APMP.QM-S10

Elements in Food Supplement

Final Report

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Abstract

The Supplementary Comparison APMP.QM-S10 “Elements in Food Supplement” was undertaken to demonstrate the capability of participating national metrology institutes (NMIs) and designated institutes (DIs) in measuring the mass fraction of the analytes at mg/kg levels in a test sample of food supplement by various analytical techniques.

Mineral food supplements are commercially available and marketed in forms of tablets, capsules, powders, solutions, etc. In cases where the intake from the diet is insufficient or where consumers consider their diet requires supplementation, mineral food supplements serve to supplement the daily diet. The amounts of the minerals should be properly declared in the labelling of the products. The use of reliable methods for measurement of minerals is important in safeguarding the quality of these products and the public health.

According to the information from the BIPM Key Comparison Database (KCDB), a few NMIs have made Calibration and Measurement Capabilities (CMCs) claims related to the analysis of elements in food/nutritional supplements. In this regards, the Government Laboratory, Hong Kong (GLHK) proposed to coordinate a new supplementary comparison (APMP.QM-S10) for the determination of elements in food supplement at the APMP TCQM meeting in November 2015. At the CCQM IAWG Meeting held in April 2016, the proposed study was further discussed and the Chair of APMP TCQM eventually approved the proposed supplementary comparison for 2016/17 with a study number of APMP.QM-S10 in May 2016.

During the call for participation of APMP.QM-S10, GLHK received enquiries about the participation of metrology institutes in a pilot study instead of the supplementary comparison. To address such concern, GLHK discussed the issue with the Chair of CCQM IAWG and proposed an APMP pilot study which is conducted in parallel with APMP.QM-S10 using the same test material for analysis. The Chair of APMP TCQM finally approved the proposed pilot study with a study number of APMP.QM-P31 in December 2016.

The study is based on the analysis of Zinc, Manganese, Calcium and Magnesium in food supplement, which are the micronutrients essential for good health and are the elements commonly formulated in food supplements. Zinc and Manganese are categorised as “transition elements”, and Calcium and Magnesium are classified as “alkali and alkaline earth elements”. Its aim is to demonstrate the capability of participating national metrology institutes (NMIs) and designated institutes (DIs) in measuring the mass fractions the analytes at mg/kg levels in a test sample of food supplement by various analytical techniques. The mass fractions of the analytes reported on a dry mass basis will be used for comparability purpose.

The supplementary comparison facilitates participating national metrology institutes (NMIs) and designated institutes (DIs) in making claims on the analysis of relevant “transition elements” and “alkali and alkaline earth elements” in appropriate food matrices (e.g. food supplements) on the Calibration and Measurement Capabilities (CMCs) as listed in Appendix C of the Key Comparison Database (KCDB) under the Mutual Recognition Arrangement of the International Committee for Weights and Measures (CIPM MRA). Participants are requested to complete the pertinent Inorganic Core Capabilities Tables as a means of providing evidence for their CMC claims.

For registration of APMP.QM-S10, totally 14 institutes registered for the examination of the Zinc, Manganese, Calcium and Magnesium. For submission of results, all institutes submitted the results for Zinc and Manganese, and 12 institutes submitted the results for Calcium and Magnesium.

For examination of Zinc, Manganese, Calcium and Magnesium, most of the participants used microwave-assisted acid digestion methods for sample dissolution. A variety of instrumental techniques including inductively coupled plasmas mass spectrometry (ICP-MS), isotope dilution inductively coupled plasmas mass spectrometry (ID-ICP-MS), inductively coupled plasmas optical emission spectrometry (ICP-OES), flame atomic absorption spectrometry (FAAS), and instrumental neutron action analysis (INAA) were employed by the participants for determination. For this supplementary comparison, inorganic core capabilities have been demonstrated by the concerned participants with respect to methods including ICP-MS (without isotope dilution), ID-ICP-MS, ICP-OES, FAAS and INAA on the determination of elements (Zinc, Manganese, Calcium and Magnesium) in a food matrix of food supplement.

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1. Introduction

The United States Congress has defined the term “dietary supplement” in the Dietary Supplement Health and Education Act (DSHEA) of 1994 [1]. A dietary supplement is a product taken by mouth that contains a dietary ingredient intended to supplement the diet. DSHEA places dietary supplements in a special category under the general umbrella of “foods” not drugs, and requires that every supplement be labelled a dietary supplement. Besides, the European Commission has established harmonised rules to help ensure that food supplements are safe and properly labelled [2]. The definition of “food supplements” means foodstuffs the purpose of which is to supplement the normal diet and which are concentrated sources of nutrients or other substances with a nutritional or physiological effect, alone or in combination, marketed in dose form, namely forms such as capsules, pastilles, tablets, pills and other similar forms, sachets of powder, ampoules of liquids, drop dispensing bottles, and other similar forms of liquids and powders designed to be taken in measured small unit quantities. In the EU, food supplements are regulated as foods. The main EU legislation is Directive 2002/46/EC related to food supplements containing vitamins and minerals. The CODEX Alimentarius Commission has also adopted the “Guidelines for Vitamin and Mineral Food Supplements CAC/GL 55-2005” [3]. The guidelines apply to vitamin and mineral food supplements intended for use in supplementing the daily diet with vitamins and/or minerals, where these products are regulated as foods.

Mineral food supplements are commercially available and marketed in forms of tablets, capsules, powders, solutions, etc. In cases where the intake from the diet is insufficient or where consumers consider their diet requires supplementation, mineral food supplements serve to supplement the daily diet. The amounts of the minerals should be properly declared in the labelling of the products. The use of reliable methods for measurement of minerals is important in safeguarding the quality of these products and the public health.

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The supplementary comparison facilitates participating NMIs and DIs in making claims on the analysis of relevant “transition elements” and “alkali and alkaline earth elements” in appropriate food matrices (e.g. food supplements) on the CMCs as listed in Appendix C of the KCDB under the Mutual Recognition Arrangement of the International Committee for Weights and Measures (CIPM MRA). Participants are requested to complete the pertinent Inorganic Core Capabilities Tables as a means of providing evidence for their CMC claims.

2. Participating Institutes

For APMP.QM-S10, totally 14 institutes registered for the APMP Supplementary Comparison. The lists showing the countries’ names of the participating NMIs/DIs in alphabetical order are given in Table 1.

Table 1. APMP.QM-S10: List of participating NMIs/DIs

No.	Institute	Country	Contact person	Results submitted for measurand
1	INTI Instituto Nacional de Tecnología Industrial- Lab. Metales y Análisis Inorgánico.	Argentina	Nadia Hatamleh	Zn, Mn, Ca, Mg
2	DRiCM Designated Reference Institute for Chemical Measurements	Bangladesh	Mala Khan	Zn, Mn, Ca, Mg

No.	Institute	Country	Contact person	Results submitted for measurand
3	NRC National Research Council Canada	Canada	Zoltan Mester, Lu Yang	Zn, Mn, Ca, Mg
4	NIM National Institute of Metrology, P. R. China	China	Chao Wei	Zn, Mn, Ca, Mg
5	GLHK Government Laboratory, Hong Kong	Hong Kong, China	Yuk-Tai Tsoi	Zn, Mn, Ca, Mg
6	INRIM Istituto Nazionale di Ricerca Metrologica	Italy	Luigi Bergamaschi	Zn, Mn
7	KEBS Kenya Bureau of Standards	Kenya	Tom Oduor Okumu	Zn, Mn, Ca, Mg
8	INACAL National Institute for Quality	Peru	Christian Uribe	Zn, Mn, Ca, Mg
9	VNIIFTRI Russian Metrological Institute of Technical Physics and Radio Engineering	Russian Federation	Aleksei Stakheev	Zn, Mn, Ca, Mg
10	HSA Health Sciences Authority	Singapore	Richard Shin	Zn, Mn, Ca, Mg
11	JSI Jožef Stefan Institute / Department of Environmental Sciences	Slovenia	Radojko Jaćimović	Zn, Mn, Ca, Mg
12	NIMT National Institute of Metrology (Thailand)	Thailand	Usana Thiengmanee	Zn, Mn
13	INRAP National Institute for Research and Physical and Chemical Analysis	Tunisia	Hanen Klich	Zn, Mn, Ca, Mg
14	VMI Vietnam Metrology Institute	Vietnam	Ngô Huy Thành	Zn, Mn, Ca, Mg

Note:

(i) INRIM and NIMT did not submit the results for Ca and Mg.

3. Samples and Instructions to Participants

3.1. Materials

About 20 kg of food supplement tablets was purchased from the local market. The food supplement tablets were synthetically produced according to the manufacturer’s formulation. Preliminary analysis of the food supplement tablets has been conducted to confirm that the levels of the target analytes were fit for the intended purpose. The food supplement tablets were blended to give powder. The powder was subjected to a sieving process through two calibrated sieves (200 and 100 µm respectively). The sieved powder (particle sizes: 100 – 200 µm) was thoroughly homogenised in a 3-dimensional mixer for 5 days. The material was irradiated using ^{137}Cs gamma source at a dose of about 1 kGy for disinfection. The irradiated material was packed into pre-cleaned and nitrogen-flushed high density polyethylene bottles, each of about 25 g. About 250 bottles of sample were prepared. Finally, each bottle of sample was vacuum-sealed in a polypropylene bag. All prepared bottles of sample are stored at room temperature (20 ± 5°C) prior to distribution or use.

3.2. Homogeneity and Stability Study

The homogeneity study was conducted after the testing material was bottled and irradiated. 10 bottles of the test material (conditioned at 20 ± 5 °C) were randomly selected from the whole lot of bottles prepared. Two test portions of 0.5 g were taken from each bottle for analysis.

For analysis of Zinc, Manganese, Calcium and Magnesium, the test portions were digested using microwave-assisted acid digestion. Following validated procedures, the digested samples and method blanks were analysed using standard additions with ICP-AES.

ANOVA technique was applied to assess the between-bottle heterogeneity and the standard uncertainty originated from the between-bottle heterogeneity was calculated using the equation (1) given below in accordance with ISO Guide 35:2006 [4]. The results are summarised in Table 2.

$$u_{\mathrm{bb}} = \sqrt{\frac{MS_{\mathrm{within}}}{n}} . \sqrt[4]{\frac{2}{\nu_{MS_{\mathrm{within}}}}} \qquad (1)$$

where

u_{bb}: standard uncertainty due to between-bottle heterogeneity

MS_{within}: mean square within bottles variance

$\nu_{MS_{\mathrm{within}}}$: degree of freedom of MS_{within}

n: number of replicates

Table 2.   Summary of homogeneity study results

Measurand	ANOVA test		Relative standard uncertainty due to between-bottle (in)homogeneity, u_{bb} (%)
	F-statistics	Critical value	
Zn	1.13	3.02	0.28
Mn	0.74	3.02	0.37
Ca	2.17	3.02	0.23
Mg	1.14	3.02	0.27

The homogeneity study results indicated that no significant inhomogeneity was observed in the test material. The test material was considered fit for the purpose of the supplementary comparison.

Long-term and short-term stability studies were conducted for the test material using the same analytical procedures as for the homogeneity study. The long-term stability is associated with the behavior of the test material under storage in participating laboratories while the short-term stability studies aimed to show the stability of the material during its transport. The long-term stability was conducted at the storage temperature (20 ± 5 ºC) on the classical approach covering the period from the distribution of test material to the deadline for submission of results. The short-term stability of the food supplement was conducted by two bottles of sample were randomly taken from the reference temperature (about -20 ºC) to the simulated transport temperatures (conditioned at 20 ± 5 °C and 40 ± 5 °C) on three occasions (1, 2 and 4 weeks) over the study period. Each bottle of sample was analysed in duplicate for monitoring the sample instability. The stability check was conducted on "*isochronous*" approach that allowed all measurements of the stability study to take place under repeatability conditions (one run with one calibration).

The trend-analysis technique proposed by ISO Guide 35:2006 [4] was applied to assess the stability of the test material at 20 ºC and 40 ºC. The basic model for the stability study is expressed as the equation (2).

$$Y = \beta_0 + \beta_1 X + \varepsilon \qquad (2)$$

where β_0 and β_1 are the regression coefficients; and ε denotes the random error component. With appropriate t-factors, β_1 (slope) can be tested for significance of deviation from zero. Table 3 summarizes the results of the stability tests at 20 ºC and 40 ºC respectively.

Table 3. Summary of stability study results

Measurand	**p-value for the slope**		
	Short-term stability		Long-term stability
	20 ºC	40 ºC	20 ºC
Zn	0.994	0.701	0.182
Mn	0.253	0.683	0.984
Ca	0.335	0.112	0.088
Mg	0.448	0.790	0.207

As all p-values were greater than 0.05, it was concluded that the corresponding slope was not significantly deviated from zero at 95% level of confidence. In other words, no instability was observed for the test material at 20 ºC and 40 ºC during the testing period. The test material was considered fit for the purpose of the supplementary comparison.

To monitor the highest temperature that the test material would be exposed to during the transportation, temperature recording strips were sent along with the test material to the participating institutes. According to the information provided by the participants in the Sample Receipt Forms, the maximum temperatures that the test material experienced were all below 40 ºC.

3.3. Instructions to Participants

Participants were free to choose any analytical methods for examination. They were advised to mix the sample thoroughly before processing. A sample size of at least 0.5 g was recommended for testing. Participants were requested to perform at least three independent measurements on three separate portions of the sample and to determine the mass fractions of the analytes of interest. For the determination of dry mass correction, a minimum of three separate portions (recommended size to be about 1 g each) of the sample shall be taken and placed over anhydrous calcium sulphate (DRIERITE®) in a desiccator at room temperature for a minimum of 20 days until a constant mass is reached. Participants were also advised to carry out dry mass correction and analysis of the test material at the same time.

Participants were asked to report the mean value of at least three independent measurements of the mass fractions of measurands in mg/kg for Zinc, Manganese, Calcium and Magnesium on a dry mass basis and its associated uncertainty (combined standard uncertainty at 1 sigma level). Participants were requested to provide (i) description of analytical methods (including sample dissolution procedures if any); (ii) details of the uncertainty estimation (including complete specification of the measurement equations and description of all uncertainty sources and their typical values); and (iii) sources and purity of any reference materials used for calibration purposes.

4. Methods of Measurement

For examination of Zinc, Manganese, Calcium and Magnesium, most of the participants used microwave-assisted acid digestion methods for sample dissolution. A variety of instrumental techniques including inductively coupled plasmas mass spectrometry (ICP-MS), isotope dilution inductively coupled plasmas mass spectrometry (ID-ICP-MS), inductively coupled plasmas optical emission spectrometry (ICP-OES), flame atomic absorption spectrometry (FAAS), and instrumental neutron action analysis (INAA) were employed by the participants for determination. For APMP.QM-S10, the methods of measurement used by the participants are summarised in Table 4 respectively, and the information about dry mass correction are shown in Table 5 respectively.

Table 4. APMP.QM-S10: Summary of methods of measurement used by the participants

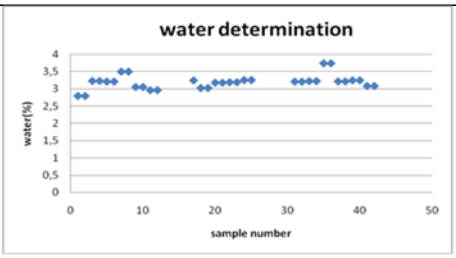
Institute (Country)	Analyte	Dissolution method	Calibration method	Analytical instrument	Reference material used for calibration
INTI (Argentina)	Zn, Mn, Ca, Mg	Microwave-assisted digestion (HNO_3/HF/HCl/H_3BO_3)	Gravimetric standard addition	ICP-OES	Zn: NIST SRM 3168a Zinc standard solution Mn: NIST SRM 3132 Manganese standard solution Ca: NIST SRM 3109a Calcium standard solution Mg: NIST SRM 3131a Magnesium standard solution
DRiCM (Bangladesh)	Zn, Mn, Ca, Mg	Microwave-assisted digestion (HNO_3)	Gravimetric standard addition	FAAS	Zn: (AppliChem A2469,0500) Zinc standard solution Mn: (Scharlau MA01110100) Manganese standard solution Ca: (Fluka 69349) Calcium standard solution Mg: (AppliChem A2455,0500) Magnesium standard solution
NRC (Canada)	Zn, Mn, Ca, Mg	Microwave-assisted digestion with 3 ml HF, 15 ml HNO_3 and 3 ml H_2O_2 and 3 ml HCl	Zn and Mg: Triple ID and gravimetric standard additions Mn and Ca: gravimetric standard additions	HR-ICP-MS and ICPOES	Zn: NRC Zn Mn: NRC Mn Ca: NIST SRM 3109a Mg: NIST SRM 3131a
NIM (China)	Zn, Mn, Ca, Mg	Microwave-assisted digestion (HNO_3/HF)	External Curve	ICP-OES	Zn: NIM CRM GBW08620 Zinc standard solution Mn: NIM CRM GBW(E)080157 Manganese standard solution Ca: NIM CRM GBW(E)060080 Calcium Carbonate

Institute (Country)	**Analyte**	**Dissolution method**	**Calibration method**	**Analytical instrument**	**Reference material used for calibration**
					Mg: NIM CRM GBW(E)080126 Magnesium standard solution
GLHK (Hong Kong, China)	Zn, Mn, Ca, Mg	Microwave-assisted digestion (HNO_3/HCl)	Gravimetric standard addition	ICP-OES	Zn: NIST SRM 3168a Zinc standard solution Mn: NIST SRM 3132 Manganese standard solution Ca: NIST SRM 3109a Calcium standard solution Mg: NIST SRM 3131a Magnesium standard solution
INRIM (Italy)	Zn, Mn	No dissolution	Gravimetric comparator standard	Instrumental Neutron Activation	Zn: NIST SRM 3168a Zinc standard solution Mn: NIST SRM 3132 Manganese standard solution
KEBS (Kenya)	Zn, Mn, Ca, Mg	Microwave-assisted digestion (HNO_3)	Gravimetric standard addition	Single Quad ICP-MS	Zn: Multielement standard solution 6 for ICP (Fluka 43843) Mn: Multielement standard solution 6 for ICP (Fluka 43843) Ca: Multielement standard solution 6 for ICP (Fluka 43843) Mg: Multielement standard solution 6 for ICP (Fluka 43843)
INACAL (Peru)	Zn, Mn, Ca, Mg	Microwave-assisted digestion (HNO_3/H_2O_2/HCl)	Gravimetric single-point internal standard addition	ICP-OES	Zn: NIST SRM 3168a Zinc standard solution Mn: NIST SRM 3132 Manganese standard solution Ca: NIST SRM 3109a Calcium standard solution Mg: KRISS CRM 105-02-017 Magnesium standard solution
VNIIFTRI (Russian Federation)	Zn, Mn, Ca, Mg	Microwave-assisted digestion (HNO_3)	Gravimetric standard addition	High resolution ICP-OES	Zn: Zinc ICP Standard (993 ± 5) mg/kg Certipur CRM, Merck, Germany Mn: Manganese ICP Standard (998 ± 5) mg/kg Certipur CRM, Merck, Germany Ca: Calcium ICP Standard (986 ± 5) mg/kg Certipur CRM, Merck, Germany Mg: Magnesium ICP Standard (997 ± 5) mg/kg Certipur CRM, Merck, Germany
HSA (Singapore)	Zn, Mn, Ca, Mg	Microwave-assisted digestion (HNO_3/H_2O_2/HF)	Zn: IDMS using ^{67}Zn (94.60%) isotopic spike Mn: Gravimetric standard addition using indium (In) as internal standard Ca: Gravimetric standard addition	Zn and Mg: ICP-HR-MS Mn: ICP-MS Ca: ICP-OES	Zn: NIST SRM 3168a Zinc standard solution Mn: NIST SRM 3132 Manganese standard solution Ca: NIST SRM 3109a Calcium standard solution Mg: NIST SRM 3131a Magnesium standard solution

Institute (Country)	Analyte	Dissolution method	Calibration method	Analytical instrument	Reference material used for calibration
			Mg: IDMS using ^{25}Mg (98.81%) isotopic spike		
JSI (Slovenia)	Zn, Mn, Ca, Mg	N/A (non-destructive)	k_0-method of INAA	TRIGA Mark II research reactor, absolutely calibrated HPGe detector	IRMM-530R Al-0.1%Au alloy
NIMT (Thailand)	Zn, Mn	Microwave-assisted digestion (HNO_3/HCl)	Zn: Isotope dilution-ICP-MS Mn: Gravimetric standard addition	ICP-MS/MS	Zn: NIST SRM 3168a Zinc standard solution Mn: NIST SRM 3132 Manganese standard solution
INRAP (Tunisia)	Zn, Mn, Ca, Mg	Microwave-assisted digestion (HNO_3/H_2O_2)	Standard calibration	ICP-AES	Zn: NIST SRM 3168a Zinc standard solution Mn: NIST SRM 3132 Manganese standard solution Ca: NIST SRM 3109a Calcium standard solution Mg: NIST SRM 3131a Magnesium standard solution
VMI (Vietnam)	Zn, Mn, Ca, Mg	Wet digestion by HNO_3	Standard addition	ICP-MS	Zn: KRISS CRM 105-02-032 Mn: KRISS CRM 105-02-018 Ca: KRISS CRM 105-02-007 Mg: Perkin Elmer

Table 5. APMP.QM-S10: Information reported by the participants for dry mass correction

Institute (Country)	Amount and number of sample aliquots taken for dry mass correction	Correction for dry mass (%)	Uncertainty for dry mass correction
INTI (Argentina)	5 sample aliquots of 1.0 g each.	98.72%	$U_{exp.}$: 0.05% (k=2)
DRiCM (Bangladesh)	2.0±0.0002g with three (03) replications were taken. According to AOAC 934.01.	10.7% of weighted sample	0.02% (Expanded Uncertainty)
NRC (Canada)	1.0 g of three subsamples were taken.	Dry mass correction factor (=dry weight/initial weight) is 0.9808±0.0003 (mean, 1SD).	0.0003
NIM (China)	~1g, n=5	98.79%~98.83%.	0.04% (k=2)
GLHK (Hong Kong, China)	Amount: 1 g/aliquot Number of sample aliquots: 3	Analysis of Zn, Mn, Ca and Mg: 98.9% of weighted sample	Analysis of Zn: 0.01% of the combined standard uncertainty; Analysis of Mn: 0.01% of the combined standard uncertainty; Analysis of Ca: 0.01% of the combined standard uncertainty; Analysis of Mg: 0.01% of the combined standard uncertainty
INRIM (Italy)	3 samples of about 500 mg were used for moisture determination. The procedure suggested by the technical protocol was not applied because no stabile weight was reached after 20 days in desiccator. A thermo-balance (Mettler Toledo HC 103) was used for the mass correction.	The correction for dry mass obtained was 2.7%	associated uncertainty u=0.4%
KEBS (Kenya)	The sample was dried over drierite (anhydrous $CaSO_4$) for twenty five days for dry mass correction.	N/A	N/A
INACAL (Peru)	3 sample aliquots of 1 g each	The dry mass correction is calculated with the formula: 100/(100-Ms), where Ms is the moisture. The result for dry mass correction is: 1,030	The relative standard uncertainty for the dry mass correction is 1,2 %
VNIIFTRI (Russian Federation)	6 aliquots of approximately 1.5 g of the sample	Correction for dry mass was 0.53 % of weighted sample.	Standard uncertainty for dry mass correction was 0.02 % of weighted sample.

Institute (Country)	**Amount and number of sample aliquots taken for dry mass correction**	**Correction for dry mass (%)**	**Uncertainty for dry mass correction**
HSA (Singapore)	~1.0 g, n = 3	Mean moisture content 1.16 (%) or 0.98838	0.00020
JSI (Slovenia)	Aliquots varied from 1.1 to 1.3 g. 4 aliquots were taken in this study.	The dry mass obtained for APMP.QM-S10 Food supplement from four replicates was 98.0285% (1.9715% moisture content). Results for all elements were multiplied with the correction factor for dry mass 1.0201 (100/98.0285=1.0201).	The relative uncertainty of F_{dry_mass} is 0.15 %.
NIMT (Thailand)	Weight taken: Approximately 1 g of samples Number of sample aliquots taken: 3	Dry mass: 99.0% of weighted sample	0.06%
INRAP (Tunisia)	The amount of sample is 1 g The number of sample aliquot taken for elemental analysis is 16		The uncertainty for the dry mass correction is estimated to 0.15%
VMI (Vietnam)	N/A	N/A	N/A

5. Results and Discussion

5.1. General

The reported results for Zinc, Manganese, Calcium and Magnesium sorted in an ascending order are presented in Tables 6, 7, 8 and 9 respectively. All measurement results were reported on a dry mass basis for comparability purpose.

Table 6. APMP.QM-S10: Reported results for Zinc

Institute (Country)	Reported value (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor k (95% level of confidence)	Expanded uncertainty (mg/kg)	Analytical instrument / Method
KEBS (Kenya)	Not detected	-	-	-	Single Quad ICP-MS / GSA
DRiCM (Bangladesh)	10147.74	542.5	2	1085	FAAS / Gravimetric standard addition (GSA)
VMI (Vietnam)	10573	160	2	320	ICP-MS / Standard addition
NIMT (Thailand)	10700	120	2	240	ICP-MS/MS / IDMS
HSA (Singapore)	10984	140	2	281	ICP-HR-MS / IDMS
GLHK (Hong Kong, China)	11000	138	2	275	ICP-AES / GSA
JSI (Slovenia)	11061	258	2	516	k_0-INAA
NRC (Canada)	11070	280	2	560	HR-ICP-MS and ICP-OES / Triple IDMS and GSA
NIM (China)	11210	44	2	90	ICP-OES / External curve
INACAL (Peru)	11233	168	2	337	ICP-OES / GSA
INRIM (Italy)	11371	193	2	387	INAA
INTI (Argentina)	11831	273	2	546	ICP-OES / GSA
VNIIFTRI (Russian Federation)	12760	540	2	1080	HR-ICP-OES / GSA
INRAP (Tunisia)	13215	263	2	527	ICP-AES / Standard calibration

Table 7. APMP.QM-S10: Reported results for Manganese

Institute (Country)	Reported value (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor k (95% level of confidence)	Expanded uncertainty (mg/kg)	Analytical instrument / Method
KEBS (Kenya)	Not detected	-	-	-	Single Quad ICP-MS / GSA
DRiCM (Bangladesh)	3299.79	35	2	70	FAAS / GSA
VMI (Vietnam)	3585	27	2	54	ICP-MS / Standard addition
HSA (Singapore)	3686	45	2	90	ICP-MS / Gravimetric standard addition
NIMT (Thailand)	3700	77	2	160	ICP-MS/MS / GSA
NRC (Canada)	3700	70	2	140	HR-ICP-MS and ICP-OES / GSA
INRIM (Italy)	3700	52	2	104	INAA
GLHK (Hong Kong, China)	3710	58	2	115	ICP-AES / GSA
JSI (Slovenia)	3722	94	2	188	k_0-INAA
NIM (China)	3730	22	2	50	ICP-OES / External curve
INACAL (Peru)	3836	58	2	115	ICP-OES / GSA
INTI (Argentina)	3941	148	2	296	ICP-OES / GSA
VNIIFTRI (Russian Federation)	3950	160	2	320	HR-ICP-OES / GSA
INRAP (Tunisia)	3988	80	2	161	ICP-AES / Standard calibration

Table 8. APMP.QM-S10: Reported results for Calcium

Institute (Country)	Reported value (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor k (95% level of confidence)	Expanded uncertainty (mg/kg)	Analytical instrument / Method
KEBS (Kenya)	2415	32	2	64	Single Quad ICP-MS / GSA
INRAP (Tunisia)	110095	2468	2	4936	ICP-AES / Standard calibration
JSI (Slovenia)	112408	3396	2	6792	k_0-INAA
INTI (Argentina)	117835	2824	2	5648	ICP-OES / GSA
NRC (Canada)	119000	1100	2	2200	HR-ICP-MS and ICP-OES / GSA
GLHK (Hong Kong, China)	120000	2160	2	4320	ICP-AES / GSA
NIM (China)	120000	960	2	2000	ICP-OES / External curve
HSA (Singapore)	120030	1667	2	3334	ICP-OES / Gravimetric standard addition
INACAL (Peru)	120912	1814	2	3627	ICP-OES / GSA
VNIIFTRI (Russian Federation)	121000	5100	2	10200	HR-ICP-OES / GSA
DRiCM (Bangladesh)	123662.08	1173	2	2346	FAAS / GSA
VMI (Vietnam)	166321	1846	2	3692	ICP-MS / Standard addition

Table 9. APMP.QM-S10: Reported results for Magnesium

Institute (Country)	Reported value (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor k (95% level of confidence)	Expanded uncertainty (mg/kg)	Analytical instrument / Method
KEBS (Kenya)	680	16	2	32	Single Quad ICP-MS / GSA
VMI (Vietnam)	64229	1679	2	3358	ICP-MS / Standard addition
JSI (Slovenia)	64582	1822	2	3644	k_0-INAA
NRC (Canada)	64800	700	2	1400	HR-ICP-MS and ICP-OES / Triple IDMS and GSA
NIM (China)	65300	640	2	1300	ICP-OES / External curve
INRAP (Tunisia)	65389	1226	2	2452	ICP-AES / Standard calibration
DRiCM (Bangladesh)	65527.45	1805.5	2	3611	FAAS / GSA
INTI (Argentina)	65958	2050	2	4100	ICP-OES / GSA
GLHK (Hong Kong, China)	65980	1090	2	2180	ICP-AES / GSA
HSA (Singapore)	65985	890	2	1780	ICP-HR-MS / IDMS
INACAL (Peru)	66190	993	2	1986	ICP-OES / GSA
VNIIFTRI (Russian Federation)	68600	1950	2	3900	HR-ICP-OES / GSA

5.2. Calculation of the reference mass fraction values and associated uncertainties

In order to establish the degrees of equivalence (DoE) of the measurement results submitted by the participants of APMP.QM-S10, a supplementary comparison reference value (SCRV) was calculated for each measurand as a consensus value of the reported results [5]. Moreover, all submitted results should be included in the comparison report and a DoE calculated for each one.

GLHK, as the coordinating laboratory, prepared and circulated the 1st Initial Result Summary to the participants on 20 April 2017 for checking any transcription and typographical errors. Participating institutes are requested to review their own results and inform the coordinating laboratory, together with reasons, if they identify any measurement problems which could explain errors on the reported results. GLHK discussed the measurement results shown in the 1st Initial Result Summary at the CCQM IAWG Meeting (24 – 25 April 2017). Among other issues, the observations on calibrants' traceability and the dry mass correction methodology used by some participants aroused specific concern in the meeting. As a follow-up, the coordinating laboratory asked for participants' clarification to address the findings. The observations and clarifications provided by some participants are shown as follows:

Table 10. Observations and clarification provided by some participants

Institute (Country)	Observations	Clarification provided by participant
INRIM (Italy)	Calibrants' details are incomplete	Participant supplemented additional information to clarify the traceability of calibrants used for the analysis.
VNIIFTRI (Russian Federation)	Calibrants are originated from commercial supplier	Participant confirmed the use of commercial standards as calibrants.
DRiCM (Bangladesh)	Calibrants are originated from commercial supplier	Participant confirmed the use of commercial standards as calibrants.
KEBS (Kenya)	(i) Calibrants are originated from commercial supplier (ii) Dry mass correction was not mentioned in the record	Participant confirmed the use of commercial standards as calibrants and the sample was dried over drierite (anhydrous $CaSO_4$) for twenty five days for dry mass correction.
VMI (Vietnam)	(i) One calibrant (Mg) is originated from commercial supplier (ii) "N/A" was recorded for dry mass correction	Participant did not response to enquiries.

According to the Technical Protocol, participants requested to report their results on a dry mass basis. It is noted that the result submitted by VMI was not mentioned to perform any dry mass correction for its result. In this regard, all results submitted by VMI (Zn, Mn, Ca and Mg) were excluded on technical grounds in the calculation of SCRV.

With reference to the discussion within the CCQM IAWG meetings held on 24-25 April 2017 and 26-28 September 2017 and the minutes of the meetings, the values based on commercial calibrants should be excluded from the calculation of SCRV, noting that they do not comply with the CIPM MRA requirement for SI traceability. Therefore, the results submitted by DRiCM (Zn, Mn, Ca and Mg), KEBS (Zn, Mn, Ca and Mg), VMI (Mg) and VNIIFTRI (Zn, Mn, Ca and Mg) were excluded in the calculation of SCRV. Besides, these participants would need to satisfy the review of any future CMCs that appropriate calibrants were being used.

Based on the valid measurement results, GLHK prepared and circulated the Draft A Report to the participants on 5 March 2018 for checking and comments. The coordinating laboratory received two replies related to the addition of participants' name in acknowledgement, revised the inconsistency of a result of one participant shown in the respective result table and its corresponding SCRV, and suggestion to calculate u(SCRV)s using additional statistical model specified in the reference document "CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, Version: 10". GLHK discussed the revised measurement results shown in the Draft A Report at the CCQM IAWG Meeting (16-18 April 2018) with two uncertainty calculation models (MADe and MADe+) for median. Through the discussion, u(SCRV)s of this comparison were confirmed to use MADe in the meeting.

With reference to the valid measurement results shown in Tables 6-9, the consensus values and their dispersion of the participants' results calculated using the following different statistical quantifiers are summarised in Table 11.

- Arithmetic mean, standard deviation
- Median, MADe [median absolute deviation (MAD) multiplied by 1.483]

As shown in Table 11, a good agreement was observed among the consensus values calculated as the arithmetic mean and median for Zn, Mn, Ca and Mg.

Table 11. APMP.QM-S10: Results of various consensus values and their dispersion (unit: mg/kg)

Measurand	Arithmetic mean (Note i)	Standard deviation	n	Standard uncertainty (Note ii)
Zn	11 368	713	10	226
Mn	3 771	111	10	35
Ca	117 535	4 029	8	1 425
Mg	65 523	601	8	213
Measurand	**Median (Note i)**	**MADe**	**n**	**Standard uncertainty of MADe (Note iii)**
Zn	11 140	219	10	87
Mn	3 716	24	10	9
Ca	119 500	1 440	8	636
Mg	65 674	508	8	224

Notes:

(i) The measurement results that were not included in the calculation of arithmetic mean and median are as follows:

Zinc: DRiCM, KEBS, VMI and VNIIFTRI

Manganese: DRiCM, KEBS, VMI and VNIIFTRI

Calcium: DRiCM, KEBS, VMI and VNIIFTRI

Magnesium: DRiCM, KEBS, VMI and VNIIFTRI

(ii) The standard uncertainty is calculated as follows:

$$\text{standard uncertainty} = \frac{\text{standard deviation}}{\sqrt{n}}$$

where n is the participants' results included in the calculation.

(iii) The standard uncertainty is calculated as follows:

$$\text{standard uncertainty} = 1.25 \times \frac{\text{MADe}}{\sqrt{n}}$$

$$\text{MADe} = 1.483 \times \text{median}(|x_i - \text{SCRV}|)$$

where n is the participants' results included in the calculation.

As the arithmetic mean is not robust to the presence of extreme values, where leaving them in has the effect of skewing the mean values, this statistical quantifier is not recommended to be used as the estimation of SCRV. On the other hand, the median is a simple and robust estimator of SCRV. To this end and the discussion in April 2018 IAWG Meeting, the median and the standard uncertainty derived from MADe were recommended to be the SCRV and u(SCRV) respectively. The standard uncertainty derived from MADe was calculated using the equation (3), where n is the number of participants' results included in the calculation. Following the CCQM Guidance Note [5], the supplementary comparison expanded uncertainty was calculated as U(SCRV) = 2 × u(SCRV). The calculated SCRV, u(SCRV) and U(SCRV) are summarised in Table 12.

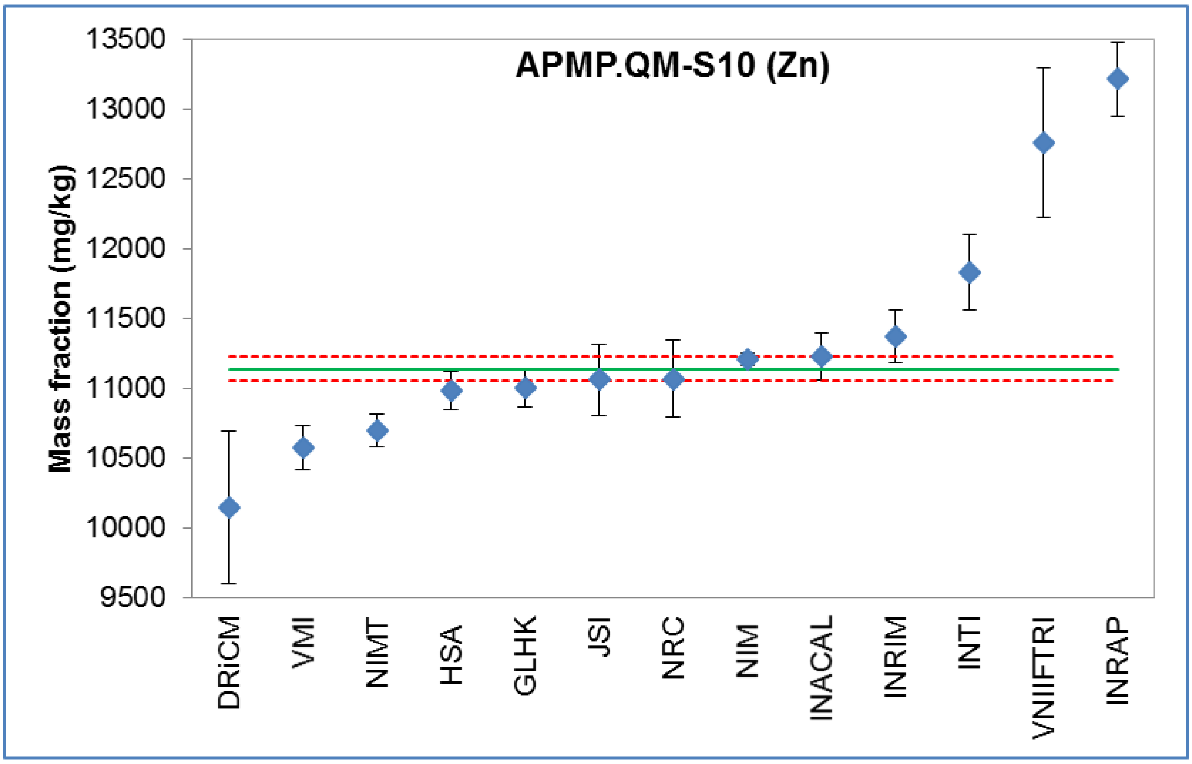
$$u(\mathrm{SCRV}) = 1.25 \times \frac{\mathrm{MADe}}{\sqrt{n}} \qquad (3)$$

Table 12. Calculated SCRV, *u*(SCRV) and *U*(SCRV)

Measurand	SCRV	*u*(SCRV)	*U*(SCRV)	*U*(SCRV)
Zn	11 140 mg/kg	87 mg/kg	174 mg/kg	1.6%
Mn	3716 mg/kg	9 mg/kg	19 mg/kg	0.5%
Ca	119 500 mg/kg	636 mg/kg	1 273 mg/kg	1.1%
Mg	65 674 mg/kg	224 mg/kg	449 mg/kg	0.7%

For ease of reference, the measurement results of the APMP.QM-S10 are presented in Figures 1-4 with the respective SCRV (as median) and u(SCRV). The solid horizontal line in red is the proposed SCRV and the dashed lines show the standard uncertainty of the proposed reference value, u(SCRV). The error bar line of an individual participant's result covers the reported result ± standard uncertainty.

Figure 1. APMP.QM-S10: Participants' reported results and measurement uncertainties for Zinc (unit: mg/kg)



Notes:

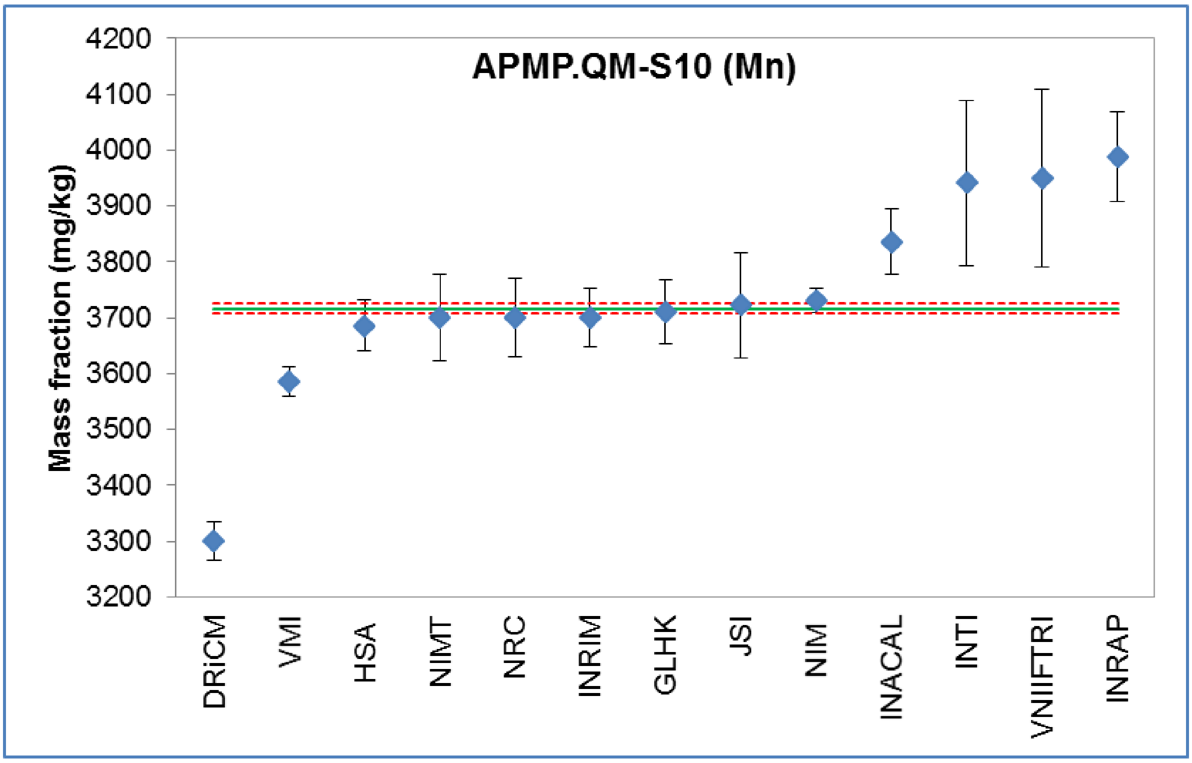
(i) Participants' results are displayed with error bars representing reported standard uncertainties. The solid green line is the proposed SCRV (as median) of the participants' results and the red dashed lines indicate the range of the standard uncertainty, *u*(SCRV).

(ii) APMP.QM-S10: 14 institutes registered and 14 institutes submitted the results.

(iii) KEBS reported "not detected" for Zn, the result submitted by KEBS was not shown in Figure 1.

(iv) The result submitted by DRiCM, KEBS, VMI and VNIIFTRI were excluded in the calculation of SCRV. Please refer to Section 5.2 for details.

Figure 2. APMP.QM-S10: Participants' reported results and measurement uncertainties for Manganese (unit: mg/kg)



Notes:

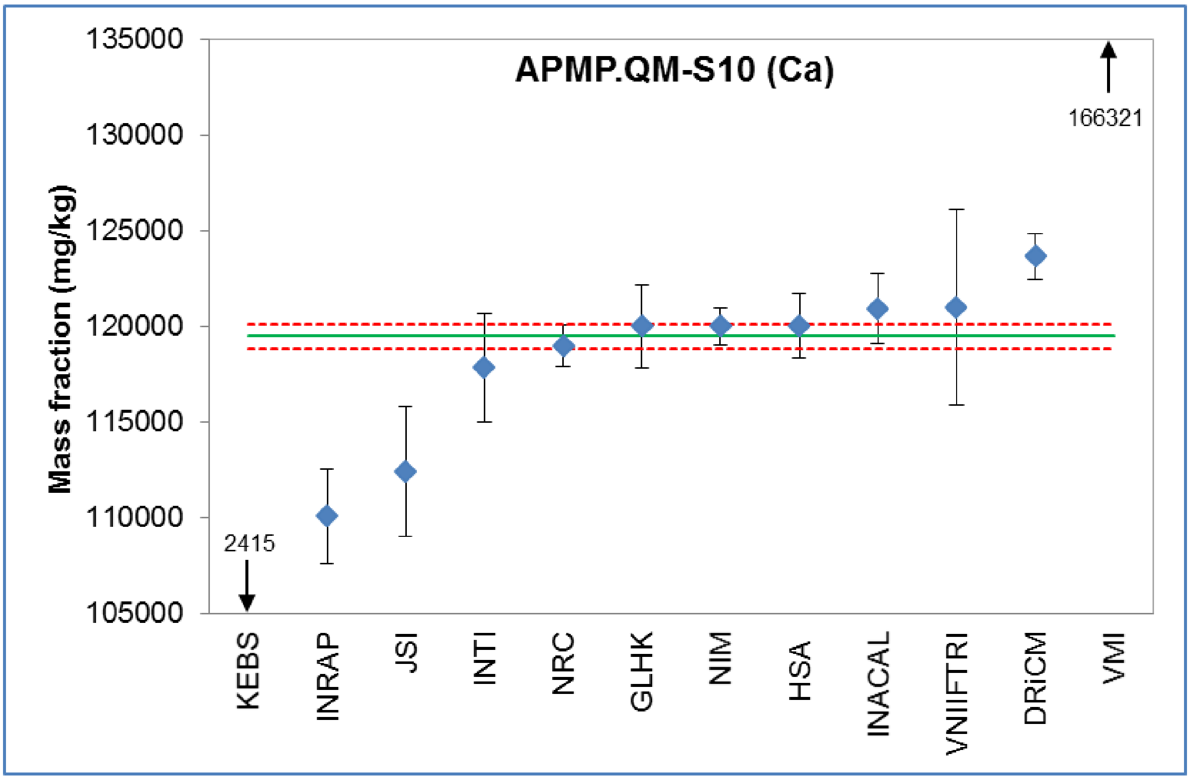
(i) Participants' results are displayed with error bars representing reported standard uncertainties. The solid green line is the proposed SCRV (as median) of the participants' results and the red dashed lines indicate the range of the standard uncertainty, *u*(SCRV).

(ii) APMP.QM-S10: 14 institutes registered and 14 institutes submitted the results.

(iii) KEBS reported "not detected" for Mn, the result submitted by KEBS was not shown in Figure 2.

(iv) The result submitted by DRiCM, KEBS, VMI and VNIIFTRI were excluded in the calculation of SCRV. Please refer to Section 5.2 for details.

Figure 3. APMP.QM-S10: Participants' reported results and measurement uncertainties for Calcium (unit: mg/kg)



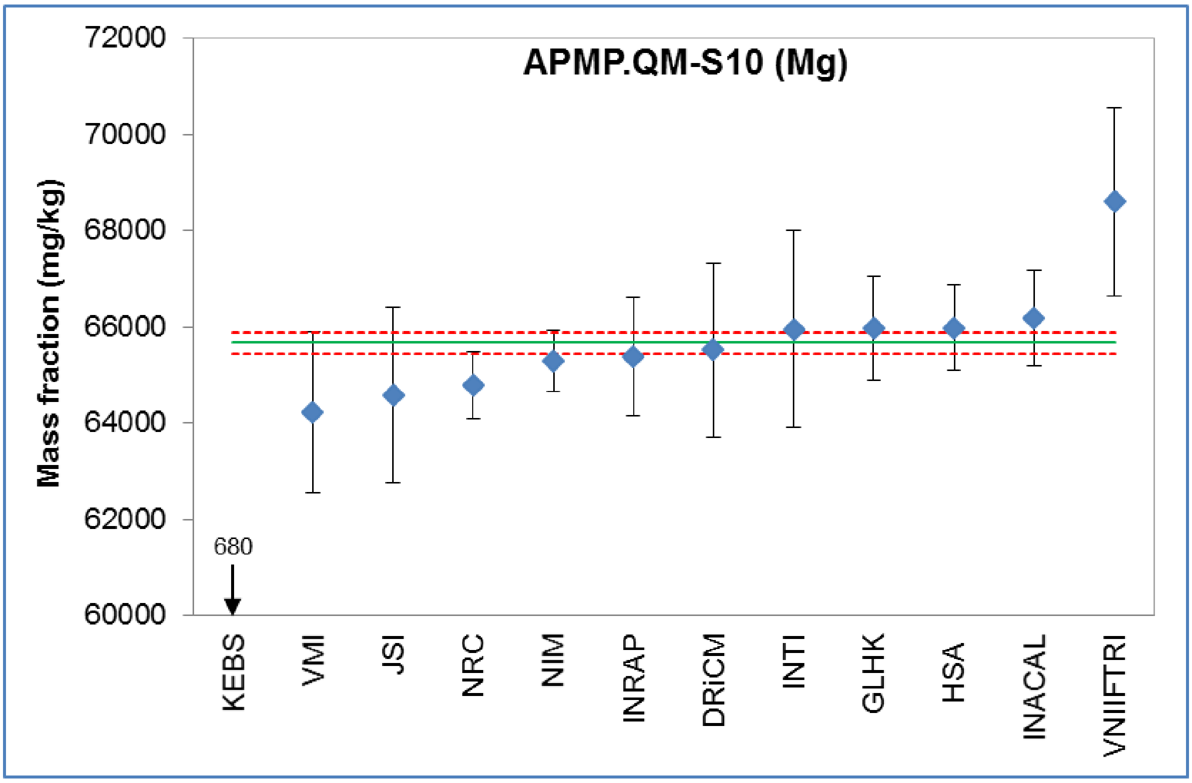
Notes:

(i) Participants' results are displayed with error bars representing reported standard uncertainties. The solid green line is the proposed SCRV (as median) of the participants' results and the red dashed lines indicate the range of the standard uncertainty, *u*(SCRV).

(ii) APMP.QM-S10: 14 institutes registered and 12 institutes submitted the results.

(iii) The result submitted by DRiCM, KEBS, VMI and VNIIFTRI were excluded in the calculation of SCRV. Please refer to Section 5.2 for details.

Figure 4. APMP.QM-S10: Participants' reported results and measurement uncertainties for Magnesium (unit: mg/kg)



Notes:

(i) Participants' results are displayed with error bars representing reported standard uncertainties. The solid green line is the proposed SCRV (as median) of the participants' results and the red dashed lines indicate the range of the standard uncertainty, *u*(SCRV).

(ii) APMP.QM-S10: 14 institutes registered and 12 institutes submitted the results.

(iii) The result submitted by DRiCM, KEBS, VMI and VNIIFTRI were excluded in the calculation of SCRV. Please refer to Section 5.2 for details.

5.3. Equivalence statements

According to the CCQM Guidance Note [2], the degree of equivalence (DoE) and its uncertainty of a measurement result reported by a participating NMI/DI with respect to the SCRV can be calculated using the following equations (4)-(5):

$$d_i = (x_i - \mathrm{SCRV}) \quad (4)$$

$$U(d_i) = 2 \cdot \sqrt{u^2(x_i) + u^2(\mathrm{SCRV})} \quad (5)$$

where

x_i is the reported value from the i^{th} participant (i = 1 to n);

d_i is the difference between the reported value and the SCRV; and

$U(d_i)$ is the expanded uncertainty (k = 2) of the difference d_i at a 95% level of confidence.

It is possible for the values of d_i and $U(d_i)$ published in this report to differ slightly from the values of d_i and $U(d_i)$ that can be calculated using the equations given in (4)-(5). These differences arise from the necessary rounding of the SCRV and u(SCRV) prior to their publication in Tables 13 to 16. The relative values of d_i and $U(d_i)$ are expressed as percent of SCRV. The equivalence statements for APMP.QM-S10 based on the proposed SCRV are given in Tables 13 to 16 and are shown graphically in Figures 5 to 8.

Table 13. APMP.QM-S10: Equivalence Statement for Zinc based on the use of median as the robust estimation of SCRV

Institute	**Reported value, x_i (mg/kg)**	**Reported standard uncertainty, $u(x_i)$ (mg/kg)**	**Difference from SCRV, d_i (mg/kg)**	**$U(d_i)$ (mg/kg)**	**$\frac{d_i}{U(d_i)}$**	**d_i relative value (%)**	**$U(d_i)$ relative value (%)**
DRiCM	10147.74**	542.5	-992.26	1098.73	-0.90	-8.91	9.9
VMI	10573**	160	-567	363.83	-1.56	-5.09	3.3
NIMT	10700	120	-440	295.93	-1.49	-3.95	2.7
HSA	10984	140	-156	329.20	-0.47	-1.40	3.0
GLHK	11000	138	-140	325.81	-0.43	-1.26	2.9
JSI	11061	258	-79	544.27	-0.15	-0.71	4.9
NRC	11070	280	-70	586.15	-0.12	-0.63	5.3
NIM	11210	44	70	194.22	0.36	0.63	1.7
INACAL	11233	168	93	377.98	0.25	0.83	3.4
INRIM	11371	193	231	423.05	0.55	2.07	3.8
INTI	11831	273	691	572.79	1.21	6.20	5.1
VNIIFTRI	12760**	540	1620	1093.79	1.48	14.54	9.8
INRAP	13215	263	2075	553.76	3.75	18.63	5.0

Notes:

* KEBS reported “not detected” for Zn, the equivalence statement of KEBS was not shown in Table 13.

** The result submitted by DRiCM, VMI and VNIIFTRI were excluded in the calculation of SCRV. Please refer to Section 5.2 for details.

Table 14. APMP.QM-S10: Equivalence Statement for Manganese based on the use of median as the robust estimation of SCRV

Institute	**Reported value, x_i (mg/kg)**	**Reported standard uncertainty, $u(x_i)$ (mg/kg)**	**Difference from SCRV, d_i (mg/kg)**	**$U(d_i)$ (mg/kg)**	$\frac{d_i}{U(d_i)}$	**d_i relative value (%)**	**$U(d_i)$ relative value (%)**
DRiCM	3299.79**	35	-416.21	72.47	-5.74	-11.20	2.0
VMI	3585**	27	-131	57.17	-2.29	-3.53	1.5
HSA	3686	45	-30	91.93	-0.33	-0.81	2.5
NIMT	3700	77	-16	155.14	-0.10	-0.43	4.2
NRC	3700	70	-16	141.25	-0.11	-0.43	3.8
INRIM	3700	52	-16	105.68	-0.15	-0.43	2.8
GLHK	3710	58	-6	117.51	-0.05	-0.16	3.2
JSI	3722	94	6	188.93	0.03	0.16	5.1
NIM	3730	22	14	47.83	0.29	0.38	1.3
INACAL	3836	58	120	117.51	1.02	3.23	3.2
INTI	3941	148	225	296.59	0.76	6.05	8.0
VNIIFTRI	3950**	160	234	320.55	0.73	6.30	8.6
INRAP	3988	80	272	161.10	1.69	7.32	4.3

Notes:

* KEBS reported “not detected” for Zn, the equivalence statement of KEBS was not shown in Table 14.

** The result submitted by DRiCM, VMI and VNIIFTRI were excluded in the calculation of SCRV. Please refer to Section 5.2 for details.

Table 15. APMP.QM-S10: Equivalence Statement for Calcium based on the use of median as the robust estimation of SCRV

Institute	Reported value, x_i (mg/kg)	Reported standard uncertainty, $u(x_i)$ (mg/kg)	Difference from SCRV, d_i (mg/kg)	$U(d_i)$ (mg/kg)	$\frac{d_i}{U(d_i)}$	d_i relative value (%)	$U(d_i)$ relative value (%)
KEBS	2415*	32	-117085	1274.39	-91.88	-97.98	1.1
INRAP	110095	2468	-9405	5097.46	-1.85	-7.87	4.3
JSI	112408	3396	-7092	6910.23	-1.03	-5.93	5.8
INTI	117835	2824	-1665	5789.64	-0.29	-1.39	4.8
NRC	119000	1100	-500	2541.65	-0.20	-0.42	2.1
GLHK	120000	2160	500	4503.60	0.11	0.42	3.8
NIM	120000	960	500	2303.56	0.22	0.42	1.9
HSA	120030	1667	530	3568.69	0.15	0.44	3.0
INACAL	120912	1814	1412	3844.78	0.37	1.18	3.2
VNIIFTRI	121000*	5100	1500	10279.10	0.15	1.26	8.6
DRiCM	123662.08*	1173	4162.08	2669.03	1.56	3.48	2.2
VMI	166321*	1846	46821	3905.23	11.99	39.18	3.3

Note:

* The result submitted by DRiCM, KEBS, VMI and VNIIFTRI were excluded in the calculation of SCRV. Please refer to Section 5.2 for details.

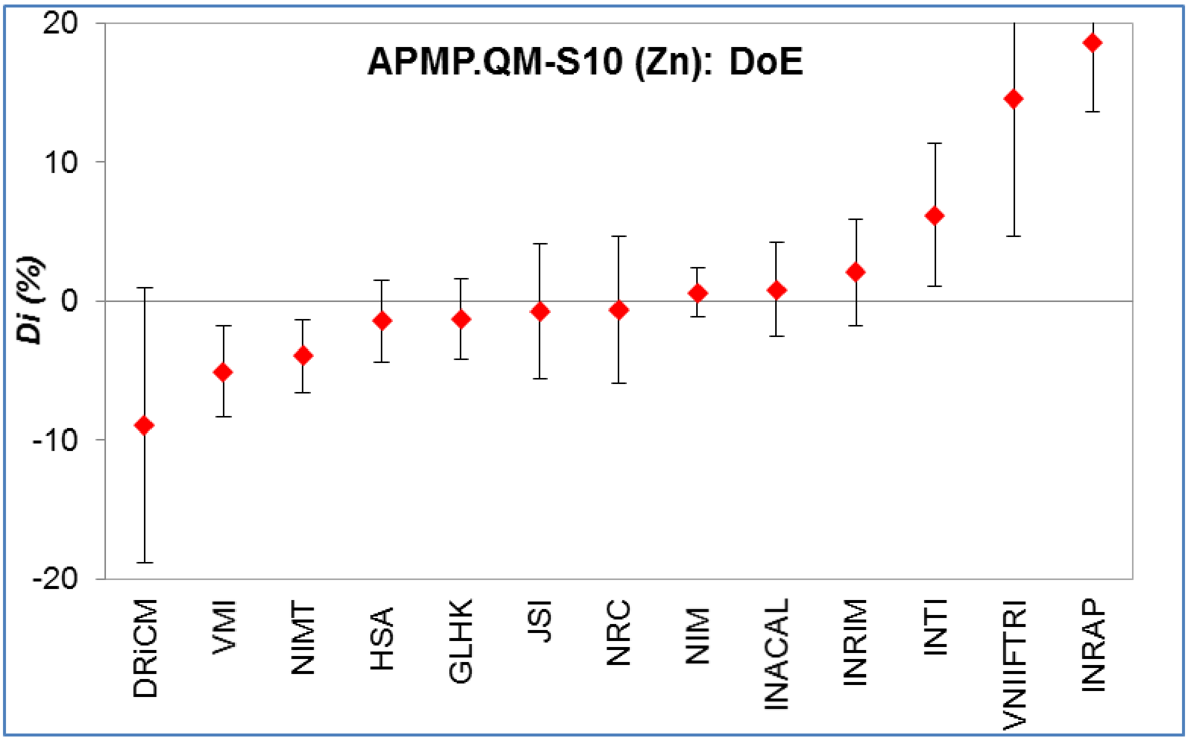
Table 16. APMP.QM-S10: Equivalence Statement for Magnesium based on the use of median as the robust estimation of SCRV

Institute	Reported value, x_i (mg/kg)	Reported standard uncertainty, $u(x_i)$ (mg/kg)	Difference from SCRV, d_i (mg/kg)	$U(d_i)$ (mg/kg)	$\frac{d_i}{U(d_i)}$	d_i relative value (%)	$U(d_i)$ relative value (%)
KEBS	680*	16	-64994	450	-144.40	-98.96	0.7
VMI	64229*	1679	-1445	3388	-0.43	-2.20	5.2
JSI	64582	1822	-1092	3672	-0.30	-1.66	5.6
NRC	64800	700	-874	1470	-0.59	-1.33	2.2
NIM	65300	640	-374	1356	-0.28	-0.57	2.1
INRAP	65389	1226	-285	2493	-0.11	-0.43	3.8
DRiCM	65527.45*	1805.5	-146.05	3639	-0.04	-0.22	5.5
INTI	65958	2050	285	4125	0.07	0.43	6.3
GLHK	65980	1090	307	2226	0.14	0.47	3.4
HSA	65985	890	312	1836	0.17	0.47	2.8
INACAL	66190	993	517	2036	0.25	0.79	3.1
VNIIFTRI	68600*	1950	2927	3926	0.75	4.46	6.0

Note:

* The result submitted by DRiCM, KEBS, VMI and VNIIFTRI were excluded in the calculation of SCRV. Please refer to Section 5.2 for details.

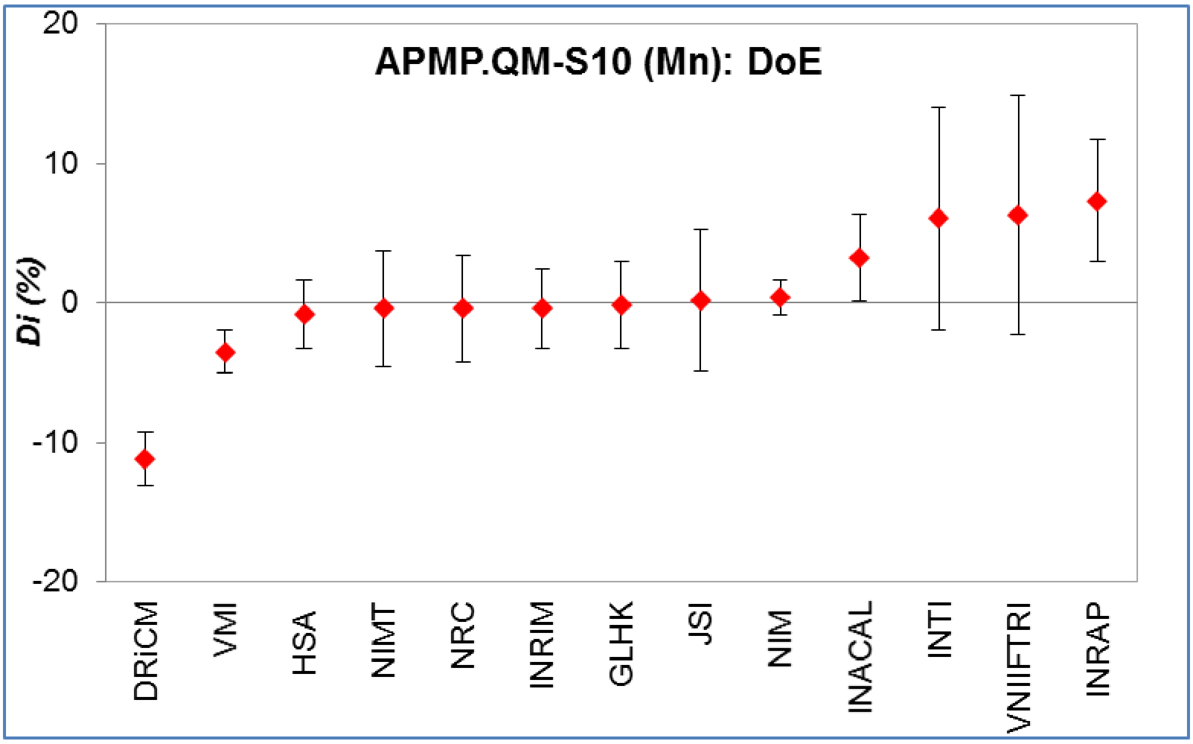
Figure 5. APMP.QM-S10: Equivalence Statement for Zinc based on the use of median as the robust estimation of SCRV



Note:

(i) The half of each bar indicates $U(d_i)$, relative value (%).

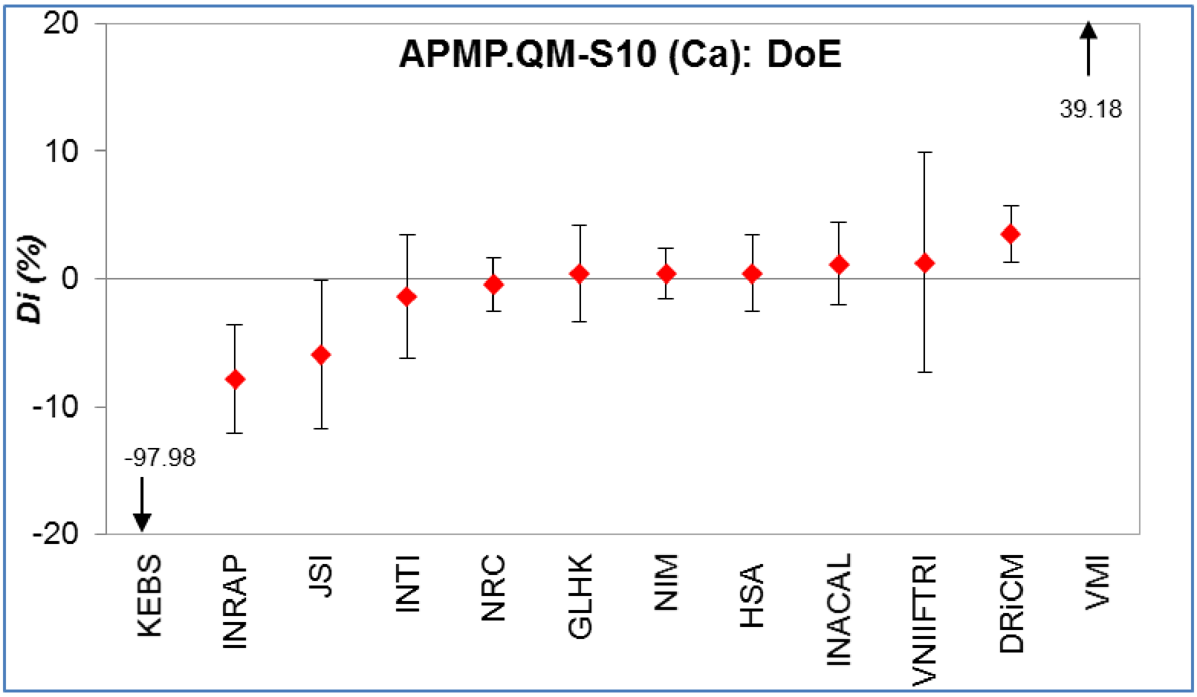
Figure 6. APMP.QM-S10: Equivalence Statement for Manganese based on the use of median as the robust estimation of SCRV



Note:

(i) The half of each bar indicates $U(d_i)$, relative value (%).

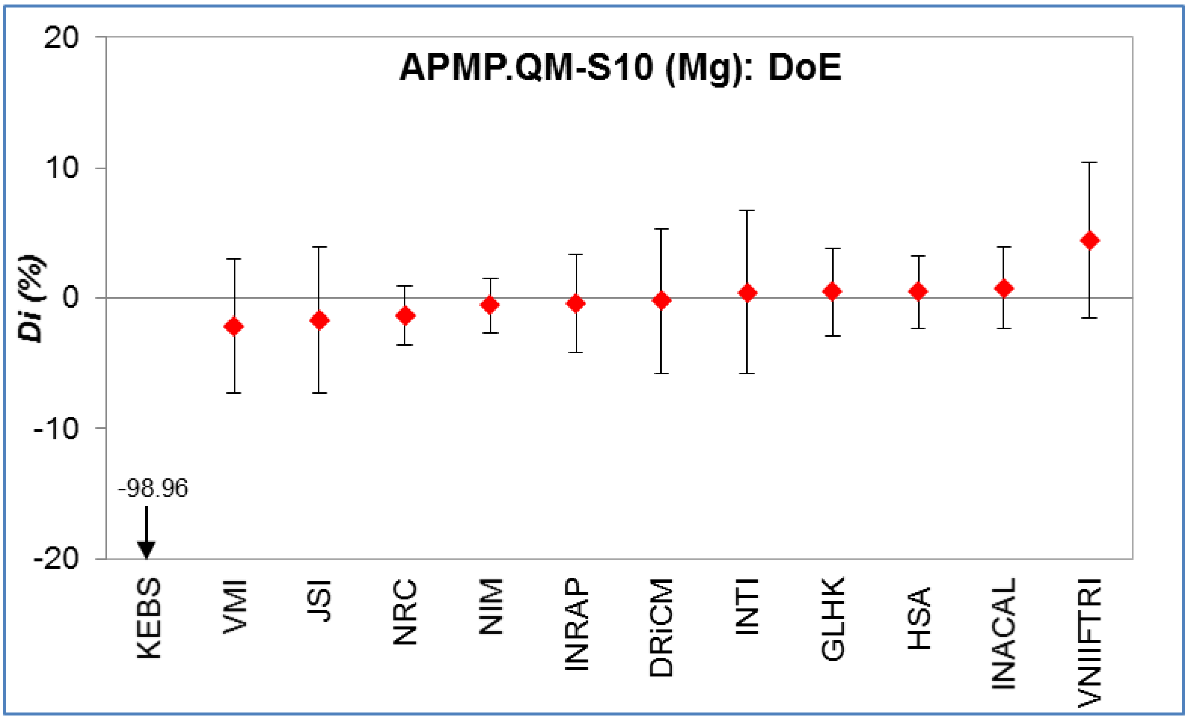
Figure 7. APMP.QM-S10: Equivalence Statement for Calcium based on the use of median as the robust estimation of SCRV



Note:

(i) The half of each bar indicates $U(d_i)$, relative value (%).

Figure 8. APMP.QM-S10: Equivalence Statement for Magnesium based on the use of median as the robust estimation of SCRV



Note:

(i) The half of each bar indicates $U(d_i)$, relative value (%).

6. Demonstration of Core Capabilities

As agreed in previous CCQM IAWG meetings, a system of Core-Capabilities for inorganic analysis would be employed in key/supplementary comparisons starting from CCQM-K75 onward. This strategy is to improve the efficiency and effectiveness of key/supplementary comparisons to support CMC claims. With the use of the system, new CMC claims can be supported by describing core capabilities that are required to deliver the claimed measurement service and by referencing core capabilities that were successfully demonstrated by participation in relevant key/supplementary comparisons. In this connection, all participants were requested to submit their Inorganic Core Capabilities (CCs) Tables to the coordinating laboratory for compilation. On 15 April 2017, VMI submitted their Report Form but the CCs Table was not included. Two reminders were sent on 16 August 2017 and 08 December 2017 but no further reply, therefore, the corresponding participant's information was not included in the Summary Table. The returns are summarized in the Appendix.

7. Acknowledgements

The contributions from the contract persons and/or analysts of participating NMIs/DIs, as listed below, are highly appreciated and acknowledged.

Institute	Contact person and/or analysts
INTI	Nadia Hatamleh, Mabel Puelles and Hernán Lozano
DRiCM	Mala Khan
NRC	Lu Yang, Indu Gedara Pihillagawa, Kenny Nadeau and Zoltan Mester
NIM	Chao Wei and Xiao Li
GLHK	Della Wai-mei Sin, Alvin Wai-hong Fung, Yuk-tai Tsoi, Ping-yuk Cheung and Kam-yiu Tsui
INRIM	Luigi Bergamaschi
KEBS	Tom Oduor Okumu
INACAL	Christian Uribe
VNIIFTRI	Aleksei Stakheev
HSA	Richard Shin, Sim Lay Peng, Fransiska Dewi, Benny Tong and Leung Ho Wah
JSI	Radojko Jaćimović
NIMT	Usana Thiengmanee
INRAP	Hanen Klich, Jebali Raouf, Najet Chaabene and Soumaya Chaieb
VMI	Huy Thành Ngô

The coordinating laboratory would like to thank Dr. Mike Sargent (CCQM IAWG Chair) and Prof. Ma Liandi (APMP/TCQM Chair) for providing guidance throughout the course of the study.

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Appendix

Inorganic Core Capabilities Table
Summary Table

APMP Study: APMP.QM-S10 Elements in Food Supplement

Institutes (s): NRC (Mn, Ca), KEBS (Zn, Mn, Ca, Mg), HSA (Mn), NIMT (Mn)

Method: ICP-MS / HR-ICP-MS (without isotope dilution)

Analyte(s): Zn, Mn, Ca, Mg

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.*	NIMT	NRC, KEBS, HSA	NRC: contamination is controlled by preparing samples in class-10 or class-100 clean room and use of high purity reagents
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.*	NIMT	NRC, KEBS, HSA	NRC: Mix acids microwave digestion was performed
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.*	HSA	NRC, KEBS, NIMT	NRC: Mix acids microwave digestion was performed NIMT: Not only nitric acid, but also hydrochloric acid was employed for achieving clear digest, under microwave condition used.
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	KEBS, HSA, NIMT		
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, HSA, NIMT		
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, HSA, NIMT		

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
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.*	NRC, KEBS, HSA, NIMT		NRC: High resolution was used to resolve the polyatomic interferences.
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		KEBS, HSA	HSA: Standard addition was used.
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.*	NIMT	NRC, KEBS, HSA	NRC: Adequate sensitivity KEBS: The signals for manganese and zinc were too low and therefore the two elements could not be quantified during the measurements.
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	HSA, NIMT	NRC, KEBS	NRC: Rinsed with 3% HCl and 1% HNO_3 solution, and no significant memory effect was observed.
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.*	NIMT	NRC, KEBS, HSA	NRC: High resolution was used to resolve the polyatomic interferences.
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.*	KEBS	HSA	HSA: Standard addition was used.
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	KEBS, HSA, NIMT	NRC	
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	KEBS, HSA, NIMT	NRC	

Inorganic Core Capabilities Table
Summary Table

APMP Study: APMP.QM-S10 Elements in Food Supplement

Institute(s): INTI (Zn, Mn, Ca, Mg), NRC (Zn, Mn, Ca, Mg), NIM (Zn, Mn, Ca, Mg),
GLHK (Zn, Mn, Ca, Mg), INACAL (Zn, Mn, Ca, Mg), VNIIFTRI (Zn, Mn, Ca, Mg),
HSA (Ca), INRAP (Zn, Mn, Ca, Mg)

Method: ICP-OES

Analyte(s): Zn, Mn, Ca, Mg

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.*	NIM, INRAP	INTI, NRC, GLHK, INACAL, VNIIFTRI, HSA	INTI: Blank Correction NRC: Contamination is controlled by preparing samples in class-10 or class-100 clean room and use of high purity reagents GLHK: Blank control. INACAL: Blank control for digestions and measurements VNIIFTRI: Sub-boiled acid, DI water and pre-treated plastic ware were used to minimize blank.
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.*		INTI, NRC, NIM, GLHK, INACAL, VNIIFTRI, HSA, INRAP	INTI: Microwave-assisted digestion NRC: Mix acid microwave digestion was performed. NIM: HF acid was used for digestion. GLHK: Closed vessel microwave digestion with nitric acid and hydrochloric acid. INACAL: Optimization of the combination of acids for digestion VNIIFTRI: Method with nitric acid was used. Sample is digested in an acid solution. 500 mg of sample was taken into the digestion vessels, then 12 ml of sub-boiled HNO_3 (65%) were added. Heated in microwave system in 4 steps: 1 step: T = 100 ºC, p = 40 bar, power 80%, time 10 min (ramp 10 min); 2 step: T = 140 ºC, p = 40 bar, power 90%, time 10 min (ramp 5 min); 3 step: T = 160 ºC, p = 40 bar, power 90%, time 25 min (ramp 5 min); 4 step: T = 180 ºC, p = 40 bar, power 90%, time 15 min (ramp 10 min); After digestion the PTFE vessels was cooled to room temperature and then opened. INRAP: MICROWAVE DIGESTION

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
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.*	INTI, NIM, HSA	NRC, GLHK, VNIIFTRI, INRAP	NRC: Mix acid microwave digestion was performed. GLHK: Closed vessel microwave digestion with nitric acid and hydrochloric acid. VNIIFTRI: Challenge not encountered or challenge not applicable INRAP: MICROWAVE DIGESTION
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	NIM, GLHK, VNIIFTRI, HSA, INRAP	INTI	INTI: Sample Spike for Recovery Evaluation VNIIFTRI: No procedures has been used to prevent the loss of Hg
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.*	INTI, NIM, GLHK, VNIIFTRI, HSA, INRAP		
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.*	INTI, NIM, GLHK, VNIIFTRI, HSA, INRAP		
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 , 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.*	INTI, NIM, GLHK, VNIIFTRI, HSA, INRAP		
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		INTI, NRC, NIM, GLHK, INACAL, VNIIFTRI, HSA, INRAP	INTI: Gravimetric Standard Addition NRC: Good linear calibration was obtained NIM: The calibration standards were prepared with matrix-matching. GLHK: For both Zn, Mn, Ca and Mg, gravimetric standard addition approach utilizing Lu, Sc and Y as an internal standard was employed respectively. INACAL: Single-point internal standard addition VNIIFTRI: Internal standard with 3 points standard additions were used HSA: Standard addition was used.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
			INRAP: External Calibration (standard calibration)
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.*	NIM, HSA	INTI, NRC, GLHK, VNIIFTRI	INTI: Several wavelength analyzed in axial and radial view NRC: With adequate signals GLHK: For Zn, radial view was used. Zn 202.548/Sc 335.372 was selected. For Mn, radial view was used. Mn 257.610/Lu 261.541 was selected. For Ca, radial view was used. Ca 393.366/Y 371.029 was selected. For Mg, radial view was used. Mg 279.553/Y371.029 was selected. VNIIFTRI: Zn and Mn measurements were performed in Axial mode. Ca and Mg measurements were performed in Radial mode. Background reduction / quieting procedures applied.
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	NIM, HSA, INRAP	INTI, NRC, GLHK, VNIIFTRI	INTI: Wash between samples NRC: Not significant, rinsed with 3% HCl and 1% HNO_3 solution. GLHK: 1% HNO_3 rinse performed in between each sample analysis. No significant carry over observed. VNIIFTRI: No significant effect.
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.*	NIM, HSA	INTI, NRC, GLHK, VNIIFTRI, INRAP	INTI: Several wavelength analyzed, background correction, signal line reprocessing NRC: Choose wave lines without significant interference, inter element correction was applied GLHK: Several characteristic emission lines for each analyte were monitored. Matrix CRMs were also analyzed and no significant spectral backgrounds interference were observed. VNIIFTRI: Choose wave lines without significant interferences, IS correction was applied. INRAP: - using different wavelength - using spectral background correction
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.*	INRAP	INTI, NRC, NIM, GLHK, INACAL, VNIIFTRI, HSA	INTI: Use of 0.1% K (Ca and Mg) NRC: Standard additions calibration was applied NIM: The sample digestion solutions were diluted more than 40 times for removal of matrix induced signal suppression or enhancement. GLHK: Gravimetric standard addition was applied.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
			INACAL: Use of single-point internal standard addition to overcome matrix effects VNIIFTRI: Standard additions calibrations were used HSA: Standard addition was used.

Inorganic Core Capabilities Table
Summary Table

APMP Study: APMP.QM-S10 Elements in Food Supplement

Institute(s): NRC (Zn, Mg), HSA (Zn, Mg), NIMT (Zn)

Method: ID-ICP-MS

Analyte(s): Zn, Mg

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.*	NIMT	NRC, HSA	NRC: contamination is controlled by preparing samples in class-10 or class-100 clean room and use of high purity reagents
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.*	NIMT	NRC, HSA	NRC: Mix acids microwave digestion was performed
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.*	HSA	NRC, NIMT	NRC: Mix acids microwave digestion was performed NIMT: Not only nitric acid, but also hydrochloric acid was employed for achieving clear digest, under microwave condition used.
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	HSA, NIMT		
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.*	HSA, NIMT		
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.*	HSA, NIMT		
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*	NRC, HSA, NIMT		NRC: High resolution was used to resolve the polyatomic interferences.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.			
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample.*	NIMT	NRC, HSA	NRC: Samples were microwave digested prior to ICPMS analysis NIMT: It is essential for accurate IDMS and needed to mix well.
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.*	HSA, NIMT	NRC	NRC: Adequate sensitivity
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	HSA, NIMT	NRC	NRC: Rinsed with 3% HCl and 1% HNO_3 solution, and no significant memory effect was observed.
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.*	NIMT	NRC, HSA	NRC: High resolution was used to resolve the polyatomic interferences.
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	NIMT	NRC, HSA	HSA: Sample and calibration blends intensities were matched to reduce the significance of this effect.
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*		NRC, HSA, NIMT	HSA: Sample and calibration blends were bracketed with a standard solution with known isotopic composition to correct for mass bias. NIMT: Use standard solution to monitor mass bias
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*		NRC, HSA, NIMT	HSA: Exact-matching IDMS was used. NIMT: Reverse IDMS to calibrate the isotopic spike

Inorganic Core Capabilities Table
Summary Table

APMP Study: APMP.QM-S10 Elements in Food Supplement

Institute(s): DRiCM (Zn, Mn, Ca, Mg)

Method: FAAS

Analyte(s): Zn, Mn, Ca, Mg

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.*		DRiCM	DRiCM: Preparation of sample was handling in clean room. Acid contamination is a great challenge for Microwave assisted digestion. Ultra-pure acid produced by Acid Distillation Unit was used for blank correction procedure. For every experiment, two separated blank samples were measured. The blank samples were undergone through all analytical procedure stages and contain all reagents, without a sample itself.
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 FAAS.*		DRiCM	DRiCM: About 0.5 g sample was weight of into a microwave vessel. 10 ml of trace metal grade Nitric acid was added. Preparation of procedural blanks was done with the same time as well as same MW digestion system. Cold predigesting was done at room temperature until vigorous foaming subsides. Microwave digestion under operating conditions (With power setting to 1600 W, ramp temperature from ambient to 200°C in 15 min, hold at 200°C for 20 min.). Sample and standards dilution; all solutions are gravimetrically prepared. Appropriate amounts of HNO_3 were added to maintain the proportion of 10 % HNO_3 in the final solution to be analyzed. It was also used to denaturize the organo-metallic bond to metallic ion formation.
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 FAAS.*		DRiCM	DRiCM: Dissolution was carried out carefully and completely because incomplete dissolution may affect the element concentration.
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*		DRiCM	DriCM: MW with closed vessel was used to minimize the volatile element contamination
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.*	DRiCM		
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*		DRiCM	DRiCM: To avoid matrix interference some reagents were added. When determining Ca or Mg, 5 mL lanthanum solution (13.4 g $LaCl_3$. $7H_2O$ was taken volumetric flask and upto mark to 100 mL with Deionized Water) was mixed with 50 mL sample or standard before aspirating. When

ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.			determining Mn 12.5 mL of Ca Solution (0.07 g $CaCl_2$ was taken in 100 mL volumetric flask and upto the mark with DIW) was mixed with 50 mL of sample or standard. Zn was not separated from matrix, but diluted the samples to avoid matrix interference before determination.
Hydride preconcentration/matrix separation of volatile species. *Coupling of a hydride system to the FAAS and optimization of conditions.*	DRiCM		
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.*		DRiCM (Ca, Mg)	DRiCM: Trace Elements in Natural Water (SRM 1640a, Ca: 5.57; Mg: 1.05) was used for matrix matched standards (Experimental value for Ca is 5.39 ppm, Mg is 1.04 ppm)
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).*		DRiCM	DRiCM: Peak height was selected for signal processing
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		DRiCM	DRiCM: Before and after analysis, rinse with 2 % HNO_3 and pure water. For the Teflon tube, before & after it was used for digestion, it was cleaned immersed in 10 mL (1:1) HNO_3 same programing as sample used and was rinsed with pure water.
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.*	DRiCM		
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 (e.g. 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.*			DRiCM:SR, D_2 correction technique was used by default program for the Instrument.

Inorganic Core Capabilities Table
Summary Table

APMP Study: APMP.QM-S10 Elements in Food Supplement

Institute(s): INRIM (Zn, Mn), JSI (Zn, Mn, Ca, Mg)

Method: INAA

Analyte(s): Zn, Mn, Ca, Mg

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).*		INRIM, JSI	INRIM: The method for moisture correction suggested by the protocol has not been adopted because no stable weight has been obtained. For moisture analysis a thermo-balance has been used. JSI: Aliquots varied from 0.33 to 0.35 g. Samples were pelletized using a manual hydraulic press into pellets 10 mm in diameter and 2.2 mm high.
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.)*		INRIM, JSI	INRIM: No relevant problem occurs JSI: IRMM-530R Al-0.1%Au alloy in form of foil with thickness of 0.1 mm was used. Discs of about 7 mm diameter were prepared.
General applications *Procedures associated with specific method of NAA and the evaluation of the associated uncertainties for comparator NAA, k_o NAA, or other method specific parameters not described below.*		INRIM, JSI	INRIM: No relevant problem occurs JSI: 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. Concentration levels in the sample for Ca, Mg, Mn and Zn have to be suitable for INAA.
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.)*		INRIM (Ca, Mg) , JSI	INRIM: Ca and Mg were not determined. The activity produced by matrix elements with longer decay time e.g. Mn is very high, as a consequence no gamma peaks produced by Ca and Mg result detectable. JSI: For peak area evaluation, the HyperLab 2002 program was used.
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.*		INRIM, JSI	INRIM: No relevant problem occurs JSI: No difficulties in net peak areas determination were encountered for Ca-47 at 1297.1 keV, for Mg-27 at 1014.4 keV, for Mn-56 at 846.8 keV and for Zn-65 at 1115.5 keV.
Correction of fast neutron and fission interferences *Procedures used to determine the contributions from fast neutron reactions or*		INRIM, JSI	INRIM: No relevant problem occurs JSI: For Ca-47, Mn-56 and Zn-65 the threshold reactions are negligible. For Mg-27 a small

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
fission of U to the peak area of interest. The level of difficulty is related to the magnitude of the corrections needed.			contribution from Al-27(n,p)Mg-27 is taken into account.
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.*		INRIM, JSI	INRIM: Correction for neutron flux and geometry irradiation was necessary. Gold and cobalt flux monitors were used. JSI: 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.
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.*		INRIM, JSI	INRIM: No relevant problem occurs JSI: Measurements were carried out at such distances that the dead time was kept below 10 % with negligible random coincidences, and dead time correction was taken into account.
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.*		INRIM, JSI	INRIM: No relevant problem occurs JSI: Standard Al-0.1%Au (nuclide Au-198 ($T_{1/2}$=2.695 d) at gamma line of 411.8 keV) was used for axial flux gradient corrections in the sample. Radial flux gradient is negligible due to similar diameter of sample and standard. Thermal and epithermal self-shielding is negligible.
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.*		INRIM, JSI	INRIM: No relevant problem occurs JSI: The samples and standards were irradiated together (see above).
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, JSI	INRIM: No relevant problem occurs JSI: Corrections for gamma-ray attenuation in sample/standard were calculated by the Kayzero for Windows (KayWin®) software based on the sample/standard composition and geometry.

CCQM IAWG Core Capability Matrix Table

Analyte groups	**Matrix challenges**					
	Water	**High Silica content (e.g. Soils, sediments, plants, …)**	**High salts content (e.g. Seawater, urine, …)**	**High organics content (e.g. high carbon) (e.g. Food, blood/serum, cosmetics, …)**	**Difficult to dissolve metals (Autocatalysts, …)**	**High volatile matrices (e.g. solvents, fuels, ...)**
Group I and II: Alkali and Alkaline earth (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba)						
				APMP.QM-S10 (Ca, Mg)		
Transition elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ag, Cd, Ta, W, Au, Hg, Al, Ga, In, Tl, Pb, Po)						
				APMP.QM-S10 (Zn, Mn)		
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)						
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)						
Non-metals (P, S, C, N, O)						
Halogens (F, Cl, Br, I)						
Rare Earth Elements (Lanthanides, Actinides)						

Low level (e.g. below 50 µg/kg)
High level (e.g. above 50 µg/kg)