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Report of the key comparison CCQM-K108

Determination of arsenic species, total arsenic and cadmium in brown rice flour

(Final Report)

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Coordinated by NMIJ

November 2014

Abstract

The CCQM-K108 key comparison was organised by the Inorganic Analysis Working Group (IAWG) of CCQM to test the abilities of the national metrology institutes (NMIs) or the designated institutes (DIs) to measure the mass fractions of arsenic species, total arsenic and cadmium in brown rice flour. The National Metrology Institute of Japan (NMIJ) acted as the coordinating laboratory. The participants used different measurement methods, though most of them used inductively coupled plasma mass spectrometry (ICP-MS) or isotope-dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) for Cd and ICP-MS for total arsenic. Regarding arsenic speciation, all participants used ICP-MS coupled with liquid chromatography (LC). Accounting for relative expanded uncertainty, comparability of measurement results for each of total arsenic and cadmium was successfully demonstrated by the participating NMIs or DIs for the measurement of the measurand at the level of less than 0.5 mg/kg. Regarding arsenic species (inorganic arsenic and dimethylarsinic acid (DMAA)), there is, however, a remaining problem to be solved.

It is expected that arsenic, cadmium and other metals at mass fractions greater than approximately 0.1 mg/kg in rice flour can be determined by each participant using the same technique(s) employed for this key comparison to achieve similar uncertainties mentioned in the present report. Furthermore, the results of this key comparison can be utilised along with the IAWG core capability approach.

1 Introduction

Rice is rich in carbonhydrate, protein and minerals such as Fe, Cu, Zn, and is a staple food, especially in Asia. Since some arsenic compounds are considered toxic, maximum levels for As in rice are often discussed. For such discussion and a related document standard, establishing analytical methods for arsenic species is one of the key issues. NMIJ proposed the present key comparison at the IAWG meeting held April 16-17, 2012. At the CCQM meeting following the IAWG meeting, the proposal was agreed as CCQM-K108 and NMIJ was designated as the coordinating laboratory. In parallel with the key comparison CCQM-K108, pilot studies designated CCQM-P147 and APMP.QM-P21 were conducted, in which the same sample measured by the CCQM-K108 participants was also used.

The analytes in this key comparison were arsenic species, total arsenic and cadmium in brown rice flour at mass-fractions of less than 0.5 mg/kg. Each participant could use any suitable method(s) of measurement. Four measurements of each analyte had to be carried out by each participant. The homogeneity of the material used in this comparison had been investigated prior to the comparison. The comparison results were discussed at the IAWG meetings held November 5-6, 2013 and April 7-8, 2014.

Accounting for relative expanded uncertainty, comparability of measurement results for each of total arsenic and cadmium was successfully demonstrated by the participating NMIs or DIs for the measurement of the measurand at the level of less than 0.5 mg/kg. On the other hand, measurement results for each of arsenic species (inorganic arsenic and DMAA) were not in good agreement with each other; inorganic arsenic (sometimes expressed as inorgAs) means arsenite (As(III)) plus arsenate (As(V)) . Possible reasons for the inconsistency among the measurement results of the arsenic species were discussed at the IAWG meetings held November 5-6, 2013. Several points including the relation between the sum of inorganic arsenic plus DMAA and the total amount of arsenic, and possible reduction of original As(V) during treatments were raised in the meeting. After the meeting, an additional experiment among the participants in the comparison of the arsenic species was planned in order to solve the problem. Though progress

with useful information from such an experiment was provided, the problem was not completely solved. Finally the IAWG chair suggested a subsequent key comparison following CCQM-K108 (maybe CCQM-K108.1) using another brown rice flour sample.

2 List of Participants

Table 1 contains the full names of all participating NMIs and DIs.

Table 1 List of participating NMIs and DIs

No.	Participant	Country/Economy
1	**BIM** Bulgarian Institute of Metrology	Bulgaria
2	**EXHM** General State Chemical Laboratory/Hellenic Metrology Institute	Greece
3	**GLHK** Government Laboratory, Hong Kong	Hong Kong
4	**HSA** Health Sciences Authority	Singapore
5	**INDECOPI** Peru's National Institute for the Defense of Competition and the Protection of Intellectual Property	Peru
6	**INMETRO** National Institute of Metrology, Quality and Technology	Brazil
7	**INRIM** National Institute of Metrological Research	Italy
8	**INTI** National Institute of Industrial Technology	Argentina
9	**JSI** Jozef Stefan Institute	Slovenia
10	**KEBS** Kenya Bureau of Standards	Kenya
11	**NIM** National Institute of Metrology P. R. China	P. R. China
12	**NIMT** National Institute of Metrology (Thailand)	Thailand
13	**NIST** National Institute of Standards and Technology	USA
14	**NMIA** National Measurement Institute Australia	Australia
15	**NMIJ** National Metrology Institute of Japan	Japan
16	**NMISA** National Metrology Institute of South Africa	South Africa

3 Samples

The comparison material was brown rice flour containing 0.05 mg/kg to 0.5 mg/kg level (as As) of arsenite [As(III)], 0.01 mg/kg to 0.1 mg/kg level (as As) of arsenate [As(V)] and 0.005 mg/kg to 0.05 mg/kg level (as As) of DMAA), 0.05 mg/kg to 0.5 mg/kg level (as As) of total arsenic and 0.1 mg/kg to 0.5 mg/kg level of Cd. The measurands to be determined were the mass fractions (as As) of inorganic arsenic (As(III) plus As(V)), DMAA, total arsenic and Cd for the key comparison, and the mass fractions (as As) of As(III), As(V), inorganic arsenic (As(III) plus As(V)), DMAA, total arsenic and Cd for the pilot study. Each participant received a sample bottle containing approximately 20 g of the brown rice flour.

The homogeneity of the material was 0.57 % (rsd) for As(III), 0.83 % (rsd) for As(V), 0.44 % (rsd) for inorganic arsenic (As(III) plus As(V)), 0.41 % (rsd) for DMAA, 0.40 % (rsd) for total arsenic and 0.22 % (rsd) for Cd, according to the determination of 10 bottles using a sub-sample size of about 0.5 g. From the viewpoint of homogeneity, the use of more than 0.5 g sample for each measurement was strongly recommended. The sample after receiving had to be kept at the laboratory temperature.

The samples were distributed to the participants from NMIJ by EMS mail in February, 2013, except for INMETRO (second shipping in March, 2013). Finally, all samples reached their destinations safely. The contact persons are given in Table 2.

Table 2 List of contact persons of the participants

Participant	Contact person
BIM	Boriana Kotzeva
EXHM	Elias Kakoulides
GLHK	W.H. Fung and Y.Y. Choi
HSA	Richard Shin
INDECOPI	Christian Uribe
INMETRO	Janaína Marques Rodrigues and Rodrigo Caciano de Sena
INRIM	Luigi Bergamaschi
INTI	Liliana Valiente
JSI	Milena Horvat
KEBS	Tom Oduor Okumu
NIM	Wei Chao
NIMT	Sutthinun Taebunpakul and Charun Yafa
NIST	Gregory C. Turk and Stephen Long
NMIA	Jeffrey Merrick
NMIJ	Akiharu Hioki
NMISA	S.M. Linsky

4 Technical Protocol

The technical protocol, attached as Annex A, instructed participants concerning treatment of the sample, methods of measurement, reporting of results and the time schedule. The deadline for the registration of participation was originally intended to be December 7, 2012 in the original protocol; it was, however, postponed to December 21, 2012.

5 Methods of Measurement

Participants were allowed to use any suitable method(s) of measurement. Though most of the results were obtained by ID-ICP-MS or ICP-MS for Cd and by ICP-MS for total arsenic, microwave plasma optical emission spectrometry (MP-OES), atomic absorption spectrometry (AAS) and Instrumental Neutron Activation Analysis (INAA) were also employed. Regarding arsenic speciation, ICP-MS coupled with LC [so-called high performance liquid chromatography (HPLC) or ion chromatography (IC)] was used by all participants. The number of results by each method is summarized in Table 3.

Table 3 Number of results by each method for CCQM-K108

Method	Number of results reported			
	Cd	Total As	Inorganic As	DMAA
ID-ICP-MS	7			
ICP-MS	5	11		
MP-OES	1			
AAS	2	2		
INAA	1	2		
LC-ICP-MS			5	4
	Total number 16	Total number 15	Total number 5	Total number 4

6 Moisture content

Each participant was asked to measure the moisture content of the brown rice flour sample in parallel with sample analyses and to report the result as the mass fraction (as As) of each measurand on the dry mass basis. The recommended procedure was to dry the sample to constant mass in a desiccator with fresh P_2O_5 at room temperature more than 10 days. The participants were asked to extend the drying days if the mass of the sample did not reach constant, *i.e.*, if difference between masses from two consecutive measurements was more than 0.0005 g. The results of the moisture content were shown in Figure 1.

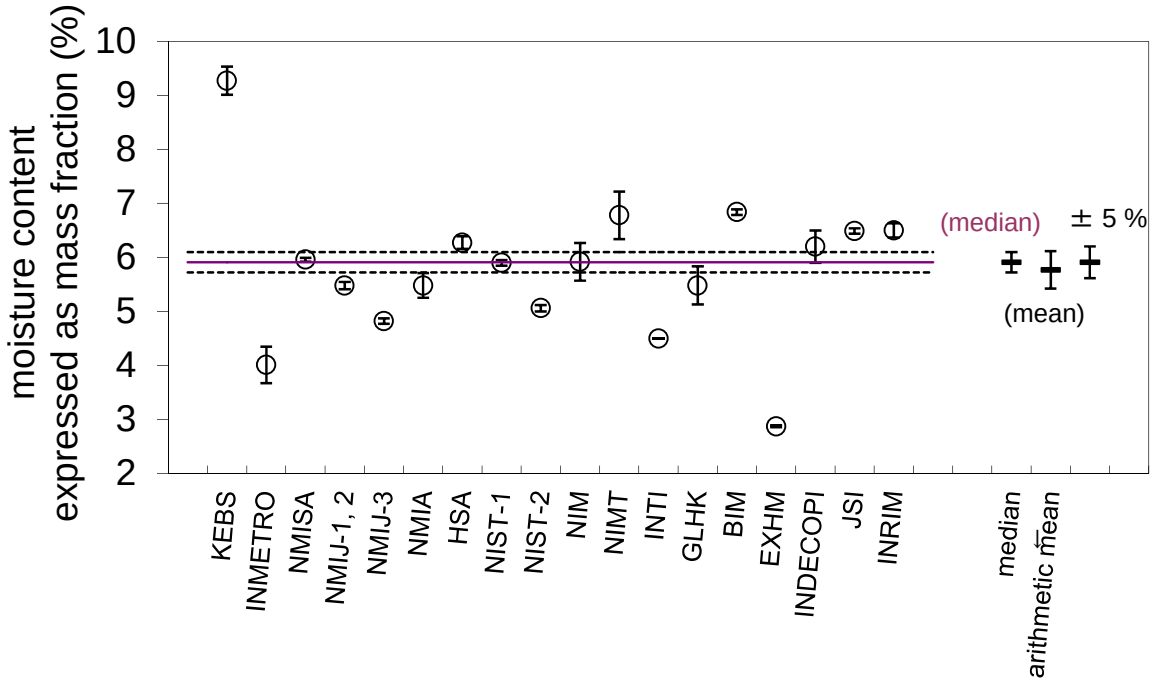

Fig. 1 Results for moisture content of CCQM-K108

The half of each bar indicates the standard uncertainty (k=1).

7 Results

Results, given in Tables 4-7, include information on the measurement methods; results are illustrated graphically in Figures 2-5. KEBS registered to the measurement of total arsenic, but reported no result for it. The half of the bar of each data in the Figures indicates the reported combined standard uncertainty (k = 1). Each Figure contains a solid, horizontal line representing the median of all data except for the additional one(s) from the participant(s) which reported more than one results; at the time of submitting the measurement results, each of such participants decided one of the reported results to be used for the key comparison reference value (KCRV) calculation. The uncertainty of the median was based on the estimate according to median($|x_i$-median$|$)/0.6745, where x_i is each reported value. The dashed, horizontal lines indicate the range of the combined standard uncertainty (k = 1) of the median. The KCRV is discussed in the following section.

In Tables 4-5, some abbreviations reported by the participants are just used as follows: ICP-Q-MS (inductively coupled plasma quadrupole mass spectrometry), ICP-CRC-MS (inductively coupled plasma collosion/reaction cell mass spectrometry), ICP-SF-MS (inductively coupled plasma sector field mass spectrometry), ICP-HR-MS (inductively coupled plasma high resolution mass spectrometry), GF-AAS (graphite furnace atomic absorption spectrometry), ETA-AAS (electrothermal atomisation atomic absorption spectrometry) and k0-INAA (k0-instrumental neutron activation analysis).

Table 4 Results for cadmium of CCQM-K108

Participant	Measurement Method	Decomposition Method (The value in [ ] indicates the sample mass used for each measurement.)	Materials used for calibration	Reported value / mass fraction (mg/kg)	Combined standard uncertainty / mass fraction (mg/kg) (k=1)
KEBS	MP-OES	[0.5 g] Dissolved in 6 mL HNO_3/then microwave digestion under pressure	NIST SRM 3108	0.3529	0.06
INMETRO	ICP-MS	[0.3 g] Microwave-assisted digestion with 5 HNO_3 and 1 H_2O_2	NIST SRM 3108	0.415	0.008716
NMIJ-2(*)	ICP-Q-MS	[0.5 g] Microwave acid digestion, 7 mL HNO_3/later, 2 mL H_2O_2	JCSS std soln.	0.4221	0.0029
NMISA	ID-ICP-MS	[0.5 g] Microwave acid digestion, 4 mL HNO_3/1 mL H_2O_2, 180 ºC	NIST SRM 3108	0.4223	0.0054
NMIJ-1 (for KCRV)	ID-ICP-MS	[0.5 g] Microwave acis digestion, 5 mL HNO_3/later, 1 mL $HClO_4$	JCSS std soln.	0.4224	0.0036
NMIA	Double ID-MS, ICP-CRC-MS & ICP-SF-MS	[0.5 g] Microwave acid digestion, 3 mL HNO_3 (69 %)/2 mL H_2O_2 (31 %)	NIST SRM 3108	0.423	0.005
HSA	ICP-HR-MS, ID-MS	[0.5 g] Microwave digestion, 2.5 mL HNO_3/0.1 mL HF/2.0 mL H_2O_2	NIST SRM 3108	0.424	0.006
NIST-1	ID-ICP-MS	[0.8 g] Digestion with 5 g HNO_3+0.5 g HF/then, microwave acid digestion with 7 g HNO_3	NIST SRM 746 (Cd metal) & NIST SRM 3108	0.4278	0.0028
NIM	ID-ICP-MS	[0.5 g] Microwave Digestion, HNO_3	GBW08612	0.4279	0.0035
NIMT-1 (for KCRV)	ID-ICP-MS	[0.5 g] Microwave digestion with HNO_3+H_2O_2+HF	NIST SRM 3108	0.432	0.008
NIMT-2(*)	ICP-MS, standard addition	[0.5 g] Microwave digestion with HNO_3+H_2O_2+HF	NIST SRM 3108	0.432	0.010
INTI	ICP-MS, standard addition	[0.5 g] Microwave digestion, 6 mL HNO_3+2 mL H_2O_2/later, further 2 mL H_2O_2	NIST SRM 3108	0.433	0.00903
BIM	ICP-MS	[0.6 g] Dissolution with 10 mL concentrated HNO_3	IMS-102 (**)	0.4381	0.023
EXHM	GF-AAS	[0.5 g] MW-asisted digestion, 7 mL HNO_3/later, 2 mL H_2O_2+0.5 mL HF	NIST SRM 3108	0.447	0.016
INDECOPI	ETA-AAS	[2.1 g] Microwave acid digestion, 10 mL HNO_3	NIST SRM 3108	0.448	0.008
JSI	k0-INAA	[0.28 g] Not applied	IRMM-530R	0.474	0.024

JCSS: Japan Calibration Service System under the Measurement Act in Japan; traceable to NMIJ.
(*): not included for the calculation of KCRV.
(**): a commercial standard solution.

Table 5 Results for total arsenic of CCQM-K108

Participant	Measurement Method	Decomposition Method (The value in [ ] indicates the sample mass used for each measurement.)	Materials used for calibration	Reported value / mass fraction (mg/kg)	Combined standard uncertainty / mass fraction (mg/kg) (k=1)
NMIA	ICP-CRC-MS & ICP-SF-MS, standard addition	[0.5 g] Microwave acid digestion, 3 mL HNO_3 (69 %)/2 mL H_2O_2 (31 %)	NIST SRM 3103a	0.304	0.008
NIST-2	ICP-MS, standard addition	[0.7 g] Microwave digestion, HNO_3+H_2O_2	NIST SRM 3103a	0.305	0.021
INDECOPI	ETA-AAS	[2.1 g] Slurry preparation, milled with 20 g of 5 % HNO_3	NIST SRM 3103a	0.306	0.008
INRIM	INAA	[0.2 g] Nothing special	Arsenic std. soln. from Inorganic Ventures (**)	0.308	0.010
INTI	ICP-MS, standard addition	[0.5 g] Microwave digestion, 6mL HNO_3+2 mL H_2O_2/later, further 2 mL H_2O_2	NIST SRM 3103a	0.313	0.01063
GLHK	ICP-MS, standard addition	[0.5 g] Microwave digestion, 4 mL HNO_3/0.2 mL H_2O_2/0.2 mL HF	NIST SRM 3103a	0.3136	0.0076
NMIJ-1(for KCRV)	internal standard, ICP-Q-MS	[0.5 g] Microwave acid digestion, 7 mL HNO_3/later, 0.5 mL HF+2 mL H_2O_2	JCSS std soln.	0.3148	0.0035
EXHM	GF-AAS	[0.5 g] MW-asisted digestion, 7 mL HNO_3/later, 2 mL H_2O_2+0.5 mL HF	NIST SRM 3103a	0.315	0.012
NIMT-2	ICP-MS, standard addition	[0.5 g] Microwave digestion with HNO_3+H_2O_2+HF	NIST SRM 3103a	0.317	0.011
JSI	k0-INAA	[0.28 g] Not applied	IRMM-530R	0.317	0.011
NMIJ-2(*)	ICP-HR-MS	[0.5 g] Microwave acid digestion, 5 mL HNO_3/later, 0.5 mL HF+1 mL $HClO_4$	JCSS std soln.	0.3178	0.0051
NIM	ICP-MS with Ge as internal std.	[0.5 g] Microwave Digestion, HNO_3	GBW08611	0.3183	0.0032
HSA	ICP-HR-MS, standard addition	[0.5 g] Microwave digestion, 2.5 mL HNO_3/0.1 mL HF/2.0 mL H_2O_2	NIST SRM 3103a	0.321	0.010
INMETRO	ICP-MS	[0.3 g] Microwave-assisted digestion with 5 HNO_3 and 1 H_2O_2	NIST SRM 3103a	0.326	0.010728
BIM	ICP-MS	[0.6 g] Dissolution with 10 mL concentrated HNO_3	IMS-102 (**)	0.3756	0.021
KEBS		Registered, but no report.		-	-

JCSS: Japan Calibration Service System under the Measurement Act in Japan; traceable to NMIJ.
(*): not included for the calculation of KCRV.
(**): a commercial standard solution.

Table 6 Results for inorganic arsenic of CCQM-K108

Participant	Measurement Method	Decomposition Method (The value in [ ] indicates the sample mass used for each measurement.)	Materials used for calibration	Reported value / mass fraction (mg/kg as As)	Combined standard uncertainty / mass fraction (mg/kg as As) (k=1)
GLHK	Hamilton PRP-X100, standard addition IC-ICP-MS	[1 g] Acid extraction, 7.5 g of 0.28 mol/L HNO_3+1 g of 30 % H_2O_2 for 3 h at 95 ºC ; oxidised to As(V)	NMIJ CRM 7912-a Arsenate [As(V)] soln.	0.2607	0.0086
NIM	Hamilton PRP-X100, HPLC-ICP-MS	[0.5 g] Microwave extraction with H_2O at 80 ºC	GBW08666 As(III), GBW08667 As(V), GBW08669 DMA	0.2785	0.0049
NIST-2	Dionex AS7, IC-ICP-MS, standard addition	[0.8 g] Microwave Extraction	NIST SRM 3103a	0.280	0.009
NIMT	ODS L-column, HPLC-ICP-MS	[0.5 g] Microwave assisted extraction with 0.02 % HNO_3 and 1 % H_2O_2 ; oxidised to As(V)	NMIJ CRM7913-a for DMAA and NMIJ CRM7912-a for As(V)	0.297	0.0099
NMIJ-3	CAPCELL PAK C18 MG column, HPLC-ICP-MS	[0.5 g] Heat assisted extraction, 0.15 mol/L HNO_3, 2 h at 100 ºC	As(III): JCSS stand. soln., As(V): NMIJ CRM 7912-a As(V) soln., DMAA: NMIJ CRM 7913-a DMAA soln.	0.2990	0.0025

JCSS: Japan Calibration Service System under the Measurement Act in Japan; traceable to NMIJ.

Table 7 Results for DMAA of CCQM-K108

Participant	Measurement Method	Decomposition Method (The value in [ ] indicates the sample mass used for each measurement.)	Materials used for calibration	Reported value / mass fraction (mg/kg as As)	Combined standard uncertainty / mass fraction (mg/kg as As) (k=1)
NIST-2	Dionex AS7, IC-ICP-MS, standard addition	[0.8 g] Microwave Extraction	NIST SRM 3103a	0.015	0.002
NIM	Hamilton PRP-X100, HPLC-ICP-MS	[0.5 g] Microwave extraction with H_2O at 80 ºC	GBW08666 As(III), GBW08667 As(V), GBW08669 DMA	0.0159	0.0005
NMIJ-3	CAPCELL PAK C18 MG column, HPLC-ICP-MS	[0.5 g] Heat assisted extraction, 0.15 mol/L HNO_3, 2 h at 100 ºC	As(III): JCSS stand. soln., As(V): NMIJ CRM 7912-a As(V) soln., DMAA: NMIJ CRM 7913-a DMAA soln.	0.0192	0.0004
NIMT	ODS L-column, HPLC-ICP-MS	[0.5 g] Microwave assisted extraction with 0.02 % HNO_3 and 1 % H_2O_2	NMIJ CRM7913-a for DMAA and NMIJ CRM7912-a for As(V)	0.020	0.0012

JCSS: Japan Calibration Service System under the Measurement Act in Japan; traceable to NMIJ.

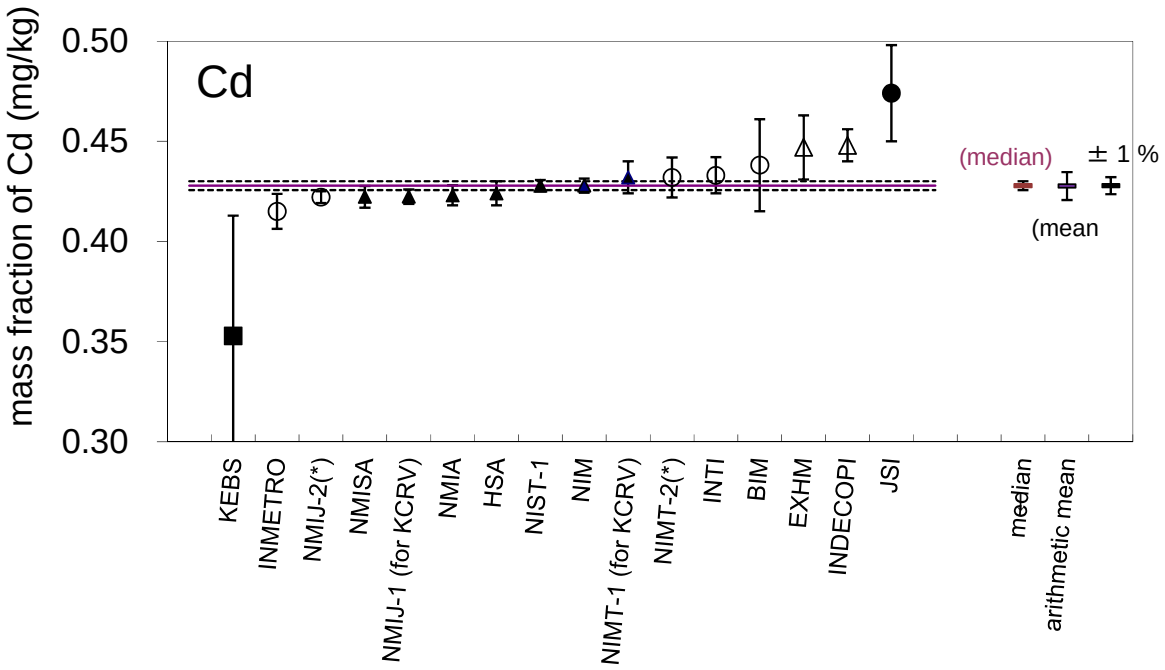

Fig. 2a Results for Cd of CCQM-K108

The half of each bar indicates the combined standard uncertainty (*k*=1).
The results indicated by (*) were not included for the calculation of KCRV.
▲: ID−ICPMS; ○: ICPMS; ●: INAA; △: AAS; ■: MPOES

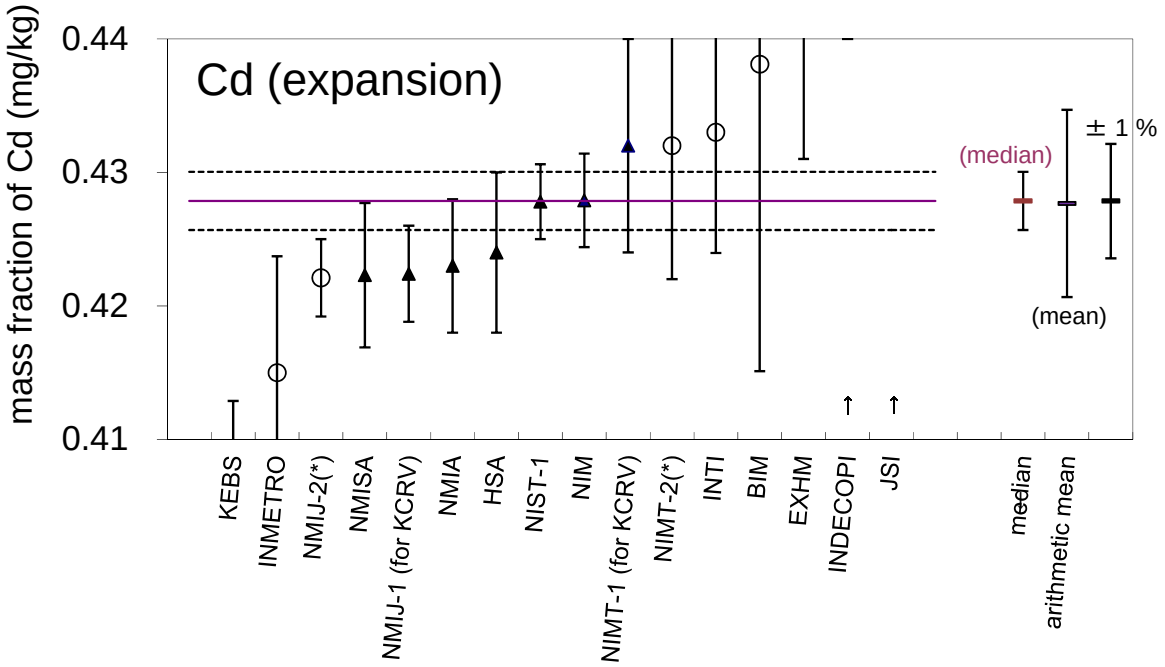

Fig. 2b Results for Cd of CCQM-K108

The half of each bar indicates the combined standard uncertainty (*k*=1).
The results indicated by (*) were not included for the calculation of KCRV.
▲: ID−ICPMS; ○: ICPMS; ●: INAA; △: AAS; ■: MPOES

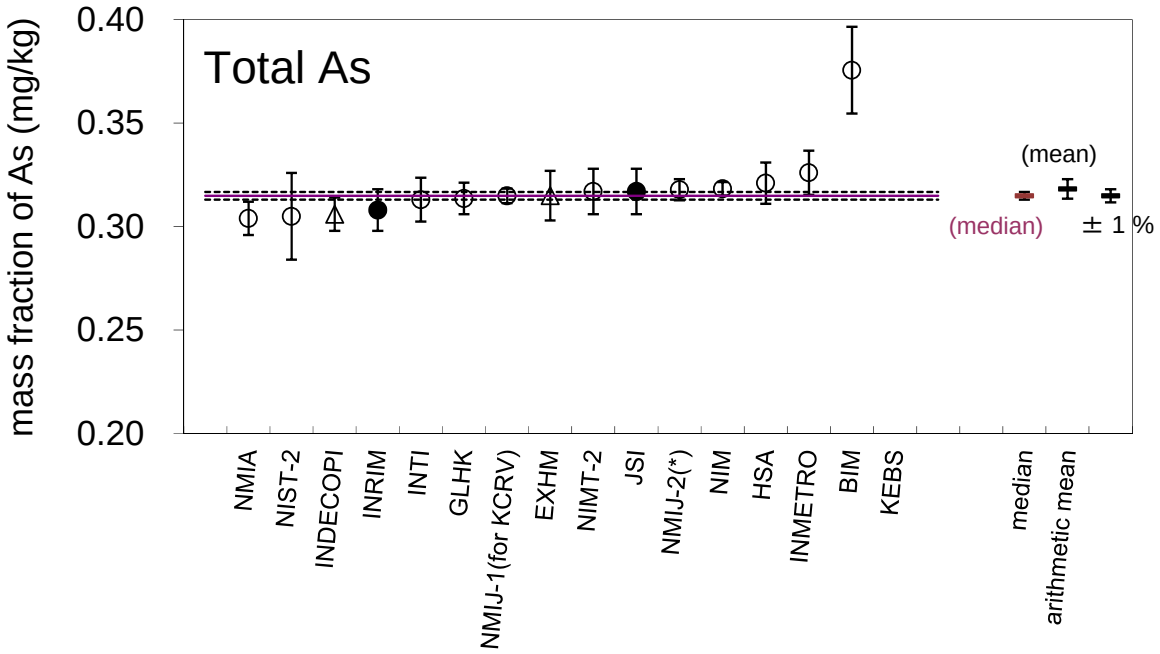

Fig. 3a Results for As of CCQM-K108

The half of each bar indicates the combined standard uncertainty (*k*=1).
The result indicated by (*) was not included for the calculation of KCRV.
○: ICPMS; ●: INAA; △: AAS

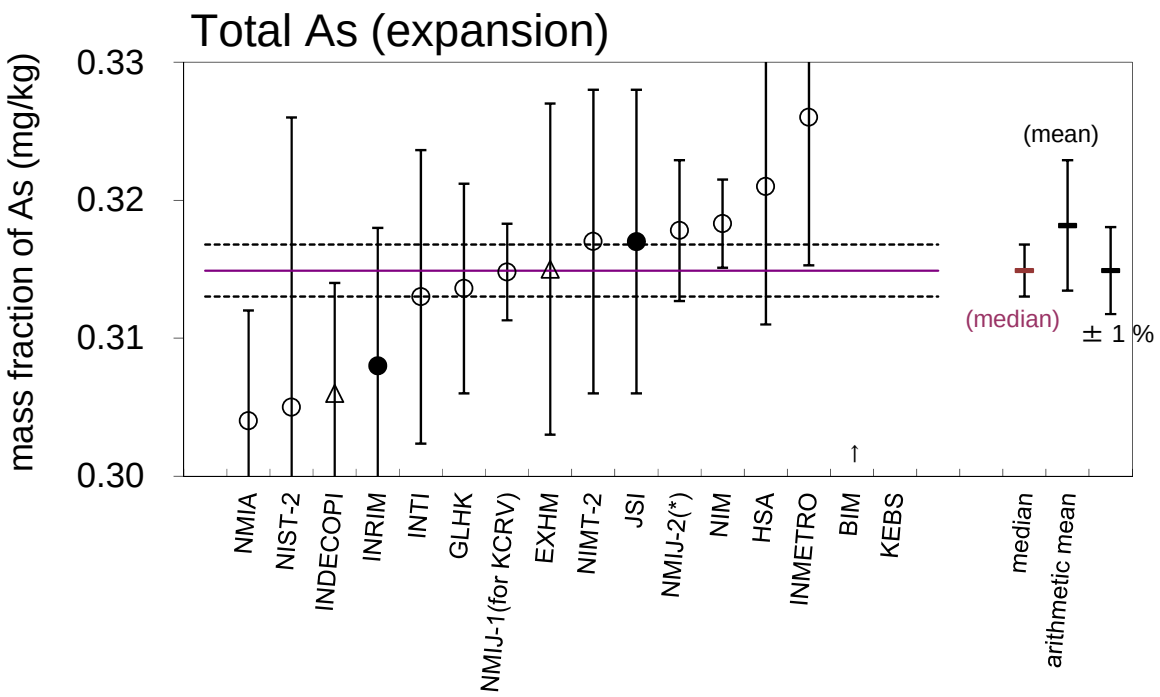

Fig. 3b Results for As of CCQM-K108

The half of each bar indicates the combined standard uncertainty (*k*=1).
The result indicated by (*) was not included for the calculation of KCRV.
○: ICPMS; ●: INAA; △: AAS

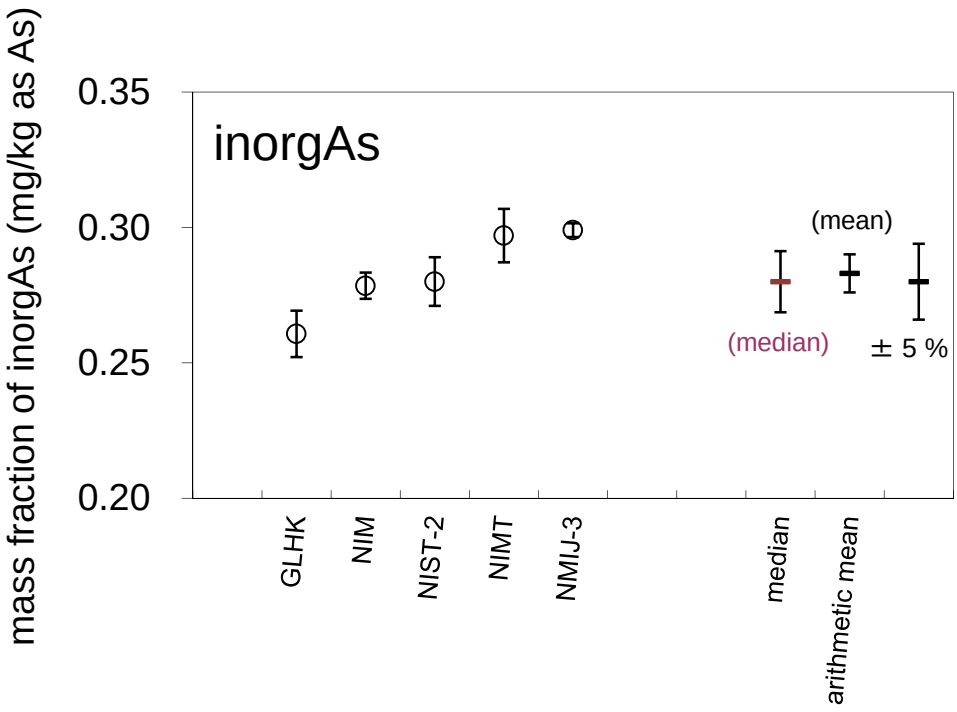

Fig. 4 Results for inorgAs of CCQM-K108

The half of each bar indicates the combined standard uncertainty

O: LC−ICP−MS

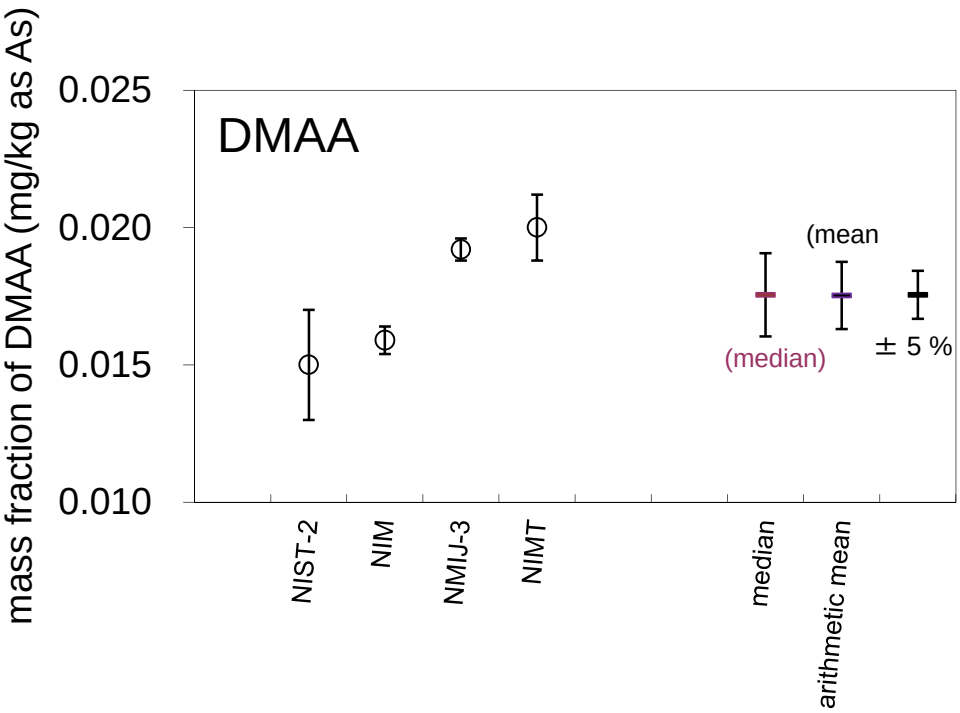

Fig. 5 Results for DMAA of CCQM-K108

The half of each bar indicates the combined standard uncertainty

O: LC−ICP−MS

8 Discussion

8.1 Total arsenic and cadmium

Regarding each of cadmium and total arsenic, no clearly observed differences among the measurement methods (including the acids used for digestion) employed are evident from the results. Most of the reported data are within ±2 % relative to the median, except for a limited number of results. In particullar, all ID-ICP-MS results for cadmium are in excellent agreement with the median.

In order to easily compare the results with each other, the key comparison reference value (KCRV) for each of cadmium and total arsenic was estimated and an equivalence statement was made. For reference, some candidates for the KCRV are shown in Table 8. The variance due to heterogeneity was not included in the calculation of each expanded uncertainty. From the viewpoint of simplicity and robustness, the median is recommended as the KCRV for each of cadmium and total arsenic in this comparison.

Table 8a. Candidates for a KCRV of cadmium for CCQM-K108

		Value / mass fraction (mg/kg)	Expanded uncertainty (k=2) / mass fraction (mg/kg)
Mean (n=14) *6	*1	0.4277	0.0140
Median (n=14)	*2	0.4279	0.0044
MMmedian (n=14)	*3	0.4274	0.0044
Weighted mean (usual weight) (n=14)	*4	0.4268	0.0030
Weighted mean (mild weight) (n=14)	*5	0.4280	0.0035

Table 8b. Candidates for a KCRV of total arsenic for CCQM-K108

		Value / mass fraction (mg/kg)	Expanded uncertainty (k=2) / mass fraction (mg/kg)
Mean (n=14)	*1	0.3182	0.0095
Median (n=14)	*2	0.3149	0.0038
MMmedian (n=14)	*3	0.3153	0.0038
Weighted mean (usual weight) (n=14)	*4	0.3156	0.0037
Weighted mean (mild weight) (n=14)	*5	0.3160	0.0043

*1 The expanded uncertainty was based on the standard deviation of the mean.
*2 The uncertainty of the median was based on the estimate from median($|x_i$-median$|$)/0.6745, where x_i is each reported value.
*3 The MMmedian was calculated according to the following:
David L. Duewer, "A robust approach for the determination of CCQM key comparison reference values and uncertainties", Working document CCQM/04-15, BIPM, 2004, (www.bipm.info/cc/CCQM/Allowed/10/CCQM04-15.pdf).
The uncertainty of the MMmedian was based on the estimate from median ($|x_i$-median$|$)/0.6745, where x_i is each reported value.
*4 The square of reciprocal of reported uncertainty was used as a weight.
*5 The reciprocal of reported uncertainty was used as a weight.
*6 n indicates the number of the results.

The degree of equivalence (DoE) and its uncertainty between a participant result and the KCRV for each of cadmium and total arsenic is calculated according to the following equations:

$D_i = (x_i - x_R)$

$U_i^2 = (k^2 u_i^2 + 2^2 u_R^2)$

where D_i is the DoE between the participant's result x_i and the KCRV, x_R, and U_i is the expanded uncertainty (coverage factor $k = 2$) of D_i calculated from both the combined standard uncertainty u_i of x_i and the standard uncertainty u_R of x_R. The calculation results are shown in Tables 9-10 and Figures 6-7. The half of each bar in the Figures indicates U_i.

Table 9 Degree of equivalence for cadmium (CCQM-K108)[*1]

Participant	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg)		D_i / mass fraction (mg/kg)	U_i / mass fraction (mg/kg)
RV	0.4279	0.0044	*k*=2		
KEBS	0.352891954	0.12	*k*=2	-0.0750	0.1201
INMETRO	0.415	0.017432	*k*=2	-0.0129	0.0180
NMIJ-2([*2])	0.4221	0.0058	*k*=2	-0.0058	0.0072
NMISA	0.4223	0.0108	*k*=2	-0.0056	0.0116
NMIJ-1 (for KCRV)	0.4224	0.0072	*k*=2	-0.0055	0.0084
NMIA	0.423	0.01	*k*=2	-0.0049	0.0109
HSA	0.424	0.012	*k*=2	-0.0039	0.0127
NIST-1	0.4278	0.0056	*k*=2	0.0000	0.0071
NIM	0.4279	0.007	*k*=2	0.0000	0.0082
NIMT-1 (for KCRV)	0.432	0.016	*k*=2	0.0041	0.0166
NIMT-2([*2])	0.432	0.02	*k*=2	0.0041	0.0205
INTI	0.433	0.01806	*k*=2	0.0051	0.0186
BIM	0.4381	0.046	*k*=2	0.0103	0.0462
EXHM	0.447	0.032	*k*=2	0.0192	0.0323
INDECOPI	0.448	0.016	*k*=2	0.0202	0.0166
JSI	0.474	0.048	*k*=2	0.0462	0.0482

[*1] Data from Table 4. [*2] Not included for the calculation of KCRV.

Table 10 Degree of equivalence for total arsenic (CCQM-K108)[*1]

Participant	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg)		D_i / mass fraction (mg/kg)	U_i / mass fraction (mg/kg)
RV	0.3149	0.0038	*k*=2		
NMIA	0.304	0.016	*k*=2	-0.0109	0.0164
NIST-2	0.305	0.042	*k*=2	-0.0099	0.0422
INDECOPI	0.306	0.016	*k*=2	-0.0089	0.0164
INRIM	0.308	0.02	*k*=2	-0.0069	0.0204
INTI	0.313	0.02126	*k*=2	-0.0019	0.0216
GLHK	0.3136	0.0152	*k*=2	-0.0013	0.0157
NMIJ-1(for KCRV)	0.3148	0.007	*k*=2	-0.0001	0.0079
EXHM	0.315	0.024	*k*=2	0.0001	0.0243
NIMT-2	0.317	0.022	*k*=2	0.0021	0.0223
JSI	0.317	0.022	*k*=2	0.0021	0.0223
NMIJ-2([*2])	0.3178	0.0102	*k*=2	0.0029	0.0109
NIM	0.3183	0.0064	*k*=2	0.0034	0.0074
HSA	0.321	0.02	*k*=2	0.0061	0.0204
INMETRO	0.326	0.021456	*k*=2	0.0111	0.0218
BIM	0.3756	0.042	*k*=2	0.0607	0.0422
KEBS					

[*1] Data from Table 5. [*2] Not included for the calculation of KCRV.

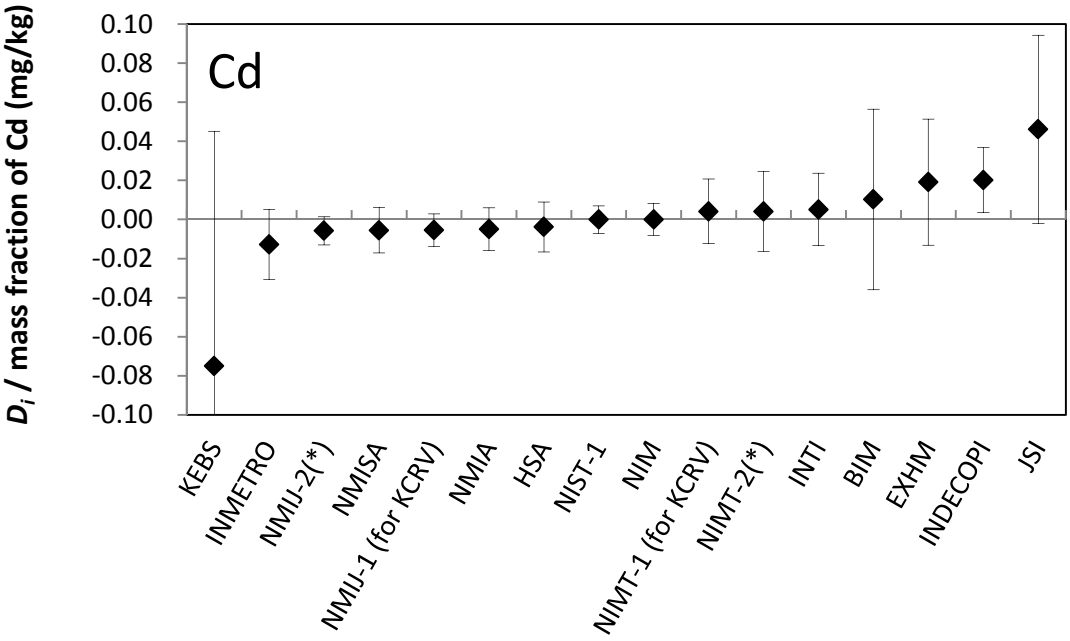

Fig. 6 Degree of equivalence D_i for cadmium

The half of each bar indicates the expanded uncertainty U_i.
The results indicated by (*) were not included for the calculation of KCRV.

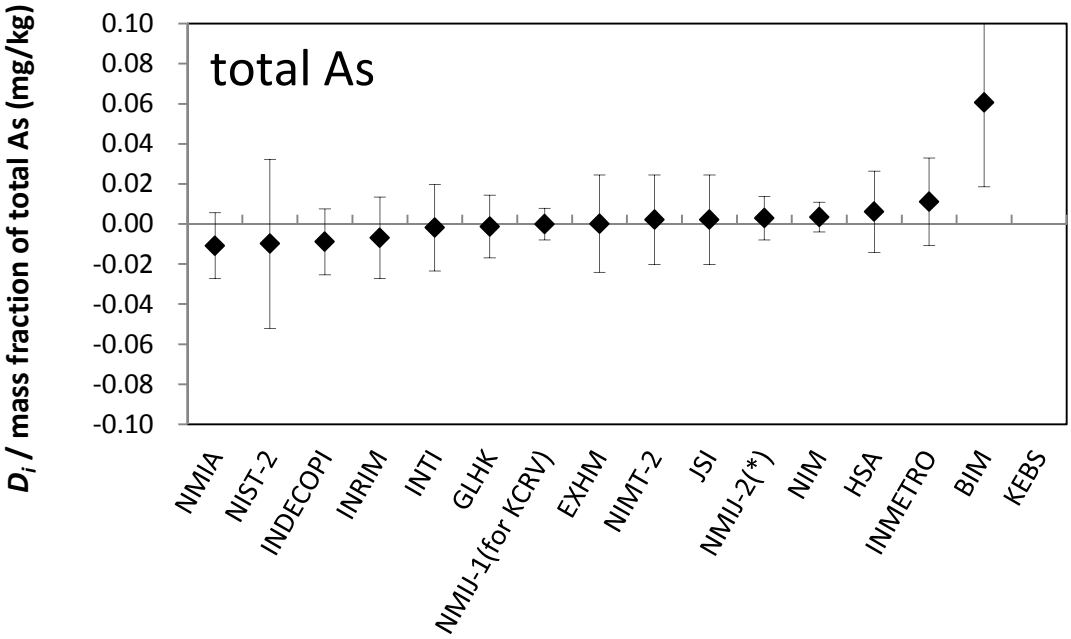

Fig. 7 Degree of equivalence D_i for total arsenic

The half of each bar indicates the expanded uncertainty U_i.
The result indicated by (*) was not included for the calculation of KCRV.

8.2 Inorganic arsenic and DMAA

Regarding each of inorganic arsenic and DMAA, the results have relatively large dispersion beyond the reported uncertainties, though the number of results is small. At the IAWG meeting held November 2013, long time was spent to investigate possible reasons for the discrepancies among the results. NMIJ demonstrated that the extraction efficiencies depended on the extracting solvents, and that the efficiency especially using water could be insufficient. Since any significant arsenic species except for inorganic arsenic and DMAA was not detected in the rice sample, the sum of inorganic arsenic and DMAA was compared with the total arsenic, when the median of the reported results for total arsenic was used (Table 11).

Table 11 Comparison of the sum of inorganic arsenic and DMAA with the total arsenic[*1]

	A	B		C (= A + B)	C / (median for total As)
	inorganic arsenic (mg/kg as As)	DMAA (mg/kg as As)	total arsenic (mg/kg)	inorganic arsenic + DMAA (mg/kg as As)	ratio of C to the median for total arsenic (0.3149 mg/kg)
NMIJ-3	0.2990	0.0192	0.3148 [*2]	0.3182	101 %
GLHK	0.2607	-	0.3136	-	-
NIM	0.2785	0.0159	0.3183	0.2944	93 %
NIMT	0.297	0.020	0.317	0.3170	101 %
NIST-2	0.280	0.015	0.305	0.2950	94 %

[*1] Data from Tables 5-7. [*2] Data of NMIJ-1.

The lower ratio (the sum of inorganic arsenic and DMAA against the total arsenic) might indicate insufficient extraction of arsenic species. Though possible reduction of original As(V) during treatments were raised in the discussion, it seemed that reduction itself had no relation to extraction efficiency. According to communications with NIMT, their extraction efficiency was *ca.* 90 % on the average and the results were corrected using NMIJ CRM 7503-a (white rice flour). Though there was no conclusion of the reasons for the discrepancies, the discussion at the meeting suggested that any additional experimental work would be necessary in order to solve the problem about such discrepancies among the participants.

Three participants (GLHK, NIM and NIMT) agreed to enforcing the additional experiment. NMIJ sent a sample bottle to each participant in inorganic arsenic and/or DMAA for CCQM-K108 who had agreed with additional work to solve the problem; the sample was same as that for CCQM-K108. NMIJ also sent the NMIJ Recommendation Method ([*]) of extraction procedures for inorganic arsenic and DMAA. NMIJ asked them to, if possible, compare results by the procedures with those by their own procedures. The sample bottles were dispatched at the end of January, 2014. The reporting from each participant was done by April 5, 2014.
([*]) the NMIJ Recommendation Method: 2 g of 0.15 mol L^{-1} nitric acid for 0.5 g sample; dry block heating at 100 °C for 2 h.

<u>The results of the additional experiment by NIMT were as follows:</u>
Arsenic species were extracted using the NMIJ Recommendation Method followed by acid digestion; this time, inorganic arsenic and DMAA were not separated. The total extracted arsenic was (0.306 ± 0.004) mg/kg (three measurements, precision). According to communications with NIMT, their extraction efficiency for CCQM-K108 had been originally *ca.* 90 % on the average and the results had been corrected using NMIJ CRM 7503-a (white rice flour); the extraction efficiency for the additional experiment was improved to *ca.* 97 % using the NMIJ Recommendation Method.

The results of the additional experiment by NIM were as follows:
NIM employed microwave extraction using 1 % HNO_3 followed by LC-ICP-MS. The column was a CAPCELL PAK C18 MG (250 mm × i.d. 4.6 mm, Shiseido Ltd.). This time the extraction efficiency was improved to 102 % using 1 % HNO_3 (Table 12) in place of water as an extraction solvent (Table 6).

Table 12 NIM's result for the the additional experiment

	inorganic arsenic (mg/kg as As)	DMAA (mg/kg as As)	inorganic arsenic + DMAA (mg/kg as As)	ratio of C to the median for total arsenic (0.3149 mg/kg)*
mass fraction as As	0.3079	0.0137	0.3216	102 %
combined standard uncertainty	0.0131	0.0008		

* C: the sum of inorganic arsenic and DMAA as Table 11.

The results of the additional experiment by GLHK were as follows:
GLHK compared their own method with the following two additional extraction methods:
(1) extraction method 1: NIST sample extraction method with modification.
Extraction using 1.25 mL of HPLC grade methanol, 3.75 mL high-purity water and 1 g 30 % H_2O_2 was carried out by holding the capped vessels at 80 ºC for 3 h in a temperature controlled water bath.
(2) extraction method 2: NMIJ sample extraction method with modification.
Extraction using 2 g of 0.15 mol L^{-1} HNO_3 and 1 g 30 % H_2O_2 was carried out by holdong the capped vessels at 100 ºC for 2 h in a temperature controlled water bath.

By using the assessment of ERM's approach (ERM: European Reference Materials) which is accounted with the measurement uncertainty, the results of their repeated analysis of inorganic arsenic (Table 13) showed no significant difference comparing with the original result reported by GLHK in CCQM-K108. GLHK reported 0.3136 mg/kg for total arsenic in CCQM-K108; there was no information about the sources from which the difference between inorganic arsenic and total arsenic came.

GLHK employed two modified extraction methods in place of the original one (Table 6). GLHK judged that there were no significant differences among three results. However, the extraction efficiency increased to some degree using the modified methods; accounting their expanded uncertainties, it seems that their results are not necessarily inconsistent with the original results of NMIJ and NIMT, and the new one of NIM. It might be possible that any results, even the original result of NIST, are consitent with each other.

Table 13 GLHK's result for the the additional experiment

	inorganic arsenic (mg/kg as As)		
	original method (from Table 6)	extraction method 1	extraction method 2
mass fraction as As	0.2607	0.281	0.278
combined standard uncertainty	0.0086	0.011	0.011

At the IAWG meeting held April 2014, all aspects on inorganic arsenic and DMAA were discussed. Though progress with useful information from such additional experiments was provided, the problem was not completely solved and any KCRV‘s for inorganic arsenic and DMAA could not be decided. Finally the IAWG chair suggested necessity of a subsequent key comparison following CCQM-K108 (maybe CCQM-K108.1) using another brown rice flour sample in order to solve the inconsistency on arsenic species.

9 Demonstrated Core Capabilities

The six Summary Tables of demonstrated core capabilities are attached as Annex B.

It is expected that total arsenic, cadmium and other metals at mass fractions greater than approximately 0.1 mg/kg in rice flour can be determined by each participant using the same technique(s) employed for this key comparison to achieve similar uncertainties mentioned in the present report. Furthermore, the results of this key comparison can be utilised along with the IAWG core capability approach.

10 Acknowledgement

The work of the key comparison was done with contributions from many scientists as well as the contact persons: Vasiliki Sxoina (EXHM), Y. T. Tsoi, C. L. Lee and M. F. Kong (GLHK), Wang Juan and Ng Sin Yee (HSA), Emily Silva Dutra (INMETRO), Laura Giordani and Giancarlo D'Agostino (INRIM), Radojko Jaćimović (JSI) , Jacqueline Kang'Iri and Tabitha Owiti Orwa (KEBS) , Chao Jingbo (NIM), Nattikarn Kaewkhomdee, Benjamat Chailap, Yanee Pharat and Pranee Phukphattanachai (NIMT), K. E. Murphy, Clay Davis and Michael Ellisor (NIST), Ian White and David Saxby (NMIA), and A. Barzev and A. Botha (NMISA).
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Annex A - Technical Protocol

CCQM-K108 & P147 Key comparison and pilot study on determination of arsenic species, total arsenic and cadmium in brown rice flour

Call for participants and technical protocol

(revised, December 4, 2012)

Introduction

Rice is rich in carbonhydrate, protein and minerals such as Fe, Cu, Zn, and is a staple food, especially in Asia. Since some arsenic compounds are considered toxic, maximum levels for As in rice are often discussed. For such discussion and a related document standard, establishing analytical methods for arsenic species is one of the key issues. The National Metrology Institute of Japan (NMIJ) proposed the present key comparison at the Inorganic Analysis Working Group (IAWG) meeting held April 16-17, 2012. At the CCQM meeting following the IAWG meeting, the proposal was agreed as CCQM-K108. The homogeneity of the material used in this comparison will be investigated prior to the comparison. In parallel with the key comparison CCQM-K108, a pilot study designated CCQM-P147 is carried out, in which the same sample measured by the CCQM-K108 participants is also used.

Samples

The comparison material is brown rice flour containing 0.05 mg/kg to 0.5 mg/kg level (as As) of arsenite [As(III)], 0.01 mg/kg to 0.1 mg/kg level (as As) of arsenate [As(V)] and 0.005 mg/kg to 0.05 mg/kg level (as As) of dimethylarsinic acid (DMAA)), 0.05 mg/kg to 0.5 mg/kg level (as As) of total arsenic and 0.1 mg/kg to 0.5 mg/kg level of Cd. The measurands to be determined are the mass fractions (as As) of inorganic arsenic (As(III) + As(V)), DMAA, total As and Cd for the key comparison, and the mass fractions (as As) of As(III), As(V), inorganic arsenic (As(III) + As(V)), DMAA, total As and Cd for the pilot study. Each participant will receive a sample bottle containing approximately 20 g of the brown rice flour. The homogeneity of the material was 0.57 % (rsd) for As(III), 0.83 % (rsd) for As(V), 0.44 % (rsd) for inorganic arsenic (As(III) + As(V)), and 0.41 % (rsd) for DMAA according to the determination of 10 bottles using a sub-sample size of about 0.5 g. The homogeneity for total As and Cd will be measured before the sample distribution. From the viewpoint of homogeneity, the use of more than 0.5 g sample for each measurement is strongly recommended. The sample after receiving should be kept at the laboratory temperature. The CCQM-P147 sample is the same as the sample for CCQM-K108.

Methods of Measurement

Each participant can use any suitable method(s) of measurement. NMIs or officially designated institutes are welcome to participate in this comparison using primary methods of measurement. Four measurements for each measurand are to be carried out by each participant. The calibrations should be carried out by using standards with metrological traceability.

Each participant's capability of the determination of arsenic species (inorganic arsenic and dimethylarsinic acid (DMAA)), total arsenic and trace metals in brown rice flour and other similar materials will be examined by the present key comparison. Each reference value will be probably a median of the submitted data from NMIs and officially designated institutes, though it will be decided after discussion in an IAWG meeting. If any participant submitted individual results by multiple methods, their best result (*i.e.*, with the smallest uncertainty) will be chose to calculate the reference value.

Determination of moisture content

The moisture content of the brown rice flour sample should be measured in parallel with sample analyses. The recommended procedure is to dry the sample to constant mass in a desiccator with fresh P_2O_5 at room temperature more than 10 days. Please extend the drying days if the mass of the sample did not reach constant, *i.e.*, if difference between masses from two consecutive measurements was more than 0.0005 g. A sample size of 0.5 g or more is recommended for the determination of moisture content. The overall drying time should be reported with the moisture content. Do not use the sample, which used for the determination of moisture content, for analysis.

Reporting

The result should be reported as the mass fraction (as As) of each measurand on the dry mass basis to NMIJ (Akiharu Hioki), accompanied by a full uncertainty budget. Any participant that chooses to use multiple methods can decide only one composite result (*e.g.*, an average value from different methods) or individual results from different methods as the reporting value(s) for each measurand. Reporting the details of the procedure (including details of sample treatment/digestion), the calibration standard and the traceability link, and the instrument(s) used is required. A reporting form will be distributed to participants. Furthermore, please choose a suitable Core Capability table from the attached example forms (no attachment at the present time) and the filled-out table should be submitted together with the measurement result; if there is no suitable table, please make a suitable one depending on the measurement method.

Time schedule

Deadline of registration of participation:	December 21, 2012
Dispatch of the samples:	March, 2013
Deadline for receiving results:	August 31, 2013
First discussion on results:	Autumn meeting, 2013

Participants

Participation is open to all interested NMIs or officially designated institutes that can perform the determination. An NMI or an officially designated institute is recommended to participate in the key comparison rather than in the pilot study as far as possible. An NMI or an officially designated institute may nominate other institutes or laboratories to participate in the pilot study. Please inform NMIJ (Akiharu Hioki) of the contact person, the shipping address, and so on using the attached registration form. Even if you do not wish to participate, please inform NMIJ of it.

We would like to ask NMIs or officially designated institutes to coordinate participation within their economies including inviting participants in the pilot study, shipping samples, and receiving the reports. The coordinating laboratory might invite some expert laboratories directly to participate in the pilot study.

Coordinating laboratory

The CCQM-K108&P147 are coordinated by NMIJ (Akiharu Hioki, Tomohiro Narukawa, Kazumi Inagaki and Shinichi Miyashita).

Contact person

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Annex B - Tables of Demonstrated Core Capabilities

Inorganic Core Capabilities
Summary Table (1)

CCQM Study: CCQM-K108 (Arsenic species, total arsenic and cadmium in brown rice flour)

Institute(s): HSA, NIM, NIMT-1, NIST-1, NMIA, NMIJ-1, NMISA

Method: ***ID-ICP-MS***

Analyte(s): Cd

Instructions:
List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.*		**All**	Method blanks were used to control contamination.
Digestion/dissolution of organic matrices *All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.*		**All**	Organic matrix containing a large amount of starch was digested.
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.*	**All**		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	**All**		
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	**All**		Some participants (NIST and NMIJ) concentrated digested samples to some degree during pretreatment, but it was not so much.
Vapor generation *Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.*	**All**		
Matrix separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	**All**		
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample.*		**All**	Spike equilibration effected the result.
Signal detection *The detection and recording of the analyte isotope signals. The degree of difficulty increases for analytes present at low concentrations, of low isotopic abundance, or that are poorly ionized.*		**All**	It was confirmed that Cd signals were well above blanks, hence this capability was not demonstrated with any degree of difficulty.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		**All**	Memory effect was always considered.
Correction or removal of isobaric/polyatomic interferences *Any techniques used to remove, reduce, or mathematically correct for interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.*		**All**	Spectral interference on the accurate measurement of the cadmium (Cd) was studied and found to be minimal for this material.
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*		**All**	Detector dead time correction was employed. Automated software detector dead time correction is sometimes used.
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*		**All**	Mass bias.effect was always considered.
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*		**All**	Many participants used double IDMS; hence direct spike calibration was not needed although claibration was still tested.. For single IDMS, the accuracy of spike concentrations were considered directly.

Inorganic Core Capabilities
Summary Table (2)

CCQM Study: CCQM-K108 (Arsenic species, total arsenic and cadmium in brown rice flour)

Institute(s): BIM(Cd,As), GLHK(As), HSA(As), INMETRO(Cd,As), INTI(Cd,As), NIM(As), NIMT-2(Cd,As), NIST-2(As), NMIA(As), NMIJ-1(As), NMIJ-2(Cd), NMIJ-2(As)

Method: ICP-MS (without Isotope Dilution)

Analyte(s): Cd, As

Instructions:
List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.*		**All**	Method blanks were used to control contamination.
Digestion/dissolution of organic matrices *All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.*		**All**	Organic matrix containing a large amount of starch was digested.
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.*	**All**		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	**All**		
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	**All**		
Vapor generation *Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.*	**All**		
Matrix separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	**All**		
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		**All**	The accuracy of concentration of calibration solution was considered.
Signal detection *The detection and recording of the analyte isotope signals. The degree of difficulty increases for analytes present at low concentrations, of low isotopic abundance, or that are poorly ionized.*		**All**	It was confirmed that signals were well distinguished from background and blanks, hence this capability was not demonstrated with any degree of difficulty.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		**All**	Memory effect was always considered.
Correction or removal of isobaric/polyatomic interferences *Any techniques used to remove, reduce, or mathematically correct for interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.*		**All**	It is required to ensure both sample digests and standards contain As in a same oxidation state, because it has been reported that As(V) is more sensitive than As(III) when measured by ICP-MS. It is required to check the interferences of $^{40}Ar^{35}Cl^{+}$ polyatomic ions.
Correction or removal of matrix-induced signal suppression or enhancement *Chemical or instrumental procedures used to avoid or correct for matrix-induced signal suppression or enhancement.*		**All**	It is needed to compensate matrix-induced signal suppression or enhancement using some techniques including sufficient dilution of the samples, a gravimetric standard addition method and an internal standard method.
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*		**All**	Detector dead time correction was employed. Automated software detector dead time correction is sometimes used.
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	**All**		

Inorganic Core Capabilities
Summary Table (3)

CCQM Study: CCQM-K108 (Arsenic species, total arsenic and cadmium in brown rice flour)

Institute(s): EXHM, INDECOPI

Method: ETA-AAS (or GF-AAS)

Analyte(s): Cd, As

Instructions:
List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.*	**All**		
Digestion/dissolution of organic matrices *All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ETA-AAS.*		**All**	Organic matrix containing a large amount of starch was digested.
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ETA-AAS.*	**All**		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	**All**		
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ETA-AAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	**All**		
Matrix separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	**All**		
Hydride preconcentration/matrix separation of volatile species. *Coupling of a hydride system to the ETA-AAS and optimization of conditions.*	**All**		
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures. Also use of matrix-matched standards to minimize effect of interferences.*		**All**	The accuracy of concentration of calibration solution was considered.
Signal detection *The detection and recording of the absorption signals of analytes. The degree of difficulty increases for analytes present at low concentrations, of low atomic absorption coefficient. Requires selection of operating conditions such as light source, absorption line, Zeeman background correction conditions. Includes selection of signal processing conditions (peak area or height).*		**All**	Zeeman background correction was employed. (EXHM(Cd,As), testing this capability with a reasonable degree of difficulty. It was confirmed that the signals were well distinguished from blank.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		**All**	Memory effect was always considered.
Optimization of the furnace temperature program *Optimization of temperature and duration of steps for sample drying, pyrolysis to remove (residual) organics, and atomization. Furnace temperature program to minimize analyte loss in the drying/pyrolysis steps, while maximizing analyte vaporization in the atomization step.*	**EXHM(Cd,As), INDECOPI(Cd)**	**INDECOPI(As)**	Optimization in order to measure slurry sample was carried out. (INDECOPI(As))
Correction or removal of matrix effects or interferences *Chemical or instrumental procedures used to avoid or correct for spectral and non-spectral interferences. Includes effects of differences in viscosity and chemical equilibrium states of analyte between the standard and sample. Selection of matrix modifier to adjust volatility of analyte and/or matrix to eliminate these effects is also included. Addition of reactive gases (eg oxygen) to the carrier gas to improve matrix separation. Also included is Zeeman or other background correction techniques to remove interference due to absorption and scattering from coexisting molecules/atoms in the sample.*	**INDECOPI(Cd,As)**	**EXHM(Cd,As)**	The use of matrix modifiers was employed to adjust analyte volatility. (EXHM(Cd,As))

Inorganic Core Capabilities
Summary Table (4)

CCQM Study: CCQM-K108 (Arsenic species, total arsenic and cadmium in brown rice flour)

Institute(s): KEBS

Method: MP-OES

Analyte(s): Cd

Instructions:
List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.*		**KEBS**	Method blanks were used to control contamination.
Digestion/dissolution of organic matrices *All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.*		**KEBS**	Organic matrix containing a large amount of starch was digested.
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.*	**KEBS**		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	**KEBS**		
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	**KEBS**		
Vapor generation *Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.*	**KEBS**		
Matrix separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	**KEBS**		
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		**KEBS**	The accuracy of concentration of calibration solution was considered.
Signal detection *The detection and recording of the analyte signals. The degree of difficulty increases for analytes present at low concentrations, or that are have weak emission lines..*		**KEBS**	It was confirmed that Cd signals were well above blanks, hence this capability was not demonstrated with any degree of difficulty.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		**KEBS**	Memory effect was always considered.
Complex spectral backgrounds *Any techniques used to remove, reduce, or mathematically correct for interferences caused by the overlap of analyte emission lines with atomic, ionic, or molecular emission from matrix components. The relative concentrations and sensitivities of the analyte and the interfering species will affect the degree of difficulty. Samples containing high concentration matrix components with large numbers of emission lines or molecular bands may increase the measurement challenge.*	**KEBS**		
Correction or removal of matrix-induced signal suppression or enhancement *Chemical or instrumental procedures used to avoid or correct for matrix-induced signal suppression or enhancement. High concentrations of acids, dissolved solids, or easily ionized elements will increase the degree of difficulty.*	**KEBS**		This method has a matrix-induced signal issue with this sample but KEBS did not attempt to address it (so not tested) leading to poor precision on measurements results.

Inorganic Core Capabilities
Summary Table (5)

CCQM Study: CCQM-K108 (Arsenic species, total arsenic and cadmium in brown rice flour)

Institute(s): INRIM(As), JSI(Cd,As)

Method: INAA

Analyte(s): Cd, As

Instructions:
List in the appropriate column (as NIST, PTB, LGC, etc.) the institutes which did or did not demonstrate each capability. Where the table includes multiple analytes add the element symbols or 'All' in parenthesis after each institute - e.g. LGC (As, Ca). Provide a brief summary of the challenges encountered in the final column, highlighting any aspects where this measurement presented an unusually high degree of difficulty. This should be a consensus agreed with all participants except where there is a valid reason for it to be different at a specific institute. This also requires explanation. Please add rows for any other capabilities which were used but which have not been included in this table.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Sample preparation *Procedures used to prepare samples for irradiation; determination of the mass basis (e.g., determination of dry mass basis); procedures to minimize sample loss during preparation; procedures to minimize contamination with the elements of interest (highest difficulty for determination of low levels of elements that are ubiquitous in the sample preparation environment).*		**All**	Moisture correction generate one of the major component of the uncertainty. (INRIM) Aliquots of about 0.27 g to 0.28 g of the sample were pelletized using a manual hydraulic press in diameter 10 mm and 3 mm high. (JSI(Cd,As))
Standards preparation *Procedures used to prepare element standards or other comparators used for standardization. (e.g., low difficulty for use of pure elements or compounds; higher difficulty for procedures involving dissolution and dilution, or dilution with solid matrices.)*		**All**	No relevant problem occurs (INRIM) IRMM-530R Al-0.1 % Au alloy in form of foil with thickness of 0.1 mm was used. Discs of about 6 mm diameter were prepared. (JSI(Cd,As))
General applications *Procedures associated with specific method of NAA and the evaluation of the associated uncertainties for comparator NAA, k_0 NAA, or other method specific parameters not described below.*		**All**	The variability of the neutron flux inside the irradiation container generate one of the major component of the uncertainty. (INRIM) A sample and standard Al-0.1 % Au were stacked together, fixed in the polyethylene vial in sandwich form and irradiated in the 250 kW TRIGA Mark II reactor. Characterization of irradiation channel in the carousel facility (CF) of TRIGA reactor and absolute calibration of the HPGe detector are needed. Optimization and validation of the k_0-INAA with different matrix certified reference materials are necessary. Concentration levels in the sample for As and Cd have to be suitable for INAA.(JSI(Cd,As))
Determination of peak areas (complex spectra/small peaks) *Procedures used to determine peak areas. (e.g., high difficulty for small peak areas on complex backgrounds or determination of areas for multiple unresolved peaks.)*		**All**	Some problem caused by small peaks compared to background, this leads to a significative contribution to the related uncertainty. (INRIM). For peak area evaluation, the HyperLab 2002 program was used. (JSI(Cd,As))
Correction for spectral interferences *Procedures used to determine peak areas from interfering nuclides and subtraction of the appropriate number of counts from the peak of interest. Level of difficulty increases with the number of corrections needed and the magnitude of the corrections relative to the total peak area.*	**All**		

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Correction of fast neutron and fission interferences *Procedures used to determine the contributions from fast neutron reactions or fission of U to the peak area of interest. The level of difficulty is related to the magnitude of the corrections needed.*	**All**		
Corrections for sample and standard geometry differences *Procedures used to determine correction factors for differences in sample and standard irradiation and counting geometries. These may include, e.g., use of flux monitors to determine irradiation geometry correction factors, and calculated correction factors based on measured thicknesses and sample-to-detector distances. Level of difficulty increases with the magnitude of the correction.*		**All**	Correction for neutron flux and geometry irradiation was necessary. Gold flux monitor was used. This correction increases the total uncertainty (INRIM). Differences in sample/standard geometry are taken into account and they are calculated by Kayzero for Windows (KayWin®) software, which was used for effective solid angle calculations and elemental concentration calculations. (JSI(Cd,As))
Corrections or uncertainty assessments for high count rates *Procedures used to correct for losses in the analyzer due to high count rates; e.g., set up and validation of loss-free counting hardware, use of mathematical corrections for pulse pileup as a function of analyzer dead time, etc. Level of difficulty increases with the magnitude of the correction.*	**All**		
Corrections for neutron absorption or scattering differences between samples and standards *Procedures used to correct for differences between neutron exposure of samples and standards associated with differences in the absorbing and scattering power; e.g., corrections derived from measurements of different amounts of materials or thicknesses of materials, or calculations based on cross-section values to correct for neutron attenuation. Level of difficulty increases with the magnitude of the correction.*	**All**		
Corrections for differences in neutron exposure of samples and standards *For some NAA applications, samples and standards are irradiated individually and corrections are needed for any differences in neutron exposures. Corrections may be based on, e.g., results from flux monitors or estimates based on knowledge of the facility.*		**Al**	The samples and standards were irradiated together.
Corrections for gamma-ray attenuation *Procedures used to correct for differences in gamma-ray attenuation between samples and standards; typically relevant only for high-z sample or standard matrices and where samples and standards differ. Level of difficulty increases with the magnitude of the correction.*	**INRIM(As)**	**JSI(Cd,As)**	Corrections for gamma-ray attenuations in sample/standard were calculated by Kayzero for Windows (KayWin®) software. (JSI(Cd,As))