|score| ≥ 3	unsatisfactory performance	(red in Annexes 6 - 9)

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

The ζ score states whether the laboratory's result agrees with the assigned value within the respective uncertainty. The denominator is the combined uncertainty of the assigned value (u_{pt}) and the standard measurement uncertainty as stated by the laboratory (u_{lab}). The ζ score includes all parts of a measurement result, namely the expected value (assigned value), its associated standard measurement uncertainty and the standard measurement uncertainty of the reported values. An unsatisfactory ζ score can either be caused by the presence of a significant bias (inaccurate measurement) or by a not realistic evaluation of the measurement uncertainty (under evaluation), or both.

The standard measurement uncertainty of the laboratory (u_{lab}) was obtained by dividing the reported expanded measurement uncertainty by the reported coverage factor, k. When no uncertainty was reported, it was set to zero (u_{lab} = 0). When k was not specified, the reported expanded measurement 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 [12].

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

The standard measurement 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": $u_{min} \leq u_{lab} \leq u_{max}$. u_{min} is set to the standard measurement uncertainty of the assigned value ($u_{min} = u_{pt}$). It is unlikely that a laboratory carrying out the analysis on a routine basis would measure the measurand with a smaller measurement uncertainty than the expert laboratories chosen to establish the assigned value.

u_{max} is set to the standard deviation accepted for the PT assessment ($u_{max} = \sigma_{pt}$). Consequently, case "a" becomes: $u_{pt} \leq u_{lab} \leq \sigma_{pt}$.

If u_{lab} is smaller than u_{min} (case "b": $u_{lab} < u_{pt}$) the laboratory may have under evaluated its measurement uncertainty. Such a statement has to be taken with care as each laboratory reported only its measurement uncertainty, whereas the uncertainty associated with the assigned value also includes the contribution for homogeneity and stability of the test item. If that is large, measurement uncertainties smaller than u_{min} are possible and plausible.

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

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

More detailed information about measurement uncertainty evaluation can be found in some international standards and other guidance documents [12-16].

6.2 General observations

Fifty-three participants from 20 countries, of which 21 NRLs, registered to this exercise (Figure 1). Seven participants (of which 1 NRL) did not report results. For total As 45 results were reported (20 from NRLs and 25 from OCLs). For iAs 39 results were reported (20 from NRLs and 19 from OCLs). Among them, one participant (NRL) reported a "*less than X*" value.

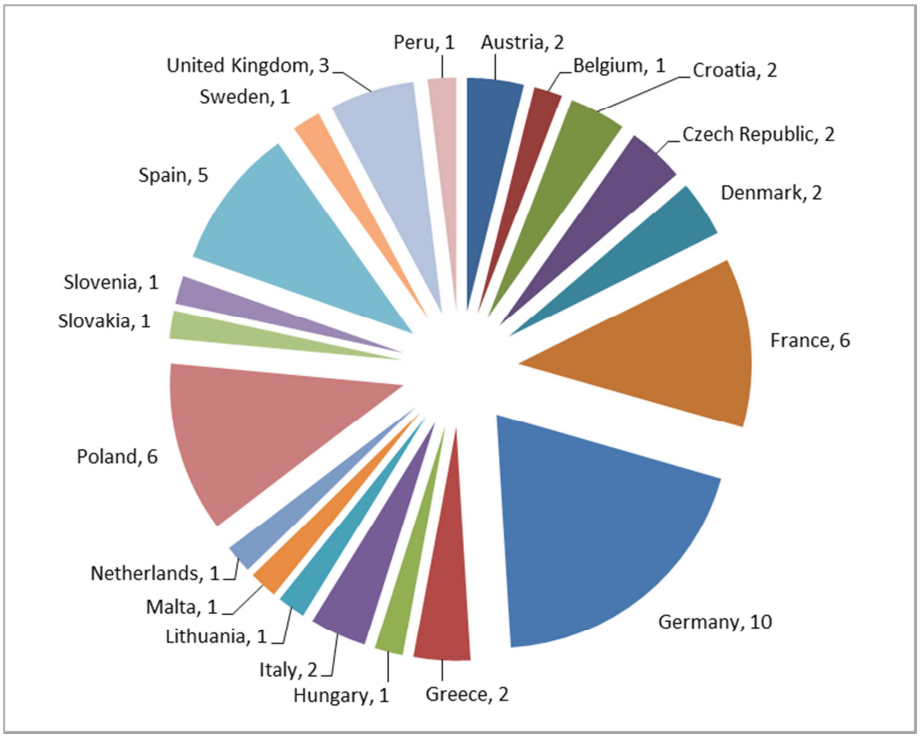

Figure 1: *Countries having registered in IRMM-PT-43. Fifty-three laboratories registered of which 46 reported results.*

6.3 Laboratory results and scorings

Annexes 6 and 7 present the reported results as tables and graphs for each measurand. NRLs and OCLs are denoted as Nxx and Lxx, respectively. The corresponding Kernel density plots, obtained using the software available from the Statistical Subcommittee of the Analytical Methods Committee of the UK Royal Society of Chemistry [17], are also included. Both for total and iAs mass fractions the Kernel density plots indicate that the distribution of the reported results follows a normal distribution (Annexes 6 and 7, respectively).

Figure 2 presents an overview of the performance of the participants, expressed as z and ζ scores, for the whole population, for OCLs and for NRLs. When taking into account the z scores, participants performed satisfactorily for the determination of the total As mass fraction (91 % satisfactory results in the total population, 95 % among NRLs and 88 % among OCLs) while a poorer performance was observed for the determination of the iAs mass fraction (55 % satisfactory results in the total population, 47 % among NRLs and 63 % among OCLs). The questionable and unsatisfactory z scores for the total As mass fraction were mostly due to a negative bias (3 out of 4); on the contrary for the iAs mass fraction all the questionable and unsatisfactory z scores (except one) were due to a positive bias.

For the total As mass fraction the performance expressed as ζ scores was slightly worse than that expressed as z scores (80 % satisfactory results in the total population, 85 % among NRLs and 76 % among OCLs), while for the iAs mass fraction the opposite was observed (63 % satisfactory results in the total population, 58 % among NRLs and 68 % among OCLs).

Most participants reported realistic measurement uncertainties, case "a" ($u_{pt} \leq u_{lab} \leq \sigma_{pt}$), for both total and iAs mass fractions (91 % and 61 %, respectively), Table 2. No laboratory reported a case "b" ($u_{lab} < u_{pt}$, possibly an under evaluation) measurement uncertainty for the total As mass fraction. In the case of the iAs mass fraction only 10 % of the reported measurement uncertainties were classified as case "b" and 29 % as case "c" ($u_{lab} > \sigma_{pt}$, possibly an over evaluation). In the whole exercise only two of the laboratories that reported a case "b" measurement uncertainty (which could penalise the ζ score) received an unsatisfactory ζ score.

Annexes 8 and 9 summarises the experimental details used by the participating laboratories in the determination of total As and iAs, respectively.

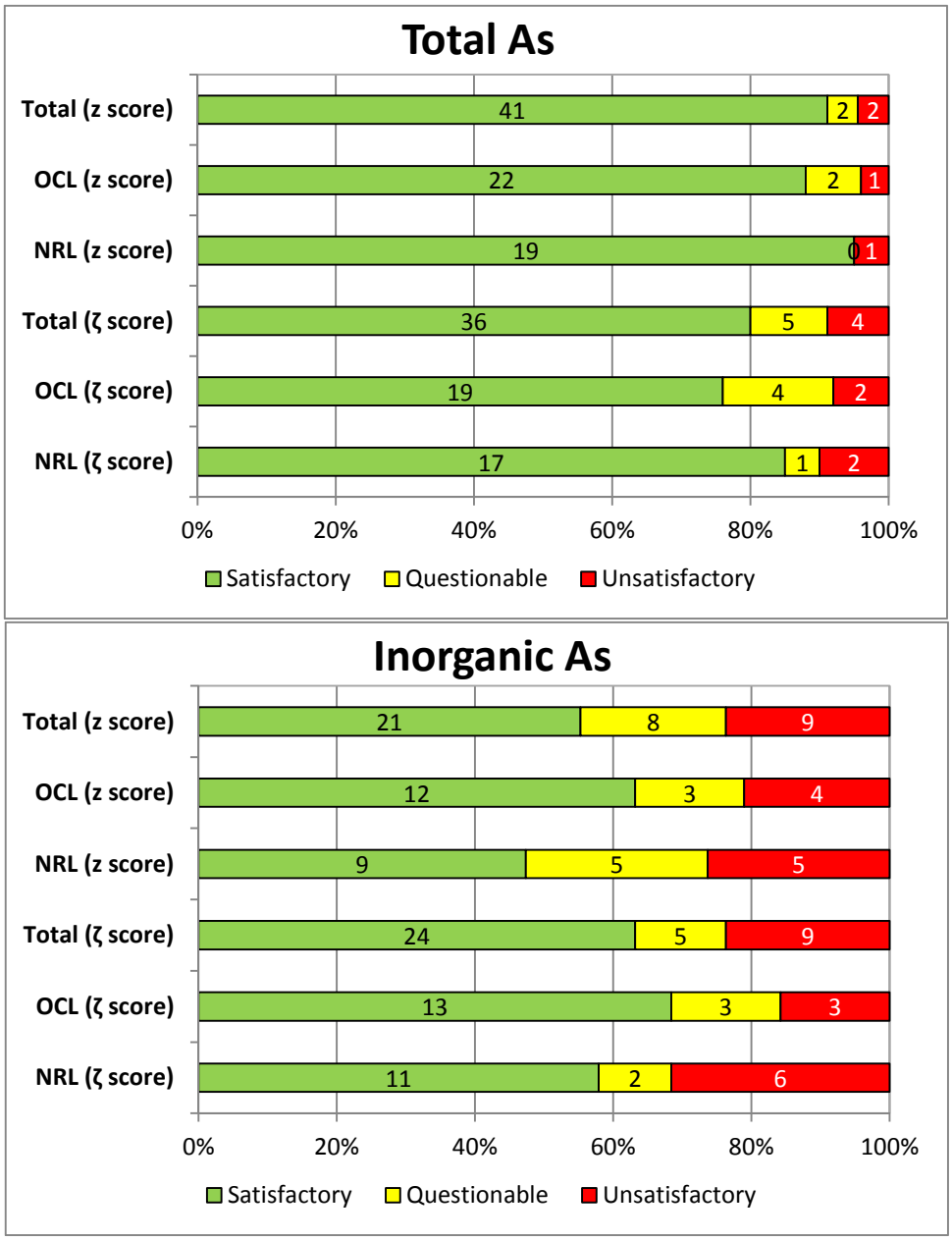

Figure 2: *Overview of scores (in % and in the number of laboratories) having satisfactory (green), questionable (yellow) and unsatisfactory performance (red).*

Table 2 – *Measurement uncertainty assessment per measurand*

	$u_{pt} \leq u_{lab} \leq \sigma_{pt}$		$u_{lab} < u_{pt}$		$u_{lab} > \sigma_{pt}$	
Total As	41 (91 %)		0		4 (9 %)	
	NRLs	**OCLs**			**NRLs**	**OCLs**
	18 (90 %)	23 (92 %)			2 (10 %)	2 (8 %)
Inorganic As	23 (61 %)		4 (10 %)		11 (29 %)	
	NRLs	**OCLs**	**NRLs**	**OCLs**	**NRLs**	**OCLs**
	13 (68 %)	10 (53 %)	2 (11 %)	2 (11 %)	4 (21 %)	7 (36 %)

Only one participant reported a "*less than*" result (N47 for iAs mass fraction). Since the reported value (< 0.08 mg kg^{-1}) was lower than X_{ref} - U_{ref} for the mentioned measurand, this statement is considered incorrect (flagged in red in Annex 7) because the laboratory should have been able to detect the iAs.

As mentioned above most of the questionable and unsatisfactory results reported for the iAs mass fraction are affected by a positive bias, probably due to contamination or to inter-conversion of arsenic species either during sample pre-treatment or during the instrumental detection of iAs:

- Inter-conversion of arsenic species during sample pre-treatment could happen if too severe conditions (high temperatures, acid concentrations, etc.) are applied. The test item used contains, according to the CRM producer [10], monomethylarsonic acid (MMA, 0.0116 ± 0.035 mg kg^{-1}) and dimethylarsinic acid (DMA, 0.180 ± 0.012 mg kg^{-1}) which could be converted, at least partially, into iAs. This could for instance explain why only four out of nine results obtained after dry ashing (temperatures between 395 and 500 °C) got a satisfactory z score, Annex 9.
- Contamination originating from the reagents could also explain the positive bias. To avoid it only reagents of the highest purity are recommended. However, if this would be the explanation for the positive bias, also the results reported for total arsenic would have been affected by it. The Youden plot (Figure 3), shows that the results reported for the total arsenic mass fraction, are randomly distributed around the assigned value and with the exception of three of them, within the accepted standard deviation for proficiency assessment, $\sigma_{pt.}$ The total arsenic mass fraction in the test item is about three times higher than that of iAs and so the interference, if present, would introduce a lower bias, relatively speaking, in the former measurand.
- Interferences linked to the instrumental approach used ($ArCl^+$ is a known interference in arsenic determinations by ICP-MS because both have an m/z of 75) may be a reason for a positive bias. However, this interference would have affected both, total and iAs.
- Not-resolved interferences due to organic species of arsenic, would mostly interfere in the determination of iAs by HG-AAS if no separation of species is carried out before the generation of the hydride. MMA and DMA can generate the hydride although normally with a lower efficiency than iAs. As mentioned above, MMA and DMA are present in the test item used in this PT. If this hypothesis would be correct, the positively biased results for the iAs mass fraction would have been mostly observed among results obtained using HG-AAS. However, as shown in Figure 3, quite a number of those results were obtained using ICP-MS.

It needs to be mentioned that six out of the ten laboratories which used HG-AAS for iAs determination which got a questionable or an unsatisfactory z score, used dry ashing to digest the sample (Annex 9) and so the positive bias could be more likely due to inter-conversion of species than to the interference of MMA and/or DMA, or to a combination of both effects.

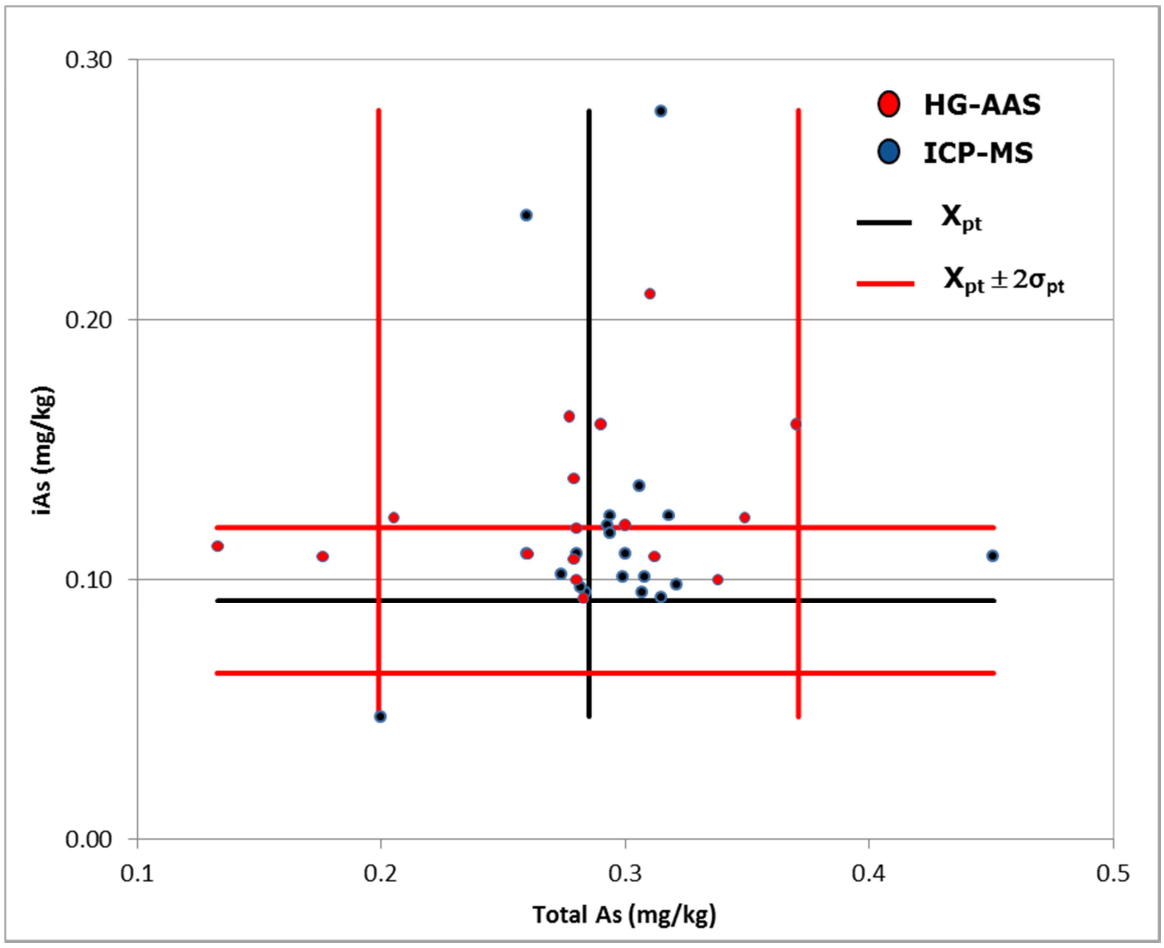

Figure 3: *Youden plot for the total and iAs mass fraction as obtained from the participants who reported values for both measurands.*

As summarised in Annexes 8 and 9 several digestion approaches (microwave (total As: 29, iAs: 15) - with open and closed vessel, wet digestion (total As: 4, iAs: 6) - in open and in pressure bomb, and dry ashing (total As: 9, iAs: 9), have been used. No significant correlation could be established between approach and performance, other than the high percentage of questionable and unsatisfactory z scores for the iAs mass fraction when dry ashing was used.

Several acids or acid mixtures were used for digestion purposes. For the total As mass fraction three out of the four laboratories to which a questionable or unsatisfactory performance was assigned used only HNO_3 during the digestion. The remaining laboratory used HNO_3 and H_2O_2 as digestion mixture. However, quite a number of participants used only HNO_3 to digest the sample and reported satisfactory results for this measurand, which indicates that this parameter alone is not responsible for the observed bias. Regarding the iAs mass fraction a slightly better performance could be identified for the use of HNO_3 + H_2O_2 as digestion mixture as the number of laboratories

using it who got satisfactory performance (seven out of ten, 70 %) was larger than for other mixtures. Inversely, the use of HCl alone does not seem to be appropriate because only one among the three laboratories that used this acid (33 %) got a satisfactory z score.

Table 3 shows the distribution of satisfactory, questionable and unsatisfactory z and ζ scores on the basis of the different instrumental approaches used for the final determination; the figures between brackets indicate the respective percentages within each particular instrumental population. Slightly better performance could be identified for participants using ICP-MS-based techniques when compared with HG-AAS and ET-AAS, for both total and iAs mass fractions.

Laboratories without experience in the analysis of iAs in food commodities could benefit of the use of standardised methods [5], [7 - 8]. Sixty-eight per cent of the laboratories that used a standardised method obtained a satisfactory z score vs 42 % among those that did not.

A HG-AAS based method has been validated recently by the JRC EURL-HM [6]. The method does not imply the use of sophisticated instrumentation, but it has the drawback of using chloroform. In this PT that extraction procedure was used by N06 which obtained a z score of 0.07 for the iAs mass fraction. Chloroform is used in other areas of analysis and if handled with proper care (in fume hood) it showed not to be of particular risk.

Also EN 16278 [5] is based on the use of HG-AAS but the method is characterised by a limit of detection (LOD) which is not low enough for the determination of iAs in rice and rice derived products.

Table 3 - *Laboratory performance by technique*

Technique	$\lvert z \rvert \leq 2$	$2 < \lvert z \rvert < 3$	$\lvert z \rvert \geq 3$	$\lvert \zeta \rvert \leq 2$	$2 < \lvert \zeta \rvert < 3$	$\lvert \zeta \rvert \geq 3$
Total As						
ICP-MS + SF-ICP-MS	23 (96 %)		1 (14 %)	21 (57 %)	2 (29 %)	1 (14 %)
HG-AAS	11 (84 %)	1 (8 %)	1 (8 %)	10 (77 %)	1 (8 %)	2 (15 %)
ET-AAS + HG-ET-AAS	6 (86 %)	1 (14 %)		4 (57 %)	2 (29 %)	1 (14 %)
iAs						
HPLC-ICP-MS + IC-ICP-MS	12 (66 %)	3 (17 %)	3 (17 %)	11 (61 %)	3 (16 %)	4 (23 %)
HG-AAS	8 (47 %)	5 (29 %)	4 (24 %)	11 (64 %)	2 (12 %)	4 (24 %)
ET-AAS + HG-ET-AAS	1 (50 %)		1 (50 %)	1 (50 %)		1 (50 %)

6.4 Analysis of the information extracted from the questionnaire

Thirty-four out of 45 (76 %) participants and 22 out of 39 (56 %) are accredited according to ISO/IEC 17025 [18] for analysis of total and iAs, respectively. Most of the laboratories (95 %) which filled in the questionnaire participate regularly in proficiency

testing rounds for this type of analysis (mostly referring to total As rather than to the iAs determination).

The experience in analysing iAs seems to make a difference: regarding performance 12 out of the 17 participants to which a no-satisfactory performance was attributed ($|z| > 2$) stated that they never carry out this speciation analysis or that they analyse only a few similar samples per year (0-50).

Participants evaluated their measurement uncertainty using one or several of the following approaches: applying the "Guide to the expression of uncertainty in measurement" (GUM [13], 10 laboratories); from their in-house method validation studies (26 laboratories); from interlaboratory comparison results (12 laboratories) and/or from precision data (13 laboratories). No correlation could be established between the different approaches and the performance in the analyses.

7. Compliance

The assigned value (X_{pt}) for inorganic arsenic (iAs) was compared to the maximum level (0.20 mg kg^{-1} wet weight for non-parboiled milled white rice) set by Regulation (EU) 2015/1006 [4]. No ML exists in European legislation for the total As mass fraction in food. Since the assigned value for iAs (0.092 mg kg^{-1} dry mass, 0.086 mg kg^{-1} wet mass if taking account of the moisture content of 6.4 % as stated by the CRM certificate) is below the respective ML the test item is considered as compliant by the PT organiser.

Summarising the answers provided by the 43 participants who reported their compliance assessment, 20 % (8 out of 41, two participants made their compliance assessment without giving a yes/no answer) stated, incorrectly, that the material was not compliant. Among them, 3 participants concluded that the material was not compliant, even though only the total As mass fraction was reported (L40, L43 and L44) while other three participants did not provide any reason for considering the test item as not compliant with the European legislation (L07, L43 and N47).

Table 4 summarises the reasons provided by the participants who considered the test item as no compliant. Highlighted participants (in green) have taken the correct compliance decision based on their reported values for iAs.

The remaining participants (33 out of 41, thus 80 %) reported a correct compliance decision.

Table 4 – *Compliance assessment: reasons for no compliance (as provided by each participant).*

Lab Code	X_{lab}	Compliance assessment
L18	0.24	ML is 0.20 mg kg^{-1} and the reporting result is 0.24 mg kg^{-1} (no uncertainty is taken into account since the method is not accredited)
L21	0.124	It does not exceed the ML set by this regulation for rice. I would reject it if it would be rice for production of infant food or similar.
L31	0.28	I would only accept the item in case of parboilded rice in view of the uncertainty of the measurement.
L40		Out of the ML : 0.20 mg kg^{-1}. [No result reported for iAs]*
L07	0.121	[No reason provided]*
L43		[No reason provided. No result reported for iAs]*
L44		[No result reported for iAs]*
N47	< 0.08	[No reason provided]*

* Observation from the PT provider.

8. Conclusion

The analytical capability of the participating laboratories for the determination of the mass fraction of total arsenic in rice was successfully demonstrated at the investigated mass fraction level, considering the overall satisfactory performance of the participating laboratories in IRMM-PT-43.

Considering the lower percentage of participating laboratories which delivered satisfactory results for inorganic arsenic, it is recommended to take actions for improving the analytical capability for its determination.

Analysis of iAs in rice can be carried out with non-sophisticated techniques but it requires a careful validation of the sample treatment. Dry ashing can be successfully used, as demonstrated by some participants, but inter-conversion of species can happen, resulting in an over evaluation of iAs. MLs for iAs in rice have entered into force since January 2016 and OCLs must be capable of a proper evaluation of this analyte in rice and rice derived products.

As a whole, participants reported realistic measurement uncertainty evaluations.

9. References

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10. Abbreviations

AAS	Atomic Absorption Spectroscopy
CRM	Certified Reference Material
ET-AAS	Electro Thermal Atomic Absorption Spectrometry
EC	European Commission
EU	European Union
GUM	Guide to the expression of Uncertainty in Measurement
HG-AAS	Hydride Generation Atomic Absorption Spectroscopy
HG-ET-AAS	Hydride Generation Electro thermal Atomic Absorption Spectroscopy
HG-ICP-OES	Hydride Generation Inductively Coupled Plasma Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
HPLC-ICP-MS	High Performance Liquid Chromatography coupled with ICP-MS
IC-ICP-MS	Ion chromatography coupled with ICP-MS
SF-ICP-MS	Sector Field Inductively Coupled Plasma Mass Spectrometry
ICP-MS (Q)	Quadrupole Inductively Coupled Plasma Mass Spectrometry
ILC	Interlaboratory Comparison
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardization
JRC	Joint Research Centre
LC-ICP-MS	Liquid Chromatography coupled with ICP-MS
LC-MS	Liquid Chromatography coupled with Mass Spectrometry
NRL	National Reference Laboratory
ML	Maximum level
OCL	Official Control Laboratory
PT	Proficiency Testing
Z-ET-AAS	Zeeman- Electro Thermal Atomic Absorption Spectrometry

Annex 1: JRC web announcement

https://ec.europa.eu/jrc/en/interlaboratory-comparison/irmm-pt-43?search&form-return

IRMM-PT-43: "Determination of the mass fractions of total (As) and inorganic arsenic (iAs) in rice"

The IRMM-PT-43 proficiency testing round (PT) focuses on the determination of the mass fractions of total and inorganic arsenic in rice. This PT supports the implementation of Regulation (EU) 2015/1006 amending Regulation (EC) 1881/2006 as regards maximum levels of inorganic arsenic in foodstuffs.

The main objective of this exercise is to assess the analytical capabilities of European official food control laboratories in the determination of total and iAs in rice.

Participation in IRMM-PT-43 is free of charge.

Please register using the following link:

https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparison=1501

Test materials and analytes

The test material to be analysed is rice. Each participant will receive one jar containing 6 g of the proficiency test item.
The measurands are the mass fractions of total As and iAs in rice.

General outline of the exercise

Participants are requested to perform two or three independent analyses using the method of their choice, and to report the mean of their measurement results, in dry mass and corrected for recovery, its associated expanded measurement uncertainty and the coverage factor *k*.
Detailed instructions will be sent together with the test item.

Schedule

Registration	Sample dispatch	Reporting of results	Report to participants
Deadline 28/02/2016	First half of March 2016	15th April 2016	July 2016

Annex 2: Invitation letter to participants

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
Standards for Food Bioscience Unit

Geel, 19 January 2016
JRC.D.5/PRO/FCR/acs/ARES

Sent by email

Subject: Proficiency testing round for the determination of the mass fractions of total (As) and inorganic arsenic (iAs) in rice – IRMM-PT-43

Dear National Reference Laboratory (NRL) representative,

The JRC-IRMM is currently organising a proficiency testing round (PT) for the **"Determination of the mass fractions of total and inorganic arsenic in rice"** (IRMM-PT-43). This PT supports the implementation of Regulation (EU) 2015/1006 amending Regulation 1881/2006 as regards maximum levels of inorganic arsenic in foodstuffs.

Many of you expressed an interest for such a PT during the recent EURL-HM workshop.

IRMM is an accredited (ISO 17043:2010) PT provider. Confidentiality of participants is guaranteed.

Participation in this PT is not mandatory for NRLs.

You may wish to inform official food control laboratories belonging to your national network about IRMM-PT-43.

Participation to this PT is free of charge.

In case you are interested register electronically for this PT using the following link:

https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparison=1501

Once you submitted your registration copy the confirmation page that will appear and send it to JRC-IRMM-IMEP@ec.europa.eu. This e-mail will be the confirmation of your participation.

The **deadline for registration is the 28th February 2016**. Samples will be sent to participants during the first half of March 2016. The deadline for submission of results is the **15th April 2016**.

Due to a limited amount of samples only 90 registrations will be accepted.

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

Yours sincerely,

Dr. Fernando Cordeiro
IRMM-PT-43 Coordinator
Cc: Franz Ulberth (Head of Unit SFB)

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

E-mail: JRC-IRMM-IMEP@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

Annex 3: Sample accompanying letter

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
Standards for Food Bioscience Unit

Geel, 07 March 2016
JRC.D5/FCR/acs/Ares(2016)1148106

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

Participation in a proficiency testing round for the determination of the mass fractions of total arsenic (As) and inorganic arsenic (iAs) in rice – IRMM-PT-43.

Dear «Title» «Surname»

Thank you for participating in the proficiency testing round (PT) IRMM-PT-43 for the determination of the mass fractions of total As and iAs in rice. This PT supports the implementation of Regulation (EU) 2015/1006 amending Regulation 1881/2006 as regards maximum levels of inorganic arsenic in foodstuffs.

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

This parcel contains:
a) One bottle containing approximately 6 g of the proficiency test item
b) A "Confirmation of Receipt" form
c) This accompanying letter.

Please check whether the bottle containing the test item remained undamaged during transport. Then, 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°C until analysis.

The measurands are the mass fractions of total As and iAs in rice.

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

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

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 687, Fax: +32-(0)14-571 865.

E-mail: JRC-IRMM-IMEP@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

- the **mean** of your two or three measurement results (mg kg^{-1}) and its associated expanded **uncertainty** (mg kg^{-1}),
- the **coverage factor**
- the **technique** used to carry out the analysis.

To calculate the moisture 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 120 ± 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.

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: **«Part_key»**. 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.

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 **15/04/2016**.

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 further questions, please contact me by e-mail: JRC-IRMM-IMEP@ec.europa.eu

With kind regards,

Fernando Cordeiro (Ph.D.)
IRMM-PT-43 Coordinator

Cc: F. Ulberth (Head of Unit)

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 687, Fax: +32-(0)14-571 865.

E-mail: JRC-IRMM-IMEP@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

Annex 4: Confirmation of receipt form

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
Standards for Food Bioscience Unit

JRC.D5/FCR/acs/Ares(2016)1148106

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

IRMM-PT-43

Determination of the inorganic arsenic (iAs) mass fraction in rice

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 (Ph.D.)

IRMM-PT-43 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

Fax : +32-14-571865
JRC-IRMM-IMEP@ec.europa.eu

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 687, Fax: +32-(0)14-571 865.

E-mail: JRC-IRMM-IMEP@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

Annex 5: Questionnaire

Milc questionnaire

Comparison for IRMM-PT-43

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

Submission Form

1. Would you accept the present test item in the European market taking into account your reported value for iAs and its maximum level (ML) set by Regulation (EU) 2015/1006?

- a) Yes
- b) No

1.1. Why?

2. To which of the three following populations do you belong?

- a) National Reference Laboratory (NRL)
- b) Official Control Laboratory (OCL)
- c) Other

3. Which digestion technique, digestion mixture, temperature and time have you used?

See table Question 3 at bottom

4. Have you followed a standardised method for the analysis of total As?

- a) Yes
- b) No

4.1. If "Yes" which one?

5. Have you followed a standardised method for the analysis of iAs?

- a) Yes
- b) No

5.1. If "Yes" which one?

6. Which approach have you followed for calibration?

- a) External calibration (no matrix matched)
- b) External calibration (matrix matched)
- c) Standard addition
- d) Bracketing
- e) Other

7. Did you correct your results for recovery?

- a) Yes
- b) No

7.1. If "No" why not?

8. Provide the estimated recovery (%) and method used for your estimation

See table Question 8 at bottom

9. Did you use a CRM for instrument calibration? Which one?

10. Did you correct your results for the moisture content?

- a) Yes
- b) No

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

10.2. If "No" why?

11. Please provide the LOD of your method (in mg/kg)

See table **Question 11** at bottom

12. Additional remarks/comments regarding the method of analysis?

13. Do you carry out this type of analysis regularly? (samples/year)

See table **Question 13** at bottom

14. How did you evaluate your measurement uncertainty?

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

14.1. Which level of confidence (%) is reflected by the coverage factor assigned to your expanded uncertainty?

15. Do you provide uncertainty statements to customers for this type of analysis?

- a) Yes
- b) No

16. Does your laboratory have a quality system?

- a) Yes
- b) No

16.1. If "Yes" specify:

- a) ISO 17025:2005
- b) ISO 9000 series
- c) Other

16.1.1. If "Other" please specify:

17. Are you accredited for the analysis of total As and/or to iAs in rice?

See table **Question 17** at bottom

18. Does your laboratory participate in PTs for this type of analysis?

- ○ a) Yes
- ○ b) No

18.1. In which ones?

19. Do you have any comments? Let us know!

Question 11

Questions/Response table	*LOD*
Total As	
iAs	

Question 13

Questions/Response table	*1- Never*	*2- 0-50*	*3- 50-250*	*4- 250-1000*	*5- >1000*
Total As					
iAs					

Question 17

Questions/Response table	*Yes*	*No*
Total As in rice		
iAs in rice		

Question 3

For the digestion technique use: 1 for Microwave (open), 2 for Microwave (closed), 3 for Open wet, 4 for Dry ashing, 5 for Pressure bomb, 6 for Other (if "Other" please specify). For the digestion mixture use: 1 for H2O2, 2 for HCl, 3 for HNO3, 4 for HClO4, 5 for HF, 6 for other (if "other" indicate which one). For digestion mixture multiple answers are possible, e.g. 1+3). Please give the concentration used for each component of the digestion mixture, e.g. 3 65%.

Questions/Response table	*Digestion technique*	*Digestion mixture*	*Temperature (celcius)*	*Time (minutes)*
Total As				
iAs				

Question 8

Please indicate which CRM was used.

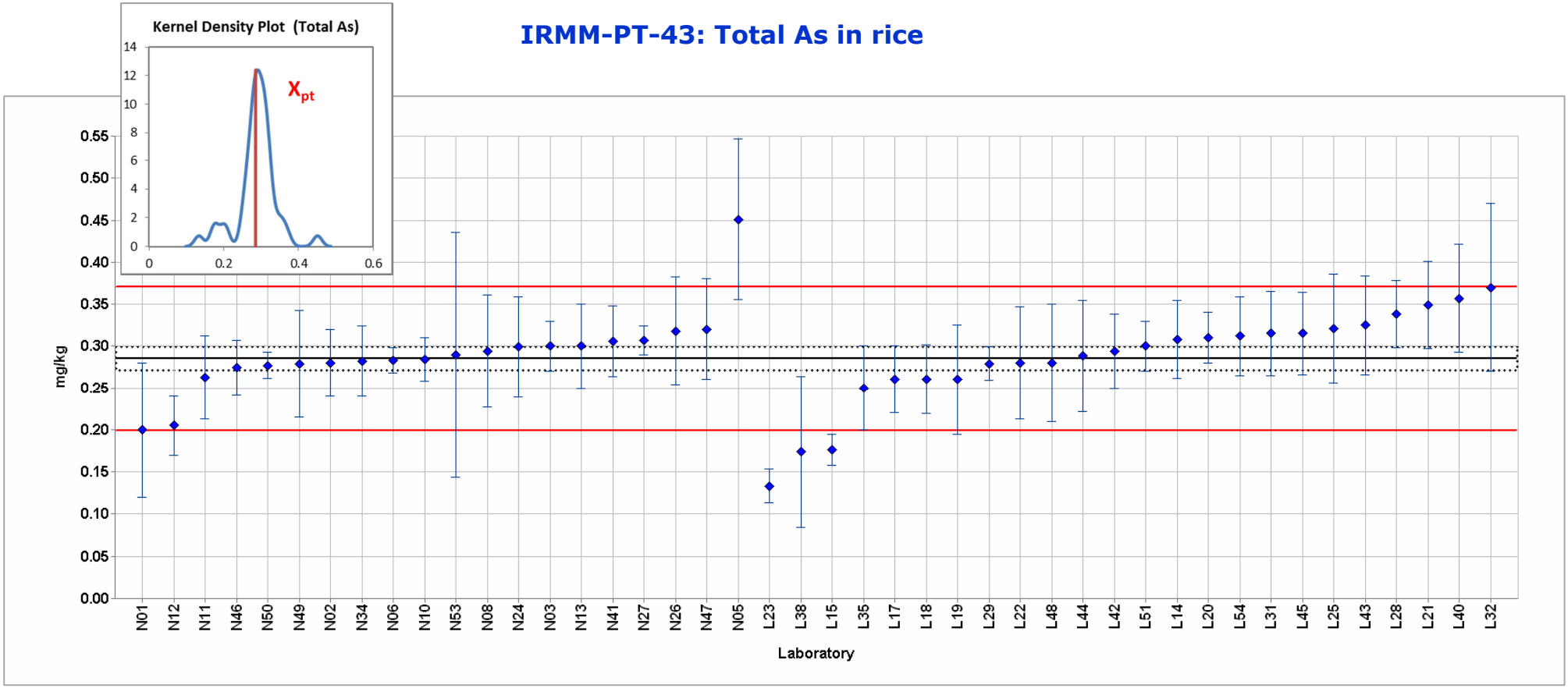
Questions/Response table	*1 - Recovery (%)*	*2 - Spiking*	*3 - Using a CRM*
Total As			
iAs			

Annex 6: Results for total arsenic (As)

Assigned values: X_{pt} = 0.285; U_{pt} = 0.014; σ_{pt} = 0.043 (all values in mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k [a]	Technique	u_{lab}	z-score [b]	ζ-score [b]	Unc [c]
L07	0.293	0.044	2	SF-ICP-MS	0.022	0.19	0.35	a
L14	0.308	0.046	2	ICP-MS	0.023	0.53	0.96	a
L15	0.176	0.018	√3	HG-AAS	0.010	-2.53	-8.70	a
L17	0.26	0.04	2	HG-AAS	0.020	-0.58	-1.18	a
L18	0.26	0.041	2	ET-AAS	0.021	-0.58	-1.15	a
L19	0.26	0.065	2	HG-AAS	0.033	-0.58	-0.75	a
L20	0.31	0.03	√3	ICP-MS	0.017	0.58	1.34	a
L21	0.349	0.052	2	HG-AAS	0.026	1.49	2.38	a
L22	0.28	0.067	2	HG-AAS	0.034	-0.12	-0.15	a
L23	0.133	0.02	1.01	HG-AAS	0.020	-3.53	-7.24	a
L25	0.321	0.065	2	ICP-MS (Q)	0.033	0.84	1.08	a
L28	0.338	0.04	√3	ET-AAS	0.023	1.23	2.20	a
L29	0.279	0.02	2	ICP-MS	0.010	-0.14	-0.49	a
L31	0.315	0.05	2	ICP-MS	0.025	0.70	1.16	a
L32	0.37	0.1	2	HG-AAS	0.050	1.98	1.68	c
L35	0.25	0.05	2	HG-AAS	0.025	-0.81	-1.35	a
L38	0.174	0.09	2	ET-AAS	0.045	-2.58	-2.44	c
L40	0.357	0.064	2	ICP-MS	0.032	1.67	2.20	a
L42	0.294	0.044	2	ICP-MS	0.022	0.21	0.39	a
L43	0.325	0.059	3	LC-MS (Q)	0.020	0.93	1.92	a
L44	0.288	0.066	2	HG-AAS	0.033	0.07	0.09	a
L45	0.315	0.049	2	ICP-MS	0.025	0.70	1.18	a
L48	0.28	0.07	2	HG-AAS	0.035	-0.12	-0.14	a
L51	0.3	0.03	2	ICP-MS	0.015	0.35	0.91	a
L54	0.312	0.047	2	HG-AAS	0.024	0.63	1.10	a
N01	0.2	0.08	2	ICP-MS	0.040	-1.98	-2.09	a
N02	0.28	0.04	2	SF-ICP-MS	0.020	-0.12	-0.24	a
N03	0.3	0.03	2	HG-AAS	0.015	0.35	0.91	a
N05	0.451	0.096	2	ICP-MS	0.048	3.86	3.42	c
N06	0.283	0.015	2	HG-ET-AAS	0.008	-0.05	-0.19	a
N08	0.294	0.067	2	ICP-MS	0.034	0.21	0.26	a
N10	0.284	0.026	2	ICP-MS	0.013	-0.02	-0.07	a
N11	0.2622	0.0498	2	SF-ICP-MS	0.025	-0.53	-0.88	a
N12	0.205	0.035	2	ET-AAS	0.018	-1.86	-4.24	a
N13	0.3	0.05	2	Z-ET-AAS	0.025	0.35	0.58	a
N24	0.299	0.06	2	ICP-MS	0.030	0.33	0.45	a
N26	0.318	0.064	2	ICP-MS	0.032	0.77	1.01	a
N27	0.307	0.0172	2	ICP-MS	0.009	0.51	1.98	a
N34	0.282	0.042	2	ICP-MS	0.021	-0.07	-0.14	a
N41	0.306	0.042	2	ICP-MS (Q)	0.021	0.49	0.95	a
N46	0.274	0.033	2	ICP-MS	0.017	-0.26	-0.61	a
N47	0.32	0.06	2	ET-AAS	0.030	0.81	1.14	a
N49	0.279	0.064	2	ICP-MS	0.032	-0.14	-0.18	a
N50	0.277	0.016	2	ICP-MS	0.008	-0.19	-0.75	a
N53	0.29	0.146	2	HG-AAS	0.073	0.12	0.07	c

[a] √3 is set when no coverage factor is reported, [b] performance: satisfactory, questionable, unsatisfactory, [c] a: $u_{pt} \leq u_{lab} \leq \sigma_{pt}$; b: $u_{lab} < u_{pt}$; and c: $u_{lab} > \sigma_{pt}$



Measurement results and associated expanded measurement uncertainties.

Assigned value (X_{pt}): black line; Assigned range ($X_{pt} \pm U_{pt}$): dashed line; Acceptance range ($X_{pt} \pm 2\sigma_{pt}$): red lines.

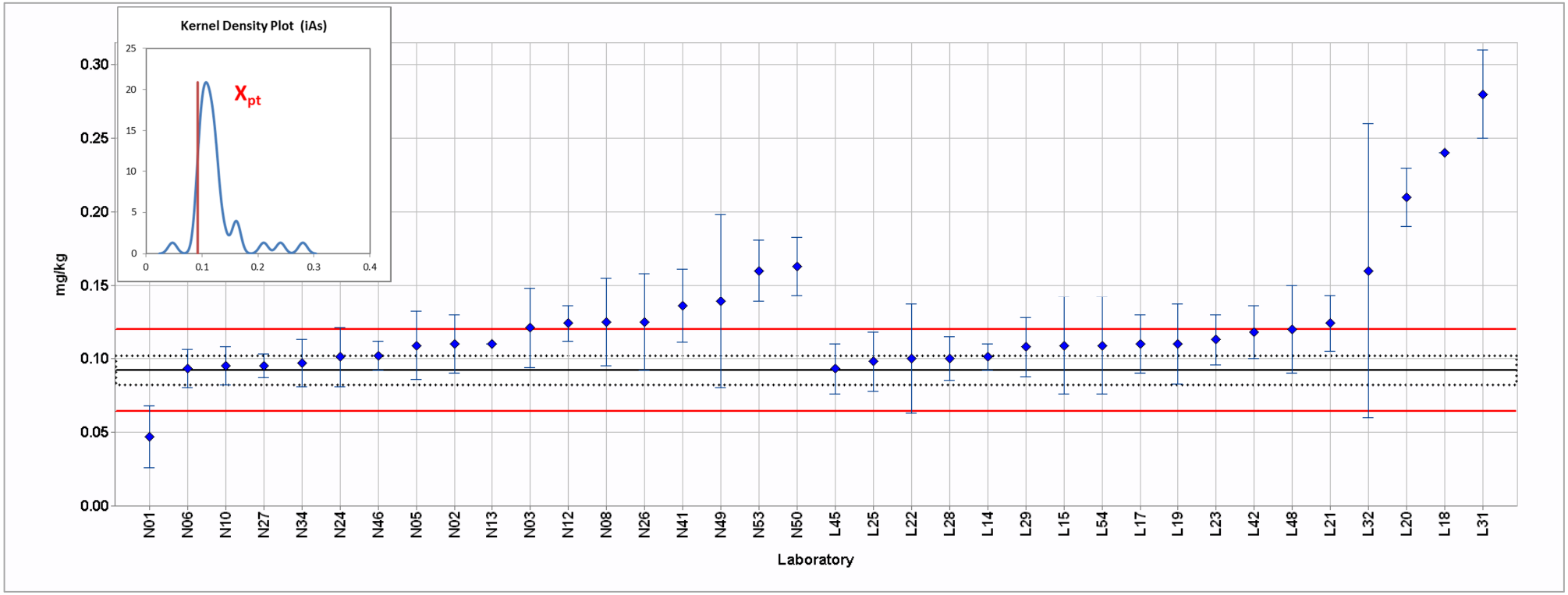
Annex 7: Results for inorganic arsenic (iAs)

Assigned values: X_{pt} = 0.092; U_{pt} = 0.010; σ_{pt} = 0.014 (all values in mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k [a]	Technique	u_{lab}	z-score [b]	ζ-score [b]	Unc. [c]
L07	0.121	0.024	2	HPLC-ICP-MS	0.012	2.10	2.23	a
L14	0.101	0.009	2	HPLC-ICP-MS	0.005	0.65	1.34	b
L15	0.109	0.033	√3	HG-AAS	0.019	1.23	0.86	c
L17	0.11	0.02	2	HG-AAS	0.010	1.30	1.61	a
L18	0.24		√3	ET-AAS	0	10.72	29.60	b
L19	0.11	0.027	2	HG-AAS	0.014	1.30	1.25	a
L20	0.21	0.02	√3	HG-AAS	0.012	8.55	9.38	a
L21	0.124	0.019	2	HG-AAS	0.010	2.32	2.98	a
L22	0.1	0.037	2	HG-AAS	0.019	0.58	0.42	c
L23	0.113	0.017	0.95	HG-AAS	0.018	1.52	1.13	c
L25	0.098	0.02	2	IC-ICP-MS	0.010	0.43	0.54	a
L28	0.1	0.015	√3	HG-AAS	0.009	0.58	0.80	a
L29	0.108	0.02	2	HG-ICP-OES	0.010	1.16	1.43	a
L31	0.28	0.03	2	HPLC-ICP-MS	0.015	13.62	11.89	c
L32	0.16	0.1	2	HG-AAS	0.050	4.93	1.35	c
L42	0.118	0.018	2	HPLC-ICP-MS	0.009	1.88	2.53	a
L45	0.093	0.017	2	HPLC-ICP-MS	0.009	0.07	0.10	a
L48	0.12	0.03	2	HG-AAS	0.015	2.03	1.77	c
L54	0.109	0.033	2	HG-AAS	0.017	1.23	0.99	c
N01	0.047	0.021	2	HPLC-ICP-MS	0.011	-3.26	-3.87	a
N02	0.11	0.02	2	SF-ICP-MS	0.010	1.30	1.61	a
N03	0.121	0.027	2	HG-AAS	0.014	2.10	2.01	a
N04	0.12	0.04	2	HG-AAS	0.020	2.03	1.36	c
N05	0.109	0.023	2	HPLC-ICP-MS	0.012	1.23	1.36	a
N06	0.093	0.013	2	HG-ET-AAS	0.007	0.07	0.12	a
N08	0.125	0.03	2	IC-ICP-MS	0.015	2.39	2.09	c
N10	0.095	0.013	2	HPLC-ICP-MS	0.007	0.22	0.37	a
N12	0.124	0.012	2	HG-AAS	0.006	2.32	4.10	a
N13	0.11		√3	HPLC-ICP-MS	0	1.30	3.60	b
N24	0.101	0.02	2	HPLC-ICP-MS	0.010	0.65	0.80	a
N26	0.125	0.033	2	HPLC-ICP-MS	0.017	2.39	1.91	c
N27	0.095	0.008	2	HPLC-ICP-MS	0.004	0.22	0.47	b
N34	0.097	0.016	2	IC-ICP-MS	0.008	0.36	0.53	a
N41	0.136	0.025	2	HPLC-ICP-MS	0.013	3.19	3.27	a
N46	0.102	0.01	2	HPLC-ICP-MS	0.005	0.72	1.41	a
N47	< 0.08			HPLC-ICP-MS				
N49	0.139	0.059	2	HG-AAS	0.030	3.41	1.57	c
N50	0.163	0.02	2	HG-AAS	0.010	5.14	6.35	a
N53	0.16	0.021	2	HG-AAS	0.011	4.93	5.85	a

[a] √3 is set when no coverage factor is reported, [b] performance: satisfactory, questionable, unsatisfactory, [c] a: $u_{pt} \leq u_{lab} \leq \sigma_{pt}$; b: $u_{lab} < u_{pt}$; and c: $u_{lab} > \sigma_{pt}$

IRMM-PT-43: iAs in rice



Measurement results and associated expanded measurement uncertainties.

Assigned value (X_{pt}): black line; Assigned range ($X_{pt} \pm U_{pt}$): dashed line; Acceptance range ($X_{pt} \pm 2\sigma_{pt}$): red lines.

Annex 8: Experimental details and scoring for total As (expressed as z scores)

Lab Code	samples / year	Accredited	LOD (mg/kg)	Standard method		Approached followed for calibration	Correct for recovery?	CRM for instrument calibration?	Correct for moisture?	Sample digestion Tech[a]	Mixture	Temp[b]	Time[c]	Technique
L07	> 1000	Yes	0.02	Yes	DIN EN 15763:2010-04	External calibration (matrix matched)	No	No	Yes	MW (C)	HNO_3	220	60	SF-ICP-MS
L14	> 1000	Yes	0.005	No		External calibration (no matrix matched)	No		Yes	MW (C)	$HNO_3+H_2O_2$	200	20	ICP-MS
L15	250-1k	Yes	0.027	Yes	64 LFGB L 00.00-19	External calibration (no matrix matched)	No		Yes	MW (C)	$HNO_3+H_2O_2$	240	30	HG-AAS
L17	50-250	Yes	0.048	No		External calibration (no matrix matched)	No	No	Yes	DA	HNO_3	400	480	HG-AAS
L18	Never	No	0.011	No		External calibration (no matrix matched)	No	No	Yes	PB	$HNO_3+H_2O_2$	180	20	ET-AAS
L19	50-250	Yes	0.005	Yes	HG-AAS	External calibration (no matrix matched)	Yes	Yes	Yes	DA	HNO_3	400	720	HG-AAS
L20	250-1k	Yes	0.002	No		External calibration (no matrix matched)	No	Yes.	Yes	MW	$HNO_3+H_2O_2$	180	20	ICP-MS
L21	0-50	Yes	0.004	No		External calibration (no matrix matched)	No	Yes	Yes	OW+DA	HNO_3	440	720	HG-AAS
L22	50-250	Yes	0.004	Yes	ISBN 83-89379-26-0	Standard addition	Yes	Yes	Yes	DA	HNO_3+MgNO_3+MgO	400	480	HG-AAS
L23	50-250	Yes	0.05	Yes	ASU§64 L00.00-19/6	External calibration (no matrix matched)	No	No	Yes	MW (C)	HNO_3	200	20	HG-AAS
L25	> 1000	Yes	0.05	Yes	DIN ISO 17294	External calibration (no matrix matched)	No		Yes	MW (C)	$HNO_3+H_2O_2$	260	60	ICP-MS (Q)
L28			0.04	Yes		Standard calibration	No							ET-AAS
L29	50-250	Yes	0.04	Yes	DIN EN ISO 17294	External calibration (no matrix matched)	No	Yes	Yes	MW	$HCl+HNO_3$	200	30	ICP-MS
L31	250-1k	Yes	0.0024	No		External calibration (no matrix matched)	Yes	No	Yes	PB	$HNO_3+H_2O_2$	320	180	ICP-MS
L32	50-250	Yes	0.025	No		External calibration (no matrix matched)	Yes	No	Yes	DA		500	240	HG-AAS
L35	50-250	Yes	0.005	Yes		External calibration (no matrix matched)	Yes	Yes	Yes	DA	HNO_3	400	840	HG-AAS
L38	0-50	No	0.04	No		External calibration (no matrix matched)	No		Yes	MW (C)	HNO_3	230	55	ET-AAS
L40		No	0.002	No		External calibration (no matrix matched)	No		No	PB	HNO_3	95	200	ICP-MS
L42	0-50	Yes	0.033	Yes	EN 13805, EN 15763	External calibration	No	Yes	No	MW (C)	$HNO_3+H_2O_2$	240	30	ICP-MS
L43	Never	No	0.01	Yes	ANSES M. ALFORT	External calibration (no matrix matched)	No		Yes	MW (C)				LC-MS (Q)
L44	0-50	No	0.015	Yes	ANSES CIME04(v.7)	External calibration (no matrix matched)	No	No	No	DA		700	360	HG-AAS
L45	50-250	Yes	0.003	No		External calibration (no matrix matched)	No	No	Yes	MW (C)	HNO_3	190	38	ICP-MS
L48	50-250	Yes	0.005	No	PN-EN 14546:2005	Other	Yes	Yes	Yes	DA	HCl	394	480	HG-AAS

Lab Code	samples / year	Accredited	LOD (mg/kg)	Standard method		Approached followed for calibration	Correct for recovery?	CRM for instrument calibration?	Correct for moisture?	Sample digestion Tech[a]	Mixture	Temp[b]	Time[c]	Technique
L51	0-50	Yes	0.05	Yes	OENORM ISO 17294-2	External calibration (no matrix matched)	No	Yes	Yes	UV apparatus	$HNO_3+H_2O_2$			ICP-MS
L54	250-1k	Yes	0.02	Yes	ASU §64 LFGB L 00.00 19/1 + L 00.00 19/6	External calibration (no matrix matched)	No	Yes	Yes	HP ashing	$HCl+HNO_3$	320	190	HG-AAS
N01	250-1k	No	0.1	No		External calibration (matrix matched)	No		Yes	MW (C)	HNO_3			ICP-MS
N02	0-50	No	0.020	Yes	SIST EN 15763	External calibration (no matrix matched)	No	Yes	Yes	MW (C)	$HNO_3+H_2O_2$	200	10+10	SF-ICP-MS
N03	0-50	Yes	0.025	Yes	EN 14546:2005	External calibration (no matrix matched)	Yes	Yes	Yes	DA	HNO_3			HG-AAS
N05	50-250	Yes	0.0006	No		External calibration (no matrix matched)	No	No	Yes	MW (C)	HNO_3	180	30	ICP-MS
N06	0-50	No	0.01	No		External calibration (no matrix matched)	Yes		Yes	MW (C)	$HNO_3+H_2O_2$	200	30	HG-ET-AAS
N08	50-250	Yes	0.002	No		External calibration (no matrix matched)	No	No	Yes	MW (C)	HNO_3	200	20	ICP-MS
N10	50-250	Yes	0.0003	No		External calibration (no matrix matched)	No	No	Yes	MW (C)	$HNO_3+H_2O_2$	150/180	20/10	ICP-MS
N11	0-50	Yes	0.0023	Yes	STN EN 15763	External calibration (no matrix matched)	Yes	No	Yes	MW (O)	$HNO_3+H_2O_2$	190	45	SF-ICP-MS
N12	0-50	No	0.030	Yes	ET-AAS	External calibration (no matrix matched)	No	Yes	Yes	MW (C)	HNO_3	200	25	ET-AAS
N13	250-1k	Yes	0.001	Yes	ISTISAN 1996/34	Other	Yes	Yes	Yes	MW (C)	$HNO_3+H_2O_2+HF$	200	28	Z-ET-AAS
N24	250-1k	Yes	0.01	Yes	EN 15763	External calibration (matrix matched)	No	No	Yes	MW (C)	HNO_3	230	20	ICP-MS
N26	50-250	Yes	0.01	Yes	EN 15763:2009	External calibration (no matrix matched)	No	No	Yes	MW (C)	$HCl+HNO_3$	190	30	ICP-MS
N27	250-1k	Yes	0.005	Yes	EN 15763 modified	External calibration (no matrix matched)	Yes	No	Yes	MW (C)	HNO_3	200	15	ICP-MS
N34	50-250	Yes	0.006	No	EN 15763	External calibration (no matrix matched)	Yes	Yes	Yes	MW (O)	HNO_3	190	10	ICP-MS
N41	0-50	Yes	0.002	No		External calibration (no matrix matched)	No	Yes	Yes	MW (C)	HNO_3	180	20	ICP-MS (Q)
N46	0-50	Yes	0.005	Yes	EN15763:2009	External calibration (matrix matched)	No	No	Yes	MW (C)	HNO_3	180	30	ICP-MS
N47	250-1k	Yes	0.05	Yes	in house validated	Standard addition	No	No	Yes	MW (C)	HNO_3	210	30	ET-AAS
N49	0-50	Yes	0.05	No	LST EN 15763:2010	External calibration (matrix matched)	No		Yes	MW (C)	$HNO_3+H_2O_2$	200	60	ICP-MS
N50	0-50	Yes	0.010	Yes	EN-15763:2009	External calibration (no matrix matched)	No		Yes	MW (C)	$HNO_3+H_2O_2$	180	30	ICP-MS
N53	0-50	No	0.045	Yes	EN 14546:2005	External calibration (no matrix matched)	No	No	Yes	DA	HNO_3	425	1020	HG-AAS

[a] MW (C) microwave closed vessel, MW (O) microwave open vessel, OV open vessel, DA Dry ashing, OW open wet, PB pressure bomb, HP high pressure, [b] Temperature in °C, [c] Time in minutes.

Annex 9: Experimental details and scoring for iAs (expressed as z scores)

Lab Code	samples / year	Accredited	LOD (mg/kg)	Standard method		Approached followed for calibration	Correct for recovery?	CRM for instrument calibration?	Correct for moisture?	Sample digestion				Technique
										Tech[a]	Mixture	Temp[b]	Time[c]	
L07	50-250	Yes	0.01	No		External calibration (matrix matched)	No	No	Yes	OV	$HNO_3+H_2O_2$	95	90	HPLC-ICP-MS
L14	250-1k	Yes	0.002	No		External calibration (no matrix matched)	No		Yes	MW (C)	$HNO_3+H_2O_2$	95	60	HPLC-ICP-MS
L15	50-250	Yes	0.053	Yes	64 LFGB, L 15.06-2	External calibration (no matrix matched)	No		Yes					HG-AAS
L17	0-50	Yes	0.017	No		External calibration (no matrix matched)	No	No	Yes	DA	HNO_3	400	180	HG-AAS
L18	Never	No		No			No	No	Yes	PB	H_2O_2+HCl	90	20	ET-AAS
L19	0-50	Yes	0.035	Yes	HG-AAS	External calibration (no matrix matched)	Yes	Yes	Yes	DA	HNO_3	400	720	HG-AAS
L20	0-50	Yes	0.02	No		External calibration (no matrix matched)	No	Yes	Yes		HCl	37	120	HG-AAS
L21	0-50	No	0.008	No		External calibration (no matrix matched)	No	Yes	Yes	OW+DA	HNO_3	440	720	HG-AAS
L22	0-50	No	0.008	No		Standard addition	Yes	Yes	Yes	DA	HNO_3+ $MgNO_3$	400	180	HG-AAS
L23	50-250	Yes	0.05	Yes	ASU §64 L 15.06-2	External calibration (no matrix matched)	No	No	Yes	Extraction	HNO_3	95	120	HG-AAS
L25	0-50		0.01	No		External calibration (no matrix matched)	No		Yes	MW(C)	HNO_3+CH_3COOH	95	90	IC-ICP-MS
L28			0.02	Yes		Standard calibration	No							HG-AAS
L29	0-50	Yes	0.03	Yes	§64 LFGB 15.06.-2	External calibration (no matrix matched)	No	Yes	Yes	Extraction	HNO_3	95	90	HG-ICP-OES
L31	0-50	No	0.003	No		External calibration (no matrix matched)	Yes	No	Yes	PB	$H_2O_2+CH_3COOH$	120	100	HPLC-ICP-MS
L32	50-250	Yes	0.06	No		External calibration (no matrix matched)	Yes	No	Yes	DA		500	240	HG-AAS
L42	Never	No	0.05	Yes	EN 16802, XPT90-140	External calibration	No	Yes	No	MW (C)	$HNO_3+H_2O_2$	90	60	HPLC-ICP-MS
L45	50-250	Yes	0.003	No		External calibration (no matrix matched)	No	No	Yes	MW (C)	$HNO_3+H_2O_2$	95	30	HPLC-ICP-MS
L48	0-50	Yes	0.011	No		Other	Yes	Yes	Yes	DA	HCl	394	240	HG-AAS
L54	0-50	Yes	0.03	Yes	64 LFGB L15.06 2	External calibration (no matrix matched)	No	Yes	Yes	Extraction	HNO_3	95	90	HG-AAS

Lab Code	samples / year	Accredited	LOD (mg/kg)	Standard method		Approached followed for calibration	Correct for recovery?	CRM for instrument calibration?	Correct for moisture?	Sample digestion Tech[a]	Mixture	Temp[b]	Time[c]	Technique
N01	50-250	No	0.1	No		External calibration (matrix matched)	No		Yes	MW (C)	H_2O	90	10	HPLC-ICP-MS
N02	0-50	No	0.050	Yes	SIST EN ISO 16278	External calibration (no matrix matched)	No	Yes	Yes	MW (C)	H_2O_2+HCl	90	25	SF-ICP-MS
N03	0-50	Yes	0.040	No		External calibration (no matrix matched)	Yes	Yes	Yes	DA	HNO_3			HG-AAS
N04	0-50	No	0.002	Yes	CEN/TS16731:2014	External calibration (no matrix matched)	Yes	Yes	Yes	MW (C)	HNO_3	95	90	HG-AAS
N05	0-50	Yes	0.0012	No		External calibration (no matrix matched)	No	No	Yes	MW (C)	HNO_3+H_2O_2	90	20	HPLC-ICP-MS
N06	50-250	Yes	0.01	Yes	SOP (IMEP-41)	External calibration (no matrix matched)	Yes		Yes	DA	HCl	425		HG-ET-AAS
N08	0-50	Yes	0.01	No		External calibration (no matrix matched)	No	No	Yes	MW (C)	HNO_3+H_2O_2	95	50	IC-ICP-MS
N10	50-250	Yes	0.006	No		External calibration (no matrix matched)	No	No	Yes	MW	H_2O_2+HCl	90	25	HPLC-ICP-MS
N12	0-50	No	0.008	Yes	HG-AAS	External calibration (no matrix matched)	No	Yes	Yes	DA	HCl + HNO_3	425	720	HG-AAS
N13		No		No		Other	Yes	Yes	Yes	MW (C)	HNO_3+H_2O_2	95	50	HPLC-ICP-MS
N24	50-250	No	0.01	Yes	EN 16802	External calibration (matrix matched)	No	No	Yes	OW	HNO_3+H_2O_2	90	90	HPLC-ICP-MS
N26	50-250	Yes	0.002	Yes	EN 16802: 2016	External calibration (no matrix matched)	No	No	Yes	OW	HNO_3+H_2O_2	90	60	HPLC-ICP-MS
N27	50-250	Yes	0.03	Yes	FprEN 16802	External calibration (no matrix matched)	Yes	No	Yes	Waterbath	HNO_3+H_2O_2	90	60	HPLC-ICP-MS
N34	0-50	No	0.01	Yes		External calibration (no matrix matched)	Yes	Yes	Yes	MW (C)	H_2O_2+HCl	90	25	IC-ICP-MS
N41	0-50	Yes	0.011	No		External calibration (no matrix matched)	No	Yes	Yes	MW (C)	H_2O	80	15	HPLC-ICP-MS
N46	50-250	No	0.003	Yes	EN16802: 2016	External calibration (matrix matched)	No	No	Yes	Waterbath		90	60	HPLC-ICP-MS
N49	Never	No		No		External calibration (matrix matched)	No		Yes	MW (C)	H_2O_2+HCl	90	25	HG-AAS
N50	0-50	Yes	0.05	Yes	EN 16278: 2012	External calibration (no matrix matched)	No		Yes	MW (C)	H_2O_2+HCl	90	30	HG-AAS
N53	0-50	No	0.028	No		External calibration (no matrix matched)	No	No	Yes	DA	HCl+$CHCl_3$	425	1020	HG-AAS

[a] MW (C) microwave closed vessel, MW (O) microwave open vessel, OV open vessel, DA Dry ashing, OW open wet, PB pressure bomb, HP high pressure, [b] Temperature in °C, [c] Time in minutes.

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