

CCQM-K108.2014 :
Determination of arsenic species and total arsenic
in brown rice flour

Final report

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Abstract

The key comparison CCQM-K108.2014 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 inorganic arsenic (i-As, sum of the amount of arsenite [As(III)] and arsenate [As(V)]), dimethylarsinic acid (DMAA), and total arsenic (total As) in brown rice flour. This was the follow-up comparison for the CCQM-K108 & CCQM-P147 (Cd, As, inorganic arsenic, and DMAA in brown rice flour).

For total As, no strong outliers among the reported values were observed, and the distribution of the results was narrow, within 3% around the median. For i-As and DMAA, the distributions of the results were slightly wider than that for total arsenic, but no strong outliers among the reported values of i-As and DMAA were observed. Two potentially bias sources, an extraction efficiency of As species (the ratio of the sum of i-As and DMAA to total As) and the quality of primary standard of DMAA, were discussed. The extraction efficiency was estimated as the ratio of the sum of i-As and DMAA to total As. In the previous comparison (CCQM-K108 & CCQM-P147), the extraction efficiency was one of the largest bias sources for i-As and DMAA. However, in this study, all the extraction efficiencies estimated from the reported values were close to 100 %. Regarding the quality of the primary standard solutions, no significant difference was observed among the primary standard solutions used by the participants. These results suggest the two potential bias sources mentioned above would not have been majors in this study, and then the technical issues in the previous comparison had been overcome.

Accounting for relative expanded uncertainty, a comparability of measurement was successfully demonstrated by the participating NMIs and DIs for the measurement of total As at the level of less than 0.7 mg/kg, i-As at the level of less than 0.6 mg/kg, and DMAA at the level of less than 0.1 mg/kg. These are expected that total arsenic and i-As at mass fractions greater than 0.1 mg/kg and DMAA at mass fractions greater than 0.005 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

From 2012 to 2014, the CCQM-K108/CCQM-P147 was organized 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 cadmium, inorganic arsenic (i-As, sum of the amount of arsenite [As(III)] and arsenate [As(V)]), dimethylarsinic acid (DMAA), and total arsenic in brown rice flour. While the results of Cd and total As were good and the reference values were suitably determined, the results of i-As and DMAA were not in agreement with each other, and then the reference values could not be determined in the comparison.

Possible reasons for the inconsistency among the reported results of the arsenic species were discussed at the IAWG meeting held November 5-6, 2013. Several technical issues including an incomplete extraction of As species, expected from the relation between the sum of inorganic arsenic plus DMAA to the total amount of arsenic, and possible reduction of As(V) during treatments were raised in the meeting. After the meeting, an additional experiment was carried out by NMIJ and the participants for verifying and overcoming the technical issues, especially for the extraction of As species, from February in 2014 to March in 2014. Through the additional experiment, some participants could improve their extraction efficiencies, but the inconsistency were still remained, and the problems could not be completely solved.

On the above background, NMIJ proposed a follow up comparison for the determination of i-As, DMAA and total As in brown rice flour at the autumn meeting of IAWG in 2014. The proposal was approved as the CCQM-K108.2014/CCQM-P171, and NMIJ was designated as the coordinating laboratory.

2. List of Participants and contact persons

All the participating NMIs and DIs and their contact persons are listed in Table 1.

All the participant, except for GLHK, reported the results for all the targets. GLHK reported the results of total As and i-As for the key comparison, and the result of DMAA for the pilot study (CCQM-P171).

3. Samples

The sample was brown rice flour, bottled in amber glass containers (ca. 20 g of material in each). The measurands to be determined were the mass fractions (as As) of inorganic arsenic (i-As, the sum of the amount of arsenite [As(III)] and arsenate [As(V)]), As(III), As(V), dimethyl arsenic acid (DMAA), and total arsenic. In this comparison, total arsenic was a mandatory measurand for all the participants, which was required for evaluating an extraction efficiency of arsenic species.

Table 1 List of participating NMIs and DIs and contact persons

No.	Participant	Contact person	Country/Economy
1	NIST National Institute of Standards and Technology	Stephen Long	USA
2	HSA Health Sciences Authority	Richard Shin	Singapore
3	BVL Federal Institute for Consumer Protection and Food Safety (BVL), designated by PTB	Timmo Kapp	Germany
4	GLHK Government Laboratory, Hong Kong	Fung Wai-hong and Chu Hei-shing	Hong Kong
5	NIM National Institute of Metrology P. R. China	Wei Chao	P. R. China
6	NIMT National Institute of Metrology (Thailand)	Sutthinun Taebunpakul and Charun Yafa	Thailand
7	NMIJ National Metrology Institute of Japan	Kazumi Inagaki	Japan

The nominal mass fractions shown in the call for participants were 0.05 mg/kg to 1.0 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, and 0.05 mg/kg to 0.5 mg/kg level of total arsenic.

The homogeneity including between- and within- bottle variances were evaluated by analyzing 3-sub sample (ca. 0.5 g each) from 10 bottles. The analytical methods used was ICP-QMS with He collision for total arsenic and ion-pair LC-ICP-QMS with He collision for inorganic arsenic and DMAA. The homogeneity was 0.55 % (rsd) for inorganic arsenic, 0.81 % (rsd) for DMAA, and 0.87 % (rsd) for total arsenic.

The samples were shipped to the participants by EMS mail in June 2015. All the participant received them without any problems.

3. Instructions to participants

A protocol, attached as Annex A, instructed the participants concerning sample treatments including the determination of moisture content, methods of measurement, reporting of results, and the time schedule.

Time schedule is summarized as follow:

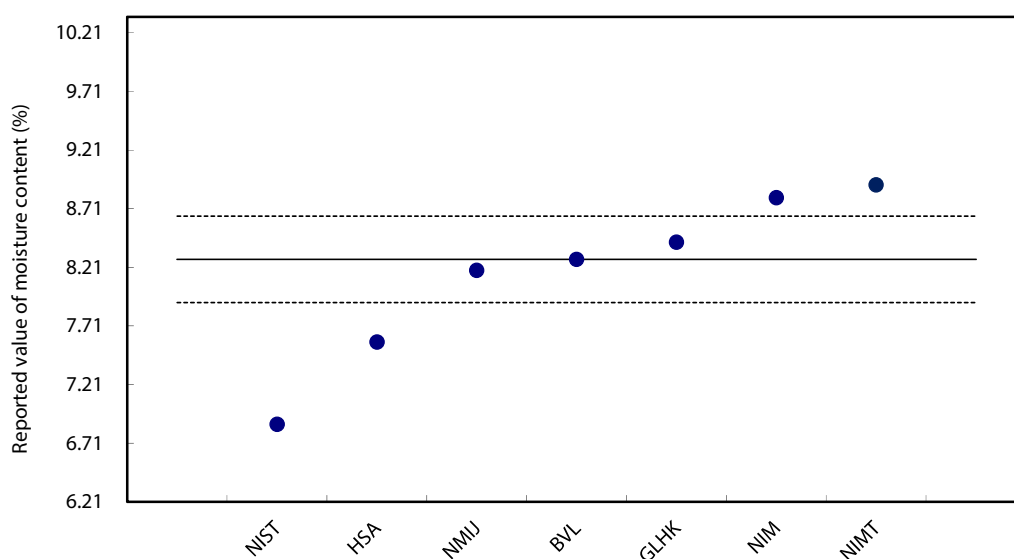
- Start of the registration: from December 17, 2014.
- Deadline for the registration: April 30, 2015.
- Shipping the sample: June 10, 2015.
- Deadline for receiving the results: August 31, 2015.
- First discussion on the results: November 17, 2015, in the autumn meeting of IAWG.

4. Summary of reported results

4.1 Moisture content

All the participants were asked to measure the moisture content in the 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 P₂O₅ 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 reported results of the moisture content were shown in Figure 1.

Figure 1 Reported values of moisture content (%)



Note: error bars of each data are the reported standard uncertainties ($k = 1$). The solid horizontal line is the median of all data and the dash lines shows the range of the standard uncertainty of the median.

4.2 Methods of Measurement and Reported Results

The methods of the measurement and reported results were summarized in Tables 2 to 4. The reported results were graphically illustrated in Figures 2 to 4.

For total As, all the participants applied ICP-MS with a microwave acid digestion. In the digestion, GLHK, HSA, and NMIJ used hydrofluoric acid with the mixture of nitric acid and hydrogen peroxide. In the measurement, NMIJ and HSA used sector field type ICP-MS (ICP-SFMS), NIMT used dynamic reaction cell type ICP-MS (ICP-DRC-MS) with a mass shift method, and the others used collision reaction cell type ICP-MS (ICP-CRC-MS). NMIJ, NIMT, and BVL applied an internal standard correction method, and GLHK, NIM, and NIST applied a standard addition method. HSA applied the combination method of an internal standard correction and standard addition.

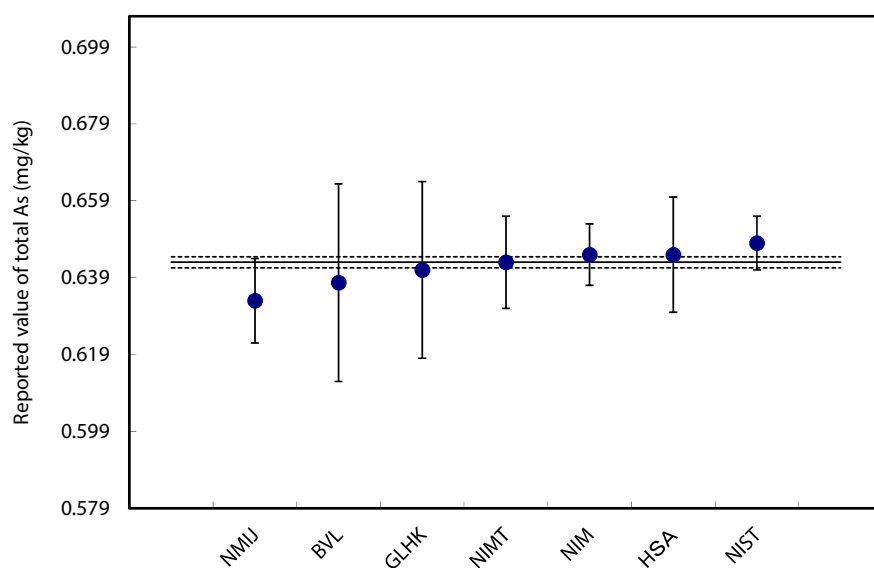
For DMAA and inorganic arsenic, all the participants applied LC-ICP-MS with a heating extraction. As the extraction method, NMIJ applied a block heating extraction with a diluted nitric acid. The others applied a microwave extraction, but different conditions of the extractions such as extracting solvents and temperatures were used in each participant. NIM used water, NIST used a mixture of water and methanol, and others used a diluted nitric acid as the extracting solvent. In the LC-ICP-MS measurement, GLHK, NIST, and BVL used anion exchange chromatograph and the others used ion pair chromatograph.

Table 2 Results for total As

Unit: mg/kg

Acronym of participant	Mass fraction	Standard u ($k=1$)	k	Preparation	Mesurement
NMIJ	0.633	0.011	2	Mw with HNO ₃ , HF& H ₂ O ₂	HR ICP-MS with Interbal STD correction
BVL	0.6377	0.0257	2	Mw with HNO ₃ & H ₂ O ₂	ICP-CRC-MS with Interbal STD correction
GLHK	0.641	0.023	2	Mw with HNO ₃ , HF& H ₂ O ₂	ICP-CRC-MS with STD addition
NIMT	0.643	0.012	2	Mw with HNO ₃	ICP-DRC-MS (mass shift)
NIM	0.645	0.008	2	Mw with HNO ₃	ICP-CRC-MS with STD addition
HSA	0.645	0.015	2	Mw with HNO ₃ , HF& H ₂ O ₂	HR ICP-MS with STD addition & Internal STD correction
NIST	0.648	0.007	2.776	Mw with HNO ₃	ICP-CRC-MS with STD addition (mixture of H ₂ &He)

Figure 2 Results for total As



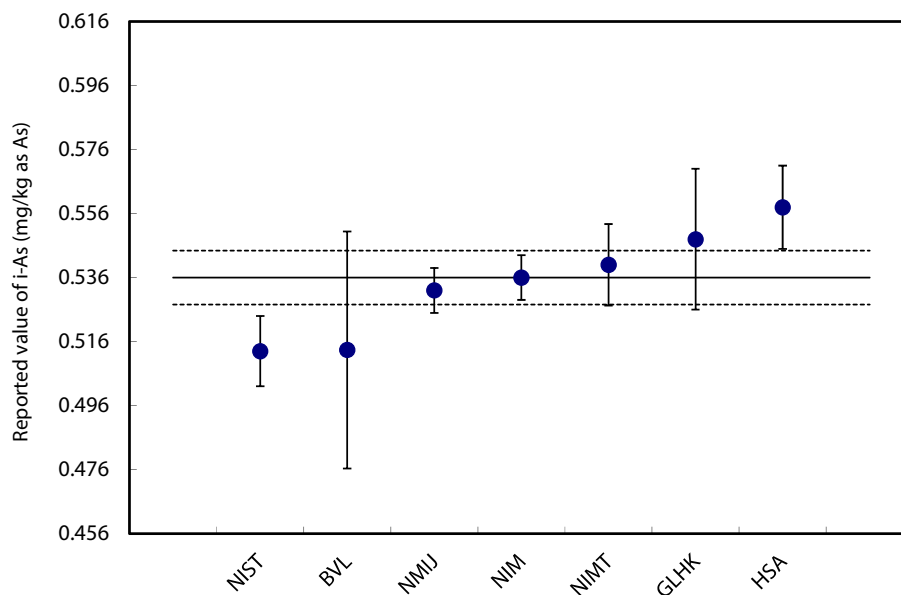
Note: error bars of each data are the reported standard uncertainties ($k=1$). The solid horizontal line is the median of all data and the dash lines shows the range of the standard uncertainty of the median.

Table 3 Results for inorganic arsenic (i-As)

Unit: mg/kg as As

Acronym of participant	Mass fraction	Standard u (k=1)	k	Extraction	Measurement
NIST	0.513	0.011	2.776	MW with water & MeOH	Gradient_anion exchange LC-ICP-MS with STD addition
BVL	0.5134	0.037	2	MW extraction with diluted acid	Anion exchange LC-ICP-MS with STD addition
NMIJ	0.532	0.007	2	Block heating with diluted acid	Ion-pair LC-ICP-MS
NIM	0.536	0.007	2	MW with water	Ion-pair LC-ICP-MS
NIMT	0.540	0.013	2	MW with diluted acid	Ion-pair LC-ICP-MS
GLHK	0.548	0.022	2	MW with diluted acid	Anion exchange LC-ICP-MS with STD addition
HSA	0.558	0.013	2	MW with diluted acid	Ion-pair LC-ICP-MS with STD addition

Figure 3 Results for inorganic arsenic (i-As)



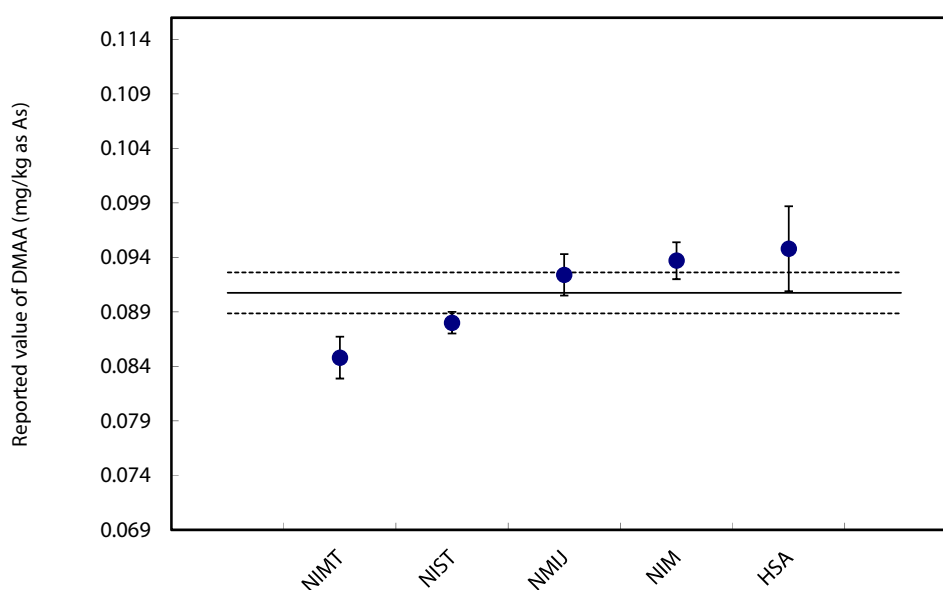
Note: error bars of each data are the reported standard uncertainties ($k = 1$). The solid horizontal line is the median of all data and the dash lines shows the range of the standard uncertainty of the median.

Table 4 Results for dimethylarsinic acid (DMAA)

Unit: mg/kg as As

Acronym of participant	Mass fraction	Standard u (k=1)	k	Extraction	Mesurement
NIMT	0.0848	0.0019	2	MW with diluted acid	Ion-pair LC-ICP-MS
NIST	0.088	0.001	2.16	MW with water & MeOH	Gradient_anion exchange LC-ICP-MS with STD addition
NMIJ	0.0924	0.0019	2	Block heating with diluted acid	Ion-pair LC-ICP-MS
NIM	0.0937	0.0017	2	MW with water	Ion-pair LC-ICP-MS
HSA	0.0948	0.0039	2	MW with diluted acid	Ion-pair LC-ICP-MS with STD addition

Figure 4 Results for dimethylarsinic acid (DMAA, the values are expressed as As)



Note: error bars of each data are the reported standard uncertainties ($k = 1$). The solid horizontal line is the median of all data and the dash lines shows the range of the standard uncertainty of the mean.

5. Discussion

5.1 Total arsenic

No strong outliers among the reported values were observed. All the data are within $\pm 3\%$ relative to the median. Candidates of the key comparison reference value (KCRV) for total As are shown in Table 5. The variance due to heterogeneity of the sample was not included in the calculation of each expanded uncertainty. From the viewpoint of simplicity and robustness, the IAWG approved use of the median as the KCRV for total arsenic in this comparison.

Table 5 Candidate KCRVs for total As

Unit: mg/kg as As

Estimator	Number of results	KCRV	$u(\text{KCRV})$
Mean ^{*1}	7	0.6418	0.0019
Median ^{*2}	7	0.6430	0.0014

^{*1} The expanded uncertainty was estimated from the standard deviation of the mean.

^{*2} The uncertainty of the median was estimated based on the following equation: $u(\text{med}(x)) = 1.25 \times \text{MAD}_E / \sqrt{n}$, where MAD_E is the estimated value of the median absolute deviation.

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

$$D_i = (x_i - x_R) / x_R$$

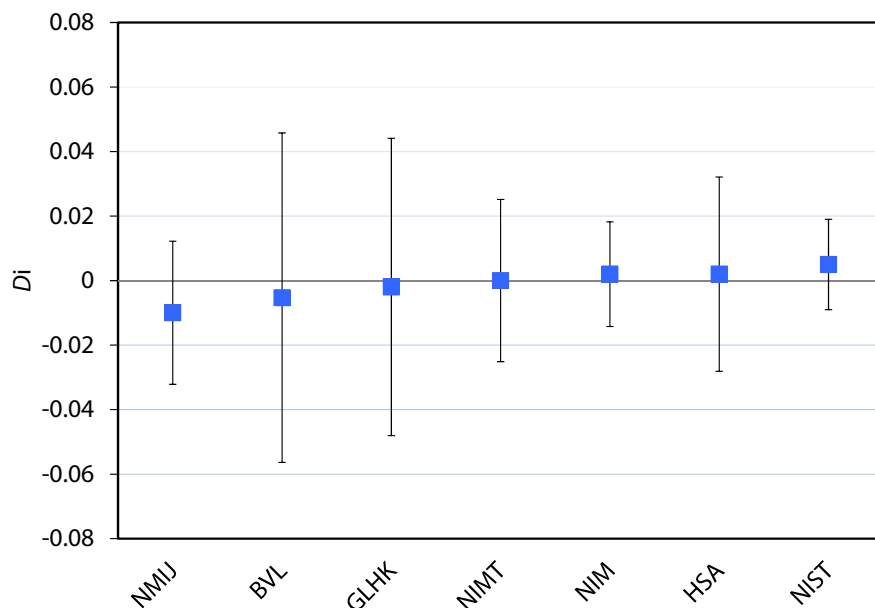
$$U_i^2 = (k^2 u_i^2 + 2^2 u_R^2) / D_i^2$$

where x_i is the participant's result, x_R is the KCRV, D_i is the relative value of the DoE, U_i is the expanded uncertainty (coverage factor $k=2$) of D_i , u_i is the combined standard uncertainty of the participant's result, and u_R is the standard uncertainty of the KCRV. The calculation results are summarized in Tables 6 and Figures 5. The half of each bar in the Figures indicates U_i .

Table 6 DoEs for the determination of total As in CCQM-K108.2014

	Mass fraction (mg/kg)	Expanded uncertainty (mg/kg)	k	D_i	$U(D_i)$	$D_i/U(D_i)$
NMIJ	0.633	0.022	2	-0.010	0.022	-0.45
BVL	0.638	0.051	2	-0.005	0.051	-0.10
GLHK	0.641	0.046	2	-0.002	0.046	-0.04
NIMT	0.643	0.025	2	0.000	0.025	0.00
NIM	0.645	0.016	2	0.002	0.016	0.12
HSA	0.645	0.030	2	0.002	0.030	0.07
NIST	0.648	0.020	2.776	0.005	0.014	0.36

Fig. 5 DoEs for Total arsenic in CCQM-K108.2014



5.2 Inorganic arsenic (i-As) and dimethyl arsenic acid (DMAA)

In the previous comparison study, it was deduced that an incomplete extraction of As species was the major source for the inconsistencies among the reported results of i-As and DMAA. Therefore, the ratios of the sum of i-As and DMAA to total As, corresponding to an estimated extraction efficiency, were evaluated. The estimated extraction efficiencies are summarized in Table 7.

Table 7 Estimated extraction efficiency in CCQM-K108.2014

	Estimated extraction efficiency (%) ^{*1}	Combined uncertainty (%) ^{*2}
NMIJ	98.6	2.2
GLHK	101.2	6.5
NIM	97.6	1.8
HSA	101.2	3.5
NIST	92.7	2.1
NIMT	97.2	2.9

^{*1} The ratios of the sum of i-As and DMAA to total As

^{*2} Combination of the uncertainty of the total As and the sum of i-As and DMAA.

All the estimated extraction efficiencies were close to 100 %, though the value of NIST was slightly lower than the others. Thus, the extraction efficiencies would not have significantly influenced on the results of i-As and DMAA in this comparison.

In the case of DMAA, the possibility of a bias regarding the primary standard used was discussed at the IAWG meetings held November 2015. Except for NIST, all the participants used CRMs as the primary standard; NIMT, HSA, and NMIJ used NMIJ CRM7913-a DMAA solution, NIM used GBW08669 DMAA solution. NIST prepared a DMAA solution from a high purity DMAA reagent and calibrated the solution by ICP-MS after decomposition. After the discussion at the IAWG meeting, NMIJ and NIST confirmed the comparability between the NIST standard solution and NMIJ CRM7913-a, no difference (less than 1 %) was observed between their concentrations. These indicate the primary standard of DMAA would not have been a major bias source in the comparison.

Both for i-As and DMAA, the distributions of the reported results slightly spread on comparing with total As, but no strong outliers among the values. Candidates of the KCRVs for i-As and DMAA are shown in Table 8 and 9, respectively.

Table 8 Candidate KCRVs for i-As

Unit: mg/kg as As

Estimator	Number of results	KCRV	$u(\text{KCRV})$
Mean ^{*1}	7	0.5343	0.0063
Median ^{*2}	7	0.5360	0.0084

^{*1} The expanded uncertainty was estimated from the standard deviation of the mean.

^{*2} The uncertainty of the median was estimated based on the following equation: $u(\text{med}(x)) = 1.25 \times \text{MAD}_E / \sqrt{n}$, where MAD_E is the estimated value of the median absolute deviation.

Table 9 Candidate KCRVs for DMAA

Unit: mg/kg as As

Estimator	Number of results	KCRV	$u(\text{KCRV})$
Mean ^{*1}	6	0.0907	0.0019
Weighted mean ^{*2}	6	0.0900	0.0017
Median ^{*3}	6	0.0924	0.0020

^{*1} The expanded uncertainty was estimated from the standard deviation of the mean.

^{*2} The square of reciprocal of reported uncertainty was used as a weight.

^{*3} The uncertainty of the median was estimated based on the following equation: $u(\text{med}(x)) = 1.25 \times \text{MAD}_E / \sqrt{n}$, where MAD_E is the estimated value of the median absolute deviation.

The variance due to heterogeneity of the sample was not included in the calculation of each expanded uncertainty. In case of i-As, no significant trend was observed in the distribution of the results. From the viewpoint of simplicity and robustness, the IAWG approved use of the median as the KCRV for i-As. On the other hand, in case of DMAA, a trend was observed in the distribution of the result. Thus, the IAWG approved use of the arithmetic mean as the KCRV for DMAA.

The degree of equivalence (DoE)s for i-As and DMAA and their uncertainties are summarized in Tables 10 and 11 and Figures 6 and 7, respectively. The half of each bar in the Figures indicates U_i .

Table 10 DoEs for the determination of i-As in CCQM-K108.2014

	Mass fraction (mg/kg)	Expanded uncertainty (mg/kg)	k	D_i	$U(D_i)$	$D_i/U(D_i)$
NIST	0.513	0.030	2.776	-0.023	0.028	-0.67
BVL	0.513	0.075	2	-0.023	0.077	-0.29
NMIJ	0.532	0.014	2	-0.004	0.022	-0.18
NIM	0.536	0.014	2	0.000	0.022	0.00
NIMT	0.540	0.026	2	0.004	0.031	0.13
GLHK	0.548	0.044	2	0.012	0.047	0.25
HSA	0.558	0.025	2	0.022	0.030	0.73

Fig. 6 DoEs for i-As in CCQM-K108.2014

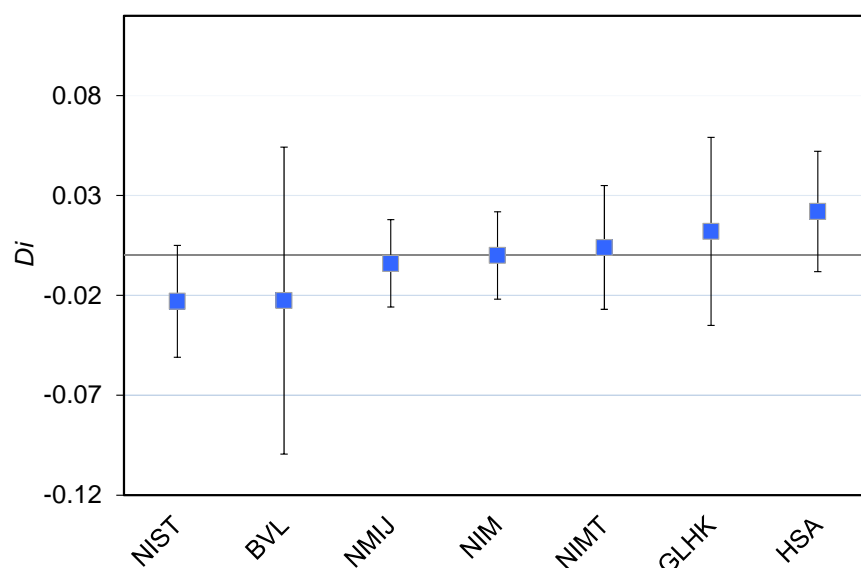
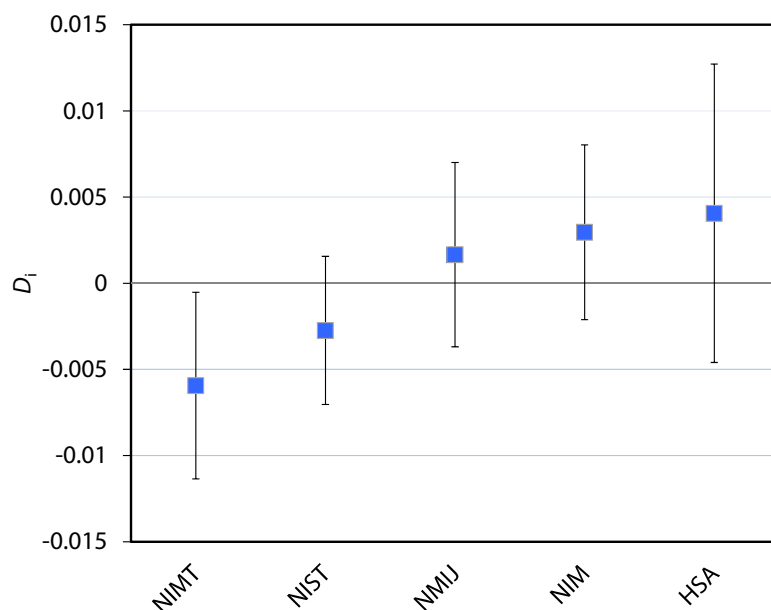


Table 11 DoEs for the determination of DMAA in CCQM-K108.2014

	Mass fraction (mg/kg)	Expanded uncertainty (mg/kg)	k	D_i	$U(D_i)$	$D_i/U(D_i)$
NIMT	0.0848	0.0039	2	-0.0059	0.0054	-1.10
NIST	0.088	0.003	2.16	-0.0027	0.0043	-0.64
NMIJ	0.0924	0.0038	2	0.0017	0.0053	0.31
NIM	0.0937	0.0034	2	0.0030	0.0051	0.58
HSA	0.0948	0.0078	2	0.0041	0.0087	0.47

Fig. 7 DoEs for DMAA in CCQM-K108.2014



9 Demonstrated Core Capabilities

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

Accounting for relative expanded uncertainty, a comparability of measurement was successfully demonstrated by the participating NMIs and DIs for the measurement of total As at the level of less than 0.7 mg/kg, i-As at the level of less than 0.6 mg/kg, and DMAA at the level of less than 0.1 mg/kg. These are expected that total As and i-As at mass fractions greater than 0.1 mg/kg and DMAA at mass fractions greater than 0.005 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: Stephen Long and Michael B. Ellisor (NIST), Sim Lay Peng, Fransiska Dewi and Richard Shin (HSA), Timo Kapp (BVL), Fung Wai-hong and Chu Hei-shing (GLHK), Wei Chao (NIM), Nattikarn Kaewkhomdee, Sutthinun Taebunpakul, Usana Thiengmanee and Charun Yafa (NIMT)

Annex A - Technical Protocol

CCQM-K108.2014 & P171 Key comparison and pilot study on determination of arsenic species and total arsenic in brown rice flour

Call for participants and technical protocol

(December 16, 2014) (revised on April 16, 2015)

Introduction

Rice is rich in carbohydrate, 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 arsenic 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 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. In parallel with the key comparison CCQM-K108, a pilot study designated CCQM-P147 was carried out, in which the same sample measured by the CCQM-K108 participants was also used. Regarding each of total arsenic and Cd for CCQM-K108, the results of almost all participants were in good agreement with each other; therefore, each reference value was suitably determined. On the other hand, regarding each of inorganic arsenic and dimethylarsinic acid (DMAA) the originally submitted results were not in good agreement with each other. In despite of additional experimental works among some participants using the comparison samples, no reference values were able to be determined for inorganic arsenic and DMAA. At the IAWG meeting held April 7-8, 2014, some possibilities of the disagreements among the results were discussed, and it was suggested that a follow-up key comparison on inorganic arsenic and DMAA in different brown rice flour would be conducted. NMIJ proposed a follow-up key comparison at the IAWG meeting held October 14-15, 2014, where possible follow-up actions were discussed. Through such discussions it is recognised that the extraction efficiencies of arsenic species depend on the kinds of rice and the extraction conditions used, although total inorganic arsenic is not usually a problem. Following the discussion at the meeting, NMIJ proposed the present key comparison CCQM-K108.2014 on determination of total inorganic arsenic and total arsenic. At the IAWG meeting held April 16-17, 2015, DMAA was also added as an analyte for the key comparison. In parallel with the key comparison CCQM-K108.2014, a pilot study designated CCQM-P171 is carried out, in which the same sample measured by the CCQM-K108.2014 participants is also used.

Samples

The comparison material is brown rice flour containing 0.05 mg/kg to 1.0 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)], 0.005 mg/kg to 0.1 mg/kg level (as As) of DMAA and 0.05 mg/kg to 1.0 mg/kg level (as As) of total arsenic. The measurands to be determined are the mass fractions (as As) of inorganic arsenic (As(III) + As(V)), total arsenic and DMAA. Participation in DMAA is optional. Participation only in total arsenic is not allowed, though participation in total arsenic is mandatory in order to discuss about the extraction efficiencies of inorganic arsenic and DMAA. Each participant may also

report individual results of As(III) and As(V) as the part of pilot study as well as inorganic arsenic, total arsenic and DMAA for discussion.

Each participant will receive a sample bottle containing approximately 20 g of the brown rice flour. The between-bottles homogeneity of the material was 0.55 % (rsd) for inorganic arsenic (As(III) + As(V)), 0.81 % (rsd) for DMAA and 0.87 % (rsd) for total arsenic 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 is strongly recommended. The sample after receiving should be kept at the laboratory temperature. The CCQM-P171 sample is the same as the sample for CCQM-K108.2014.

Methods of Measurement

The participants in the key comparison must measure both total inorganic arsenic and total arsenic using any method(s) of their choice. 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 inorganic arsenic, total arsenic and DMAA in brown rice flour and other similar materials will be examined by the present key comparison. Each reference value will be determined from the submitted data from NMIs and officially designated institutes (DIs); it will be decided after discussion in an IAWG meeting. If any participant submitted individual results by multiple methods, it should be clearly identified by the participant which result should be used for the key comparison reference value (KCRV) calculation; otherwise, their best result (*i.e.*, with the smallest uncertainty) will be chosen to calculate KCRV. Participation in the pilot study allows optional selection of the analytes including As(III) and As(V). As information for the pilot study, an NMIJ method for separation of arsenic species in brown rice is attached with this protocol. The coordinating laboratory would like to ask the participants in the pilot study to carry out comparison with their own separation procedure and, if possible, compare results with the NMIJ method.

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 P₂O₅ 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

Analysis of total arsenic is mandatory in order to discuss about the extraction efficiency of arsenic species. 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 IAWG website 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

Discussion: at April meeting, 2015

Deadline of registration of participation: April 30, 2015

Dispatch of the samples: May, 2015

Deadline for receiving results: August 31, 2015

First discussion on results: Autumn meeting, 2015

Registration will be possible even after the April meeting in 2015. Since it might take relatively long time to receive NMIJ's permission of exporting the comparison material, the coordinating laboratory will appreciate early registration, if possible, before the middle of March, 2015.

Participants

Participation is open to all interested NMIs or DIs that can perform the determination. 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. Participants shall agree to use the results each other in the result reports of the parallel comparisons; *i.e.*, the CCQM key comparison and the CCQM pilot study.

Coordinating laboratory

The CCQM-K108.2014 and CCQM-P171 are coordinated by NMIJ (Akiharu Hioki, Tomohiro Narukawa, Kazumi Inagaki and Shinichi Miyashita).

Contact person

Dr. Akiharu HIOKI

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Tel: +81-29-861-9341 Fax: +81-29-861-6857 E-mail: aki-hioki@aist.go.jp

Registration form

CCQM-K108.2014 and CCQM-P171 Determination of arsenic species and total arsenic in brown rice flour

(December 16, 2014) (revised on April 16, 2015)

We would like to participate in the key comparison CCQM-K108.2014 (open only for NMIs or officially designated institutes). The element/species to analyse are listed in the Table below.

We would like to participate in the pilot study CCQM-P171 (open only for NMIs or officially designated institutes). The element/species to analyse are listed in the Table below.

Element/species	Participation in CCQM-K108.2014 (Yes/No)	Participation in CCQM-P171 (Yes/No)
Inorganic As (As(III)+As(V))		
Total As (mandatory)*		
DMAA		
As(III)		
As(V)		

* For the key comparison, participation only in total arsenic is not allowed

Name of contact person :
(including title)

Institute/Firm :

Acronym of Institute/Firm :
(if available)

Department :

Address (for shipping) :

Country/Economy :

E-mail :

Tel :

Fax :

Date :

Signature (if possible) :

Please complete the registration form and return it to NMIJ (Akiharu Hioki) by **no later than 30 April 2015**. Early registration is welcome (if possible, before the middle of March, 2015).

Dr. Akiharu HIOKI

National Metrology Institute of Japan (NMIJ),

AIST Tsukuba Central 3-9,

1-1-1, Umezono, Tsukuba, Ibaraki, 305-8563, JAPAN

Tel : +81-29-861-9341 Fax: +81-29-861-6857 E-mail: aki-hioki@aist.go.jp

Annex B - Tables of Demonstrated Core Capabilities

Inorganic Core Capabilities
Summary Table (1)

CCQM Study: CCQM-K108.2014 (Arsenic species and total arsenic in brown rice flour)

Institute(s): NIST, GLHK, HSA, NIM, NIMT, BVL, NMIJ
Method: ICP-MS (standard addition & internal standard correction)

Analyte(s): As

Instructions:

List element symbols for analytes in the appropriate column ('Not tested' or 'Tested') for all capabilities relevant to your measurements. Provide a brief explanation of the challenges you encountered in the final column, highlighting any aspects where you believe this measurement presented an unusually high degree of difficulty. Please add rows for any other capabilities which you used but which have not been included in this table.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction <i>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.</i>		All	A method blank was prepared to control contamination. All supplies were pre-washed with an acid.
Digestion/dissolution of organic matrices <i>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.</i>		All	Closed vessel type microwave digestion system was used.
Digestion/dissolution of inorganic matrices <i>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.</i>	All		
Volatile element containment <i>All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.</i>		NIST	Use of control of similar matrix (SRM1568b) to verify recovery of As (NIST).
Pre-concentration <i>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.</i>	All		
Vapor generation <i>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.</i>	All		
Matrix separation <i>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.</i>	All		
Calibration of analyte concentration <i>The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.</i>		All	Standard addition or standard addition with internal standard correction was performed for correcting matrix effect including carbon enhancement caused

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Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
			with carbon residues in sample solutions. Adding 3 % isopropanol into both sample and standard solutions was efficient for cancelling the carbon enhancement (BVL).
Signal detection <i>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.</i>		All	
Memory effect <i>Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.</i>		All	No significant memory effect was observed, but a monitoring by periodically measuring a blank solution was required for checking any memory effect and cross-contamination in a measurement.
Correction or removal of isobaric/polyatomic interferences <i>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.</i>		All	The interference of $^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$ could be eliminated by collision cell mode, but checking the efficiency of the elimination would be required if sample solution contain a large amount of chlorine. Mathematical correction should be performed if the spectral overlapping could completely be eliminated by collision cell mode. Mass shift by reaction cell mode was also effective for avoiding the interference, but other potentially overlapping such as $^{91}\text{Zr}^+$ on $^{75}\text{As}^{16}\text{O}^+$ should be concerned (MINT).
Correction or removal of matrix-induced signal suppression or enhancement <i>Chemical or instrumental procedures used to avoid or correct for matrix-induced signal suppression or enhancement.</i>		All	Standard addition or standard addition with internal standard correction was used to compensate matrix-induced signal suppression or enhancement. The form of As species such as oxidation state in the digested solution should be concerned because it's well known the species-dependence of the sensitivity in ICP-MS (NMIJ). Carbon enhancement caused with carbon residues in sample solutions should be concerned. Standard addition method could cancel the carbon enhancement. Adding 3 % isopropanol into both sample and standard solutions was also efficient for cancelling the carbon enhancement (BVL).
Detector deadtime correction <i>Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.</i>	All		Most of ICP-MS instruments could be automatically corrected the deadtime in their firmware or operating software, but its should be confirmed to check the function is active and the correction parameter is acceptable.
Mass bias/fractionation control and correction <i>Techniques used to determine, monitor, and correct for mass bias/fractionation.</i>	All		

**Inorganic Core Capabilities
Summary Table (2)**

CCQM Study: CCQM-K108.2014 (Arsenic species and total arsenic in brown rice flour)

Institute(s): NIST, GLHK, HSA, NIM, NIMT, BVL, NMIJ

Method: LC-ICP-MS

Analyte(s): inorganic arsenic and dimethyl arsinic acid (DMAA)

Instructions:

List element symbols for analytes in the appropriate column ('Not tested' or 'Tested') for all capabilities relevant to your measurements. Provide a brief explanation of the challenges you encountered in the final column, highlighting any aspects where you believe this measurement presented an unusually high degree of difficulty. Please add rows for any other capabilities which you used but which have not been included in this table.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Extraction of species from the sample matrix <i>Single- or multi-steps procedures used to efficiently extract the analyte(s) of interest from the sample matrix with preservation of the analyte (s) integrity</i>		All	Extraction efficiency is sensitive to temperature and to the type and concentration of the acid used. When a microwave is used, the temperature homogeneity over the vessels could be a problem.
Species pre-concentration <i>Techniques and procedures used to increase the concentration of the species to be analysed by HPLC-ICP-IDMS. Includes solvent evaporation, freeze-drying, etc.</i>	All		
Achieving compatibility of LC conditions with ICP-MS <i>Selected chromatographic conditions (e.g mobile phase composition and flow rate) selected to be compatible with conventional nebulisation ICP-MS</i>		All	No special conditions were used.
Selectivity of LC separation <i>Development of separation systems to separate the target species from other species of the same element and/or to minimise matrix interferences from other compounds that co-elute with the target species and may affect its detection by ICP-MS (e.g high C-compound interference on the detection of Se and As species)</i>		All	For rice no problem, but if transferring this method to more complex matrices like an algae it becomes a vital issue.(BVL)
Spike equilibration with sample <i>The mixing and equilibration of the enriched isotopic spike with the sample</i>	All		
Characterisation of the natural species standard, including purity <i>All techniques used to know the exact concentration of the natural species standard used as a calibrant</i>		All	The standards of As (III), As (V), DMAA with metrological traceability could be used.
Transient isotope ratio precision <i>Any techniques used for improved isotope ratio precision in transient signal analysis (e.g. adequate peak area integration, isotope integration time/number of points per peak, signal intensity, etc).</i>	All		
Memory effect <i>Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.</i>		All	No serious problem was observed.
Control of procedural blank <i>All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest</i>		All	High risk of contamination by glass in the laboratory (easy to remove) and HPLC (more

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Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
<i>for species that are environmentally ubiquitous and also present at very low concentrations in the sample.</i>			difficult to remove). Checking the blank was required.
Correction or removal of isobaric/polyatomic interferences <i>Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. 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.</i>		All	Checked by injection of chloride, no overlapping with any analyzed species (BVL)
Mass bias/fractionation control and correction <i>Techniques used to determine, monitor, and correct for mass bias/fractionation.</i>	All		
Detector deadtime correction <i>Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.</i>	All		
Spike calibration <i>Techniques used to determine the analyte concentration in the enriched isotopic spike solution.</i>	All		