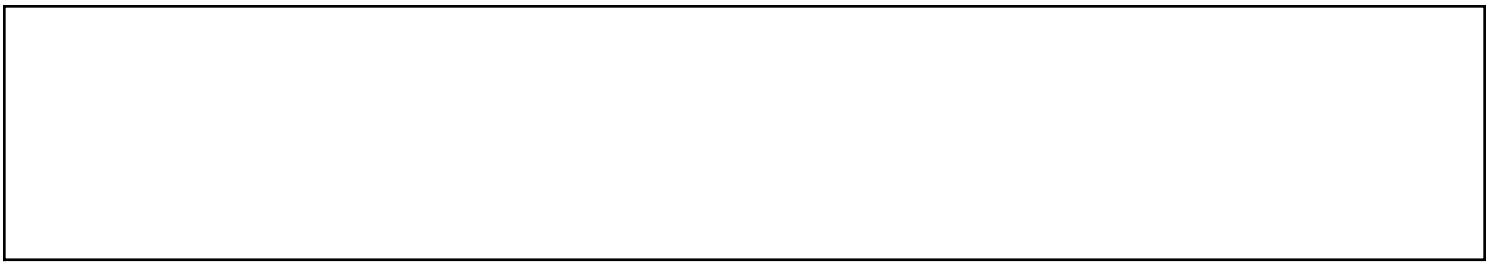
Final report of the CCQM-K145: toxic and essential elements in bovine liver



CCQM-K145: Toxic and essential elements in bovine liver

Final Report

June, 2020

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3 Finnish Environment Institute (SYKE)
4 Laboratorio Tecnológico del Uruguay (LATU)
5 Physikalisch-Technische Bundesanstalt (PTB)
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7 Russian Metrological Institute of Technical Physics and Radio Engineering (VNIIFTRI)
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10 National Metrology Institute of South Africa (NMISA)
11 Laboratoire national de métrologie et d'essais (LNE)
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13 Health Sciences Authority (HSA)
14 Research Institute of Sweden (RISE)
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CONTENTS

1. INTRODUCTION

Liver plays a major role in metabolism and acts as a source of energy for the body by storing glycogen. Also, working with other systems and organs, it is responsible for several important functions such as storing iron, detoxifying harmful substances, maintaining the hormonal balance, and producing immune factors to fight infections. Cattle seemed to be the most sensitive animal species with respect to some metal toxicities resulting from ingestion of feed material. With the growing interest and investigation in the biological effects in recent years, it is important and necessary to develop accurate and comparable analytical methods for elements in bio-samples. It has, however, been 10 years since the tissue sample (bovine liver) of CCQM-K49 key comparison. Therefore, the IAWG has included the need for such a key comparison to maintain, expand and improve core capabilities, and to support specific CMCs claim in bio-sample analysis as well.

The purpose of CCQM-K145&P183 is to ensure the comparable and traceable measurement results for essential and toxic elements such as P, S, Zn, Mn, Ni, Mo, Sr, Cr, Co, Pb, As and Hg in bovine liver among NMIs and other designated measurement bodies worldwide. The comparison has been agreed by IAWG as 6th IAWG Benchmarking Exercise with Zn and Ni as exemplary elements at the meeting in Korea in the early October 2016. The results of CCQM-K145 are expected to cover the measurement capability and support CMCs claiming for inorganic elements in the similar biological tissue materials and food samples.

34 NMIs and DIs registered in CCQM-K145 & P183. Among them, 26 institutes only registered in CCQM-K145, 4 institutes registered in both CCQM- K145 and P183. For this comparison, NIM prepared the technical protocol and result report form, and send them to each participant. By the deadline for receipt of the result report, 28 NMIs and DIs submitted their report of measurement results. As the result, Zn and Ni as exemplary elements in this 6th IAWG benchmarking, the successful results are achieved for most participants, meanwhile, good results are also obtained for other 10 elements, P, S, Mn, Mo, Sr, Cr, As, Co, Pb and Hg.

2. LIST OF PARTICIPANTS

26 institutes only registered in CCQM-K145, 4 institutes registered in both CCQM- K145 and P183. The list of all the participating institutes is shown in Table 1 according to a sequence of the time of registration.

Table 1. List of participants

No	NMI/DI/Expert institute		Country	Contact Person	K / P	Elements	Methods
1	National Research Council Canada	NRC	Canada	Dr. Lu Yang	K	P, S, Zn, Ni, Sr,Pb,As,Hg	ICP-OES, ICP-MS
2	National Institute of Standards and Technology	NIST	United States	Dr. Michael Winchester	K&P	K: Zn, Ni P: Zn, Mn, Mo,Cr,Sr,Co,As	ICP-OES ICP-MS, INAA
3	Finnish Environment Institute	SYKE	Finland	Teemu Näykki	K	Pb, Hg	ID-ICP-MS
4	Laboratorio Tecnológico del Uruguay (LATU)	LATU	Uruguay	Ramiro Pérez Zambra / Romina Napoli	K	P, Zn, Ni, Mn, Cr,Pb,Co, As,Hg	SA-ICP-OES, ID-ICP-SFMS, SA-ICP-SFMS
5	Physikalisch-Technische Bundesanstalt (PTB)	PTB	Germany	Dr. Olaf Rienitz / Dr. Janine Noordmann	K	Zn, Ni, Pb	ID-HR-ICP-MS
6	Government Laboratory (GLHK)	GLHK	Hong Kong, China	Dr. Kin-wai YEUNG, Dr. Hei-shing CHU	K	Zn, Ni	ID-ICP-MS, standard addition ICP-MS
7	Federal office of Consumer Protection and Food Safety	BVL	Germany	Dr. Timo Kapp	K&P	K: Ni, Pb, As, Hg P: Zn, Mn, Mo	ICP-MS, CV-AFS
8	Russian Metrological Institute of Technical Physics and Radio Engineering	VNIIFTRI	Russian Federation	Mr. Aleksey Stakheev	K	P, S, Zn, Ni, Mn, Mo, Cr, Sr, Pb, Co, As, Hg	ICP-OES, ICP-MS
9	National Institute of Metrology (Thailand)	NIMT	Thailand	Dr. Nattikarn Kaewkhomdee	K	Zn, Ni, Mn, Mo, Cr, Sr, Pb, Co, As, Hg	ICP-MS
10	Instituto Nacional de Calidad	INACAL	Lima, Peru	Christian Uribe/ Elmer Carrasco	K	Zn, Ni, Mn	ICP-OES
11	National Metrology Institute of South Africa	NMISA	South Africa	Angelique Botha	K	Pb, Zn, Ni, Mn, Mo, Cr, Pb	EC-ICP-MS, ID-ICP-MS
12	Laboratoire national de métrologie et d'essais	LNE	France	Paola Fisicaro	K	Zn, Ni, Cr, Pb, As, Hg	ID-ICPMS, Standard addition ICPMS
13	Instituto Nacional de Metrología de Colombia	INMC	Colombia	Diego Alejandro Ahumada Forigua	K	Zn, Ni, Pb,Hg; Mo, As	MW-ICP-MS, MW-FAAS
14	Health Sciences Authority	HSA	Singapore	Dr. Richard Shin	K	S, Zn, Ni, Mo, Cr, Pb, Hg	ID-ICP-MS, Standard addition ICP-MS
15	Research Institute of Sweden	RISE	Sweden	Conny Haraldsson	K	S, Cr, Hg	Sulphur analyser, ICP-MS
16	National Measurement Institute (Australia)	NMIA	Australia	Jeffrey Merrick	K	Zn, Ni, Mo, Cr	d-IDMS
17	LGC Limited	LGC	United kingdom	Heidi Goenaga Infante	K	Zn, Ni, Pb	ID-ICPMS
18	Jožef Stefan Institute	JSI	Slovenia	Dr. Radojko Jaćimović	K	Zn, Ni, Mn, Mo, Cr, Sr, Pb, Co, As,	k0-INAA, ICP-MS

						Hg	CV-AAS
19	Korea Research Institute of Standards and Science	KRISS	Republic of Korea	Yong-Hyeon YIM	K	Zn, Ni, Mn, Mo, Cr, Pb, Co	SA-ICP-MS, ID-ICP-MS, ICP-OES
20	Kenya Bureau of Standards	KEBS	Kenya	Tom Oduor Okumu	K&P	K: Zn, Ni, Mn, Mo, Cr, Pb P: P, Sr, Co, As, Hg	ICP-OES, ICP-MS
21	Instituto Nacional de Tecnologia Industrial	INTI	Argentina	Osvaldo Acosta; Mabel Puelles	K	P, Zn, Ni, Cr, Pb	ICP-MS, ICP-OES
22	TUBITAK Ulusal Metroloji Enstitusu	UME	Turkey	Suleyman Z. Can	K	P, Zn, Ni, Cr, Pb, As, Hg	ICP-MS
23	EXHM/GCSL-EIM	EXHM	Greece	Dr. Elias Kakoulides	K	Zn, Ni, Mn, Cr, Pb, Co, As	ICP-MS, ID-ICP-MS
24	National Institute of Metrology, Quality and Technology	INMETRO	Rio de Janeiro	Dr. Rodrigo Caciano de Sena;	K	P, S, Zn, Ni, Mn, Cr, Sr, Pb, Co, As, Hg	ICP-OES, ICP-MS
25	National Metrology Institute of Japan	NMIJ	Japan	Dr. Shin-ichi Miyashita	K	P, Zn, Ni, Mn, Cr	ID-ICP-MS, ICP-OES
26	National Institute of Research and Physical chemical analysis	INRAP	Tunisia	Mrs. Hanen KLICH	K	Zn, Ni, Mn, Mo, Cr	ICP-OES
27	National Institute of Metrology, P. R. China	NIM	China	Dr. Wang Jun	K	P, S, Zn, Ni, Mn, Mo, Cr, Sr, Pb, Co, As, Hg	ID-ICP-MS, ICP-MS, ICP-OES
28	IAEA Environment Laboratories	IAEA	Monaco	Dr. Emiliya Vasileva-Veleva	K&P	K: Zn, Pb, Hg; P: Zn, Ni, Mn, Sr, Pb, Co, As, Hg	IDMS, ICP-MS
29	Istituto Nazionale di Ricerca Metrologica	INRIM	Italy	Luigi Bergamaschi	K	Zn, Ni, Cr, Co, As	INAA
30	Ural Scientific Research Institute for Metrology	UNIIM	Russia	Egor Sobina	K	P, S, Zn, Ni, Mn, Mo, Cr, Sr, Pb, Co, As, Hg	ICP-MS, ICP-OES

For CCQM-K145, INMETRO, INTI, IAEA Environment Laboratories and BVL did not submit their result report due to the problems of sample deliver or instruments.

3. TIME SCHEDULE

Call for Participation: May, 2017
Deadline for registration: 10 June, 2017
Dispatch of the samples: June-July, 2017
Deadline for receipt of the result report: 28 February, 2018
Discussing of the result: CCQM/ IAWG Paris meeting of 2018

4. SAMPLE

Sample preparation

Liver tissues of new born healthy steers were collected and prepared under the strict protocols by the professional biological institutes. After the pretreatment of the raw materials, liver tissues were cut into portions of approximately 10 cm^3. Then, they were homogenized with a high speed mixer, frozen and lyophilized by a freeze dryer, ground with ball grinding mill. The bovine liver powder was subjected to a sieving process through 200 mesh sieve and thoroughly homogenized in a 3-dimensional mixer. The resulting final product was radiation sterilized, bottled and stored at room temperature.

The measurands to be determined are the mass fractions of P, S, Zn, Mn, Mo, Cr, Ni, Pb, Sr, Co, As and Hg. The expected mass fraction ranges of the twelve elements are listed in Table 2.

Table 2. Measurands and expected mass fraction ranges

Elements	Expected mass fraction ranges
Phosphorus	(5~50) mg/g
Sulfur	(1~30) mg/g
Zinc	(50~500) mg/kg
Nickel	(0.1~10) mg/kg
Manganese	(0.1~10) mg/kg
Molybdenum	(0.1~10) mg/kg
Chromium	(0.1~10) mg/kg
Strontium	(50~500) μg/kg
Lead	(10~300) μg/kg
Cobalt	(10~300) μg/kg
Arsenic	(1~100) μg/kg
Mercury	(1~100) μg/kg

Homogeneity test

The homogeneity of the sample was investigated by analyzing 25 bottles of the bovine liver powder and determined by ICP-OES, WD-XRF and ICP-MS, the sampling weight is about 300mg. The microwave digestion was used to the sample preparation for ICP-OES and ICP-MS analysis. Particle size distributions in the sample were determined in aqueous suspension via laser light scattering instrumentation (Malvern Mastersizer 2000). Calculated 90th percentile particle sizes was less than 50μm. ANOVA technique was applied to assess the between bottle heterogeneity and the standard uncertainty originated from the between bottle heterogeneity was calculated using the formula given below in accordance with ISO Guide 35:2006 [1]. The results are summarized in Table 3. The results based on the F test showed the homogeneity level can fit the objective of the comparison.

$$u_{bb} = \sqrt{\frac{MS_{within}}{n}} \cdot \sqrt{\frac{2}{v_{MSwithin}}} \qquad (1)$$

Where:

u_{bb}	standard uncertainty due to between bottles heterogeneity
MS_{within}	mean square of within bottles variance
$v_{MSwithin}$	degree of freedom of MS_{within}
n	number of subsample

Table 3. Summary of homogeneity study results

Measurand	ANOVA test on heterogeneity		Relative standard uncertainty due to between bottle heterogeneity, u_{bb} (%)
	F-statistics	Critical value	
P	0.57	1.96	0.50
S	1.51	1.96	0.8
Zn	0.75	1.96	0.50
Mn	1.20	1.96	0.56
Mo	1.56	1.96	0.60
Cr	1.07	1.96	1.4
Ni	1.20	1.96	1.4
Sr	1.40	1.96	0.99
Pb	1.17	1.96	1.7
Co	1.07	1.96	0.77
As	1.30	1.96	1.9
Hg	1.17	1.96	1.4

Stability monitor

The stability of the bovine liver material stored at room temperature was conducted by using ICP-OES and ICP-MS. The long-term stability of the sample was carried out continually until the deadline for submission of measurement results of this comparison. The short-term stability was conducted at 60 ºC over a week period. The stability testing results of 12 elements in the sample are shown in the Fig.1. All results of the short-term and long-term stability testing indicated that no instability was observed during the duration of the comparison, and hence the bovine liver sample was fit for the purpose of this comparison in terms of stability.

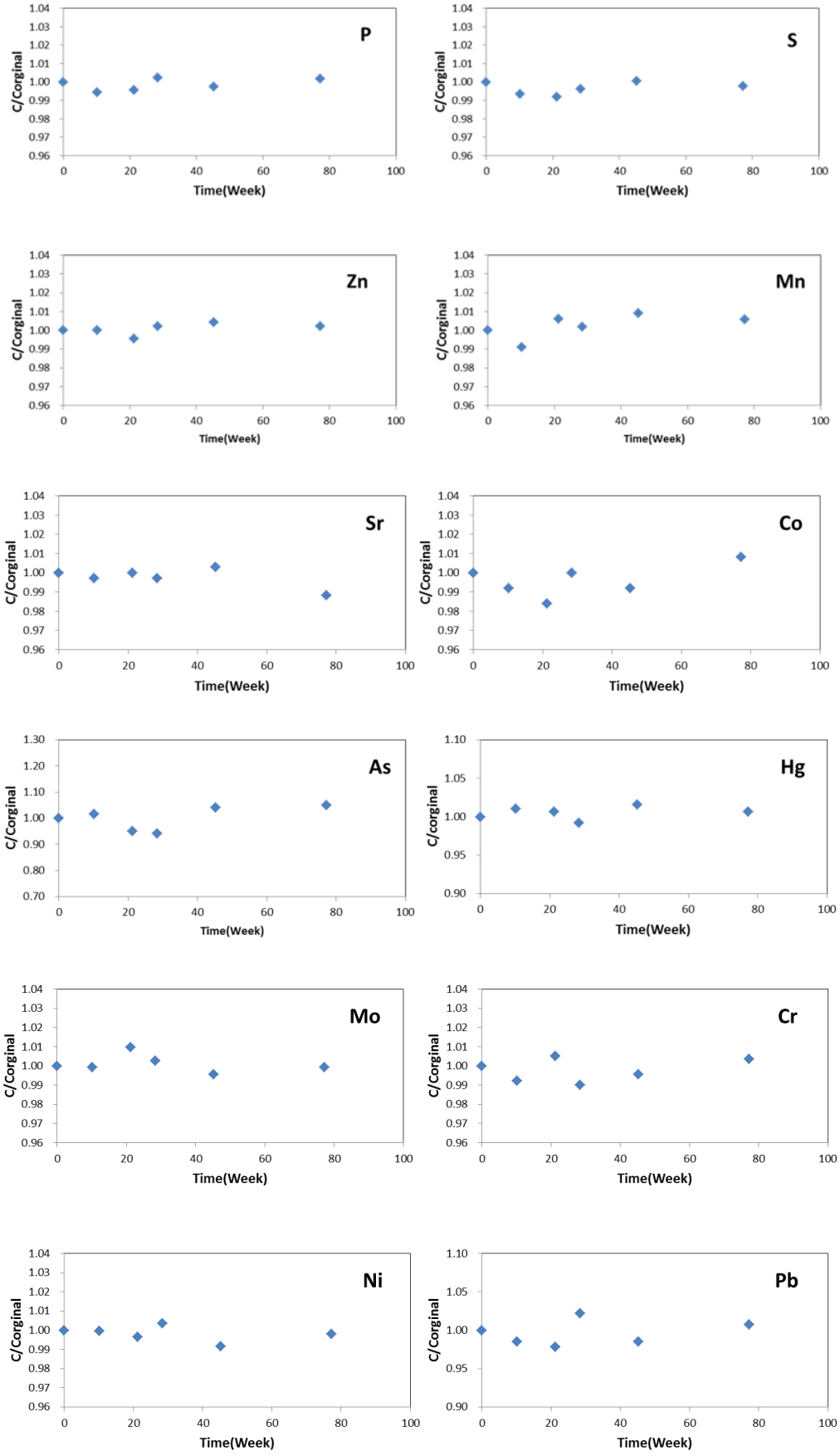

Fig.1 The results of stability monitor of 12 elements in the bovine liver sample

5. INSTRUCTIONS TO PARTICIPANTS

The instructions including technical protocol and results report form were sent to each participant by e-mail. The participants might to use any method of their choice for the measurements. Each participant received one numbered bottle containing 10g sample in each bottle. 2~3 bottles sample were sent to some participants baesd on their special requirements of using analytical methods. Each bottle was vacuum packed in aluminum-nylon pouch with temperature detector. The bovine liver sample size of at least 300mg was recommended. The lyophilized bovine liver tissue is somewhat hygroscopic, and its moisture content may be affected to change by the environmental conditions. Therefore, it was recommended that moisture determinations should be made on separate test portions taken at the same time as the portions to be analyzed. The recommended procedure was that the sample (size of 0.5~1g) was dried at 60℃ for 7 hours by using oven drying, then cooled in a desiccator to room temperature.

At least five replicate samples should be performed for each element. Calculation of the uncertainty expressed as a combined standard uncertainty and an expanded uncertainty at 95% confidence. In order to allow a sufficient evaluation of the comparison, the report was required to include a detail description of the applied method of measurement, information about sample digestion and preparation, information about the reference material used for calibration.

6. METHODS AND TRACEABILITY OF MEASUREMENT

According to the Results Report submitted by each participant, the measurement methods and source of traceability for the results are summarized in Table 4 and Table 5 respectively.

Table 4. Summary of the measurement methods

Institute	Type of preparation	Measurement method	Sample mass (g)
UNIIM	Dissolving, dilution	ICP-MS (addition method)(Zn, Ni, Mn, Mo, Cr, Co, As, Hg) ICP-OES (P, S) ID-ICP-MS (Sr, Pb)	0.3
NRC	Microwave digestion	ID-ICP-MS & standard addition ICP-OES (Zn, Ni, Sr) Standard addition ICP-OES (P, S, As) ID-ICP-MS (Pb)	0.3
NIST	Microwave digestion	IDMS (Zn, Ni)	0.5
LNE	Microwave digestion	Double IDMS (Ni, Cr, Pb, Hg) External calibration ICP-MS (Mn, Mo) Standard addition ICP-MS (As)	0.3-0.8
NIM	Microwave digestion	IDMS (Zn, Ni, Mo, Cr, Sr, Pb, Hg) Standard addition ICP-MS (P, S, Mn, Co, As) ICP-OES (Zn, P, S, Mn) XRF (Zn) AAS (Cr) MDA (Hg)	0.1-4.0
PTB	Microwave digestion & chromatographic separation	Exact matching double IDMS (Zn, Ni, Pb)	0.5

HSA	Microwave digestion	Exact matching IDMS (Zn, S, Mo, Cr, Pb, Hg) Standard addition ICP-MS (Ni)	0.3-0.5
KRISS	Microwave digestion	IDMS (Zn, Ni, Mo, Cr, Pb) Gravimetric standard addition calibration with Ga internal standard ICP-MS (Mn, Co)	0.3
NMIA	Microwave digestion	Double IDMS (Zn, Ni, Mo, Cr)	0.5
GLHK	Microwave digestion	IDMS (Zn) IDMS & standard addition (Ni)	0.5
JSI	An aliquot prepared in form of pellet (Zn, Mn, Mo, Cr,Co); Microwave digestion (Ni, Sr); Open digestion (Hg)	k0-INAA (Zn, Mn, Mo, Cr, Co) ICP-MS (Ni, Sr) CV AAS (Hg)	0.2-0.3
NIMT	Microwave digestion	Gravimetric Standard Addition ICP-MS with ISTD (Zn, Ni, Mn, Mo, Cr, Co, As) IDMS (Sr) External calibration CVAAS (Hg)	0.05-0.25
INACAL	Microwave digestion	Internal Standard & Standard Addition ICP-OES (Zn, Ni, Mn)	0.5
SYKE	Microwave digestion	Standard addition with internal standard (Rh) ICP-MS (Zn) Exact matching double IDMS (Pb) Exact matching double CV IDMS (Hg)	0.3-0.5
VNIIFTRI	Microwave digestion	Standard addition & internal standard ICP-OES (Zn, Ni) Standard addition ICP-OES (P, S, Mn) Standard addition ICP-MS (Pb, Co)	0.3-0.5
LGC	Microwave digestion	Double IDMS (Zn, Ni, Pb)	0.3-0.4
UME	Microwave digestion	IDMS (Zn, Cr, Pb, Hg) ICP-MS (Ni, P, As)	0.3
INMC	Microwave digestion	External calibration FAAS (Zn) Standard addition & internal standard ICP-MS (Ni, Mo, Pb, As, Hg)	0.25
LATU	Microwave digestion	Exact-matching IDMS (Zn, Ni, Cr, Sr, Pb) Gravimetric standard addition ICP-OES (P) Gravimetric standard addition with internal standard ICP-MS (Mn, Co)	0.3-0.7
RISE	Microwave digestion	ICP-OES (Zn) ICP-MS (Ni, Cr) CV IDMS (Hg)	0.4
INRAP	Microwave digestion	ICP-OES (Zn, Mn, Mo)	0.5
NMIJ	Microwave digestion	IDMS & standard addition ICP-MS (Zn, Ni, Cr) Standard addition ICP-MS (P, Mn)	0.3
NMISA	Microwave digestion	Double ID-ICP-MS (Zn, Ni, Mo, Cr, Pb) External calibration ICP-MS (P, Mn)	0.5
EXHM	Microwave digestion	IDMS (Zn, Ni, Cr, Pb) Standard addition ICP-MS (Mn, As, Co)	0.5
INRIM	Weighing	NAA (Zn, Mn, Cr)	1.0
KEBS	Microwave digestion	ICP-MS (Zn, Ni, Mn, Mo, Cr, Pb)	0.5

Table 5. Source of traceability for the measurement results

Institute	Calibration standard											
	Zn	**Ni**	**P**	**S**	**Mn**	**Mo**	**Cr**	**Sr**	**Pb**	**Co**	**As**	**Hg**
UNIIM	GSO CRM 10497-2014	GSO CRM 10277-2013	GSO CRM 7791-2000	GSO CRM 8746-2006	UNIIM in house characterised Mn calibrant	UNIIM in house characterised Mo calibrant	UNIIM in house characterised Cr calibrant	UNIIM in house characterised Sr calibrant	UNIIM in house characterised Pb calibrant	UNIIM in house characterised Co calibrant	CRM TraceCERT 92091(trace to NIST which has been tested regarding UNIIM primary calibration material of high-purity substance)	NIST SRM 3133
NRC	NRC-Zn	NRC-Ni	NIST SRM 3186	NIST SRM 3154	/	/	/	NRC-Sr	NRC-Pb	/	NRC-As	NIST SRM 3133
NIST	NIST SRM 3168a	NIST SRM 3136	/	/	/	/	/	/	/	/	/	/
LNE	/	LNE in house characterised Ni calibrant	/	/	/	/	NIST high purity $K_2Cr_2O_7$ standard	/	NIST SRM 982	/	NIST SRM 3103a	ERM-AE640 ERM-AE639
NIM	NIM CRM GBW08620, GBW04464	NIM CRM GBW08618	NIM CRM GBW(E) 080435	NIM CRM GBW(E) 080266	NIM CRM GBW(E) 080263	NIM in house characterised Mo calibrant	NIM CRM GBW08614	NIM CRM GBW(E) 080242	NIM CRM GBW08619, GBW04442	NIM CRM GBW(E) 080120	NIM CRM GBW(E) 080117	NIM CRM GBW08617, GBW04443
PTB	BAM-A-primary-Zn	BAM-A-primary-Ni	/	/	/	/	/	/	BAM-A-primary-Pb	/	/	/
HSA	NIST SRM 3168a	NIST SRM 3136	/	NIST SRM 3154	/	NIST SRM 3134	NIST SRM 3112a	/	NIST SRM 3128, NIST SRM 981	/	/	NIST SRM 3133

KRISS	KRISS in house characterised Zn calibrant	KRISS in house characterised Ni calibrant	/	/	KRISS in house characterised Mn calibrant	KRISS in house characterised Mo calibrant	KRISS in house characterised Cr calibrant	/	KRISS in house characterised Pb calibrant	KRISS in house characterised Pb calibrant	/	/
NMIA	NIST SRM 3168a	NIST SRM 3136	/	/	/	NIST SRM 3134	NIST SRM 3112a	/	/	/	/	/
GLHK	NIST SRM 3168a	NIST SRM 3136	/	/	/	/	/	/	/	/	/	/
JSI	IRMM 530R	NIST SRM 3136	/	/	IRMM 530R	IRMM 530R	IRMM 530R	MERCK Certipur Strontium ICP standard	/	IRMM 530R	/	NIST SRM 3133
NIMT	NIST SRM 3168a	NIST SRM 3136	/	/	NIST SRM 3132	NIST SRM 3134	NIST SRM 3112a	VHG-PSRN-100	NIST SRM 3128	NIST SRM 3113	NIST SRM 3103a	NIST SRM 3177
INACAL	SMU B37	SMU B24	/	/	SMU B21	/	/	/	/	/	/	/
SYKE	NIST SRM 3168a	/	/	/	/	/	/	/	NIST SRM 981	/	/	NIST SRM 3133
VNIIFTRI	Merck Zinc ICP Standard Certipur CRM, Yttrium ICP Standard Certipur CRM	Merck Nickel ICP Standard Certipur CRM, Yttrium ICP Standard Certipur CRM	Merck ICP Multielement Standard Solution XIV Certipur CRM	Merck ICP Multielement Standard Solution XIV Certipur CRM	Merck Manganese ICP Standard Certipur CRM	/	/	/	Merck Lead ICP Standard Certipur CRM	Merck Cobalt ICP Standard Certipur CRM	/	/
LGC	LGC in house characterised Zn calibrant	NIST SRM 3136	/	/	/	/	/	/	NIST SRM 981	/	/	/
UME	IRMM 654	NIST SRM 3136	NIST SRM 3139a	/	/	/	IRMM 624	/	NIST SRM 3128	/	NIST SRM 3103a	NIST SRM 3133, IRMM 640

INMC	NIST SRM 3168a	SMU B24	/	/	/	NIST SRM 3134	/	/	NIST SRM 3128	/	SMU B03	NIST SRM 3133
LATU	NIST SRM 3168a	NIST SRM 3136	SMU B25	/	NIST SRM 3132	/	NIST SRM 3112a	SMU B32	NIST SRM 3128 and NIST SRM 981	NIST SRM 3113	/	/
RISE	NIST SRM 3168	NIST SRM 3136	/	/	/	/	NIST SRM 136f	/	/	/	/	ERM-AE640
INRAP	NIST SRM 3168a	/	/	/	NIST SRM 3132	NIST SRM 3134	/	/	/	/	/	/
NMIJ	JCSS Zn standard solution	JCSS Ni standard solution	JCSS PO_4^{3-} standard solution	/	JCSS Mn standard solution	/	JCSS Cr standard solution	/	/	/	/	/
NMISA	NIST SRM 3168a	NIST SRM 3136	NIST SRM 3139a	/	NIST SRM 3132	NIST SRM 3134	NIST SRM 3112a	/	NIST SRM 3128	/	/	/
EXHM	NIST SRM 3168a	NIST SRM 3136	/	/	NIST SRM 3132	/	NIST SRM 3112a	/	NIST SRM 3128	NIST SRM 3113	NIST SRM 3103a	/
INRIM	NIST SRM 3168a	/	/	/	NIST SRM 3132	/	NIST SRM 3112a	/	/	/	/	/
KEBS	NIST SRM 3168a	NIST SRM 3136a	/	/	NIST SRM 3132	NIST SRM 3134	NIST SRM 3112a	/	NIST SRM 3128	/	/	/

Based on the CIPM traceability requirements and the related discussion in 2019 Paris meeting, the measurement values which not use calibrants from Metrology Institutes cannot be used for KCRV calculations, and cannot use to calculate and assess the degree of equivalence.

7. RESULTS AND DISCUSSION

7.1 General

The measurement results of 12 elements in CCQM-K145 sample reported by each participant are summarised in Table 6 ~Table 17 respectively.

Table 6. Reported results of Zn

Institute	Result (mg/kg)	*u* (mg/kg)	*U* (mg/kg)	*k*	n	Method	Moisture (%)
EXHM	420.6	11.5	23.0	2	6	IDMS(HR)	2.139
INRAP	429.71	9.48	18.96	2	14	ICP-OES HR	3.13
UNIIM	436	9	18	2	5	ICP-MS(standard addition)	3.238
LATU	453	5.6	11	2	6	IDMS(HR)	2.69
INACAL	453.1	8.8	17.6	2	5	ICP-OES(standard addition)	3.57
GLHK	453.6	7.7	15.4	2	6	IDMS(HR)	2.97
NMIA	454.1	4.2	8.6	2.04	8	IDMS(HR, QQQ)	3.1423
NIM	454.5	5.5	11	2	5	IDMS	2.505
KRISS	454.5	6.7	13.2	1.96	6	IDMS(HR)	2.65
LGC	454.5	3.9	7.8	2	6	IDMS(HR)	3.24
NMISA	454.5	6.1	12.2	2	5	IDMS(HR)	3.97
JSI	455	14	28	2	7	k0-INAA	3.1551
NIST	456.2	2.0	4.0	2.04	6	IDMS	2.45
UME	457	4	7	2	6	IDMS(HR)	4.51
HSA	459	7.1	14	2	6	IDMS	2.76
PTB	459.4	1.7	3.4	2.03	6	IDMS(HR)	3.190
RISE	460.5	3.2	6.3	2	5	ICP-OES	2.94
SYKE	460.9	11.5	23.0	2	5	ICP-MS(standard addition)	2.67
INMC	461	6.5	13	2	5	FAAS	2.593
NRC	462	5	10	2	9	IDMS(HR) ICP-OES(standard addition)	3.73
NIMT	462	13.2	27	2	5	ICP-MS(standard addition)	2.11

NMIJ	462	3	6	2	5	IDMS ICP-MS(standard addition)	3.23
KEBS	474.22	16.46	38.92	2.36	8	ICP-MS	3.7528
INRIM	491.7	10.0	20.1	2	8	NAA	4.74
VNIIFTRI	524	16	32	2	6	SA-ICP-OES	2.67
*NIM	445.4	7.7	15.5	2.0	5	XRF	/
*NIM	452	4.5	9	2	5	ICP-OES	3.23

***** NIM submitted three results using three methods. IDMS was used to calculate the KCRV.

Table 7. Reported results of Ni

Institute	**Result (mg/kg)**	***u* (mg/kg)**	***U* (mg/kg)**	***k***	**n**	**Method**	**Moisture (%)**
UNIIM	0.147	0.016	0.033	2	5	ICP-MS(standard addition)	3.238
NMISA	0.902	0.038	0.076	2	4	IDMS(HR)	3.97
EXHM	1.017	0.05	0.100	2	6	IDMS(HR)	2.139
NIMT	1.65	0.06	0.13	2	5	ICP-MS(standard addition)	2.11
JSI	1.93	0.11	0.22	2	6	ICP-MS	3.2734
INMC	1.94	0.06387	0.13	2	8	ICP-MS(standard addition)	2.593
GLHK	1.942	0.092	0.183	2	10	IDMS(HR), Gravimetric standard addition	2.97
LNE	1.958	0.075	0.15	2	5	IDMS(HR)	2.68
VNIIFTRI	1.96	0.09	0.18	2	6	SA-ICP-OES	2.67
NIST	1.984	0.020	0.047	2.31	6	IDMS	3.300
KRISS	1.993	0.033	0.067	2.06	3	IDMS(HR)	2.65
INACAL	2.01	0.06	0.13	2	5	ICP-OES(standard addition)	3.57
NMIA	2.02	0.05	0.1	2.02	14	IDMS(HR,QQQ)	3.1423
NIM	2.022	0.023	0.046	2	5	IDMS	2.859
NMIJ	2.05	0.02	0.04	2	5	IDMS ICP-MS(standard addition)	3.23
RISE	2.055	0.052	0.10	2	5	ICP-MS	2.94
NRC	2.07	0.05	0.10	2	10	IDMS(HR) ICP-OES(standard addition)	3.73
PTB	2.077	0.035	0.071	2.00	5	IDMS(HR)	3.190

LATU	2.08	0.059	0.12	2	5	IDMS(HR)	2.69
LGC	2.131	0.042	0.084	2	8	IDMS(HR)	2.83
UME	2.15	0.03	0.06	2	6	ICP-MS(HR)	4.51
HSA	2.18	0.08	0.15	2	7	ICP-MS(standard addition)	3.00
KEBS	4.63	0.94	2.22	2.36	8	ICP-MS	3.7528

Table 8. Reported results of P

Institute	**Result (mg/g)**	***u* (mg/g)**	***U* (mg/g)**	***k***	**n**	**Method**	**Moisture (%)**
UNIIM	10.65	0.24	0.49	2	5	ICP-OES	2.593
NMISA	11.203	0.092	0.184	2	7	ICP-MS(HR)	2.11
NMIJ	11.26	0.07	0.14	2	5	ICP-MS(standard addition)	3.23
NIM	11.27	0.12	0.24	2	5	ICP-OES	2.757
LATU	11.40	0.12	0.24	2	6	ICP-OES(standard addition)	3.73
UME	11.55	0.09	0.18	2	5	ICP-MS (HR)	2.94
VNIIFTRI	11.60	0.64	1.28	2	6	SA-ICP-OES	3.1551
NRC	11.70	0.30	0.60	2	5	ICP-OES(standard addition)	2.442
*NIM	11.22	0.08	0.17	2	5	ICP-MS(QQQ, standard addition)	2.5051

*****NIM submitted two results using two methods. ICP-OES was used to calculate the KCRV.

Table 9. Reported results of S

Institute	**Result (mg/g)**	***u* (mg/g)**	***U* (mg/g)**	***k***	**n**	**Method**	**Moisture (%)**
UNIIM	6.22	0.21	0.41	2	5	ICP-OES	3.238
VNIIFTRI	6.78	0.36	0.72	2	6	SA-ICP-OES	2.67
NIM	6.79	0.06	0.13	2	5	ICP-MS(standard addition)	2.5051
HSA	6.82	0.16	0.33	2	6	IDMS(HR)	2.905
NRC	7.01	0.13	0.26	2	5	ICP-OES(standard addition)	3.73
*NIM	6.74	0.07	0.14	2	5	ICP-OES	3.23

*****NIM submitted two results using two methods. ICP-MS was used to calculate the KCRV.

Table 10. Reported results of Mn

Institute	Result (mg/kg)	*u* (mg/kg)	*U* (mg/kg)	*k*	n	Method	Moisture (%)
UNIIM	5.09	0.18	0.36	2	5	ICP-MS(standard addition)	3.238
LNE	5.48	0.27	0.55	2	5	ICP-MS	2.68
JSI	5.57	0.17	0.34	2	7	k0-INAA	3.1551
EXHM	5.686	0.245	0.490	2	6	ICP-MS(HR)(standard addition)	2.139
NIMT	5.71	0.13	0.27	2	5	ICP-MS(standard addition)	2.11
INRAP	5.74	0.26	0.51	2	15	ICP-OES HR	3.13
NIM	5.75	0.06	0.12	2	5	ICP-MS(standard addition)	2.5051
KRISS	5.75	0.11	0.24	2.31	1	ICP-MS(HR)(standard addition)	2.65
INACAL	5.77	0.10	0.20	2	5	ICP-OES(standard addition)	3.57
LATU	5.79	0.12	0.24	2	6	ICP-MS(HR)(standard addition)	2.69
NMIJ	5.91	0.06	0.12	2	5	ICP-MS(standard addition)	3.23
NMISA	6.69	0.14	0.28	2	7	ICP-MS(HR)	3.97
INRIM	6.70	0.18	0.35	2	6	NAA	4.74
KEBS	6.71	0.63	1.49	2.36	8	ICP-MS	3.7528
VNIIFTRI	7.08	0.35	0.70	2	6	SA-ICP-OES	2.67
*NIM	5.79	0.06	0.12	2	5	ICP-OES	3.23

***** NIM submitted two results using two methods. ICP-MS was used to calculate the KCRV.

Table 11. Reported results of Mo

Institute	Result (mg/kg)	*u* (mg/kg)	*U* (mg/kg)	*k*	n	Method	Moisture (%)
UNIIM	1.34	0.05	0.10	2	5	ICP-MS(standard addition)	3.238
INRAP	1.36	0.066	0.13	2	15	ICP-OES(HR)	3.13
LNE	1.41	0.06	0.12	2	5	ICP-MS	2.68
NIMT	1.49	0.02	0.05	2	5	ICP-MS(standard addition)	2.11
NMISA	1.532	0.021	0.042	2	5	IDMS(HR)	3.97
KRISS	1.539	0.049	0.096	1.96	3	IDMS(QQQ)	2.65

HSA	1.546	0.021	0.042	2	6	IDMS	2.905
NMIA	1.550	0.015	0.03	2	14	IDMS(QQQ, HR)	3.1423
JSI	1.55	0.07	0.14	2	7	k0-INAA	3.1551
INMC	1.551	0.026	0.053	2	6	ICP-MS(standard addition)	2.593
NIM	1.559	0.015	0.030	2	6	IDMS	3.38
KEBS	1.91	0.11	0.26	2.36	8	ICP-MS	3.7528

Table 12. Reported results of Cr

Institute	**Result (mg/kg)**	***u*** **(mg/kg)**	***U*** **(mg/kg)**	***k***	**n**	**Method**	**Moisture (%)**
UNIIM	0.345	0.015	0.030	2	5	ICP-MS(standard addition)	3.238
NMISA	1.816	0.07	0.140	2	4	IDMS(HR)	3.97
EXHM	1.977	0.051	0.101	2	6	IDMS(HR)	2.139
NIMT	3.44	0.11	0.23	2	5	ICP-MS(standard addition)	2.11
LNE	4.13	0.15	0.30	2	5	IDMS(HR)	2.68
KRISS	4.184	0.041	0.091	2.228	3	IDMS(HR)	2.65
NMIA	4.29	0.06	0.12	2.06	14	IDMS(QQQ,HR)	3.1423
NIM	4.303	0.046	0.092	2	5	IDMS	2.859
NMIJ	4.37	0.03	0.06	2	5	IDMS ICP-MS(standard addition)	3.23
LATU	4.38	0.13	0.26	2	6	IDMS(HR)	2.69
RISE	4.39	0.079	0.16	2	5	ICP-MS	2.94
HSA	4.44	0.10	0.19	2	6	IDMS	2.757
UME	4.47	0.09	0.18	2	5	IDMS(HR)	4.45
JSI	4.55	0.14	0.28	2	6	k0-INAA	3.1551
INRIM	4.89	0.15	0.31	2	8	NAA	4.74
KEBS	5.21	0.36	0.85	2.36	8	ICP-MS	3.7528
*NIM	4.28	0.08	0.16	2	5	AAS	3.36

***** NIM submitted two results using two methods. IDMS was used to calculate the KCRV.

Table 13. Reported results of Sr

Institute	Result (μg/kg)	*u* (μg/kg)	*U* (μg/kg)	*k*	n	Method	Moisture (%)
UNIIM	319	9	18	2	5	IDMS	3.238
NIM	321.0	4.7	9.4	2	5	IDMS(Q-ICP-MS, MC-ICP-MS)	2.69
NIMT	321	9	18	2	5	IDMS(QQQ)	2.11
LATU	321.2	4.3	8.6	2	6	IDMS(HR)	2.69
NRC	323	9	18	2	10	IDMS(HR) ICP-OES(standard addition)	3.73
JSI	367	28	56	2	5	ICP-MS	3.2734

Table 14. Reported results of Pb

Institute	Result (μg/kg)	*u* (μg/kg)	*U* (μg/kg)	*k*	n	Method	Moisture (%)
EXHM	132.8	4.8	9.6	2	6	IDMS(HR)	2.139
UNIIM	141.8	4	8.0	2	5	IDMS	3.238
NIMT	142	3	6	2	5	IDMS(QQQ)	2.11
LATU	142.2	3.0	6.0	2	5	IDMS(HR)	2.69
INMC	143.4	4.3	8.7	2	6	ICP-MS(standard addition)	2.593
LNE	143.8	2.5	5.1	2	5	IDMS(HR)	2.68
LGC	143.8	1.2	2.4	2	6	IDMS(HR)	2.65
SYKE	144.0	5.0	10.0	2	5	IDMS	2.67
NIM	145.30	1.15	2.3	2	5	IDMS	2.823
KRISS	145.6	2.8	6.4	2.306	3	IDMS(HR)	2.65
UME	145.6	1.3	2.6	2	8	IDMS(HR)	4.51
HSA	145.8	2.6	5.1	2	6	IDMS	2.996
NRC	147	5	10	2	7	IDMS(HR)	3.73
PTB	147.8	2.6	5.2	2.00	5	IDMS(HR)	3.190
NMISA	150.2	2.3	4.6	2	5	IDMS(HR)	3.97
KEBS	159.49	26.09	61.69	2.36	8	ICP-MS	3.7528
VNIIFTRI	180.4	5.0	10.0	2	6	SA-ICP-MS	2.67

Table 15. Reported results of Co

Institute	Result (μg/kg)	*u* (μg/kg)	*U* (μg/kg)	*k*	n	Method	Moisture (%)
UNIIM	98.6	3.2	6.4	2	5	ICP-MS(standard addition)	3.238
VNIIFTRI	115.6	1.9	3.8	2	6	SA-ICP-MS	2.67
NIMT	121	5.6	12	2	5	ICP-MS(QQQ)(standard addition)	2.11
LATU	125.7	2.6	5.2	2	6	ICP-MS(HR)(standard addition)	2.69
NIM	126.2	1.7	3.4	2	6	ICP-MS (standard addition)	2.505
KRISS	127	5	12	2.31	1	ICP-MS(HR)(standard addition)	2.65
JSI	128	4	8	2	7	k0-INAA	3.1551
EXHM	128.5	4.9	9.7	2	6	ICP-MS(HR) (standard addition)	2.139

Table 16. Reported results of As

Institute	Result (μg/kg)	*u* (μg/kg)	*U* (μg/kg)	*k*	n	Method	Moisture (%)
EXHM	9.63	0.44	0.88	2	6	ICP-MS(HR)(standard addition)	2.139
LNE	9.8	0.6	1.2	2	5	ICP-MS(HR)(standard addition)	2.68
NIMT	10.9	0.91	1.9	2	5	ICP-MS(QQQ, standard addition)	2.11
NIM	11.24	0.42	0.83	2	5	ICP-MS, ICP-MS(standard addition)	2.505
UME	11.3	0.5	0.9	2	5	ICP-MS(QQQ)	4.51
NRC	12.97*	0.43	0.86	2	10	ICP-MS(standard addition)	3.73
INMC	19.4	1.1	2.2	2	9	ICP-MS(standard addition)	2.593
UNIIM	25.2	3.1	6.2	2	5	ICP-MS(standard addition)	3.238

* NRC found a calculation mistake for the report value.

Table 17. Reported results of Hg

Institute	Result (μg/kg)	*u* (μg/kg)	*U* (μg/kg)	*k*	n	Method	Moisture (%)
INMC	12.6	0.69	1.4	2	7	ICP-MS(standard addition)	2.593
NIMT	13.8	0.52	1.1	2	5	CV AAS(MA)	2.11
SYKE	14.96	0.75	1.50	2	5	ID-CV-ICP-MS	2.67
HSA	15.50	0.33	0.67	2	6	IDMS	2.757
NRC	15.6	2.2	4.4	2	18	IDMS(HR)	3.73
RISE	15.6	0.62	1.2	2	5	ID-CV-ICP-MS	2.94

JSI	15.9	0.5	1.0	2	7	CV AAS	3.1551
NIM	16.56	0.78	1.55	2	5	ID-ICP-MS	2.442
LNE	16.9	0.8	1.6	2	5	IDMS	2.68
UME	16.9	0.4	0.8	2	4	IDMS(HR)	4.45
UNIIM	18.2	2.1	4.2	2	5	ICP-MS(standard addition)	3.238
*NIM	15.84	0.71	1.42	2	6	DMA	2.442

***** NIM submitted two results using two methods. IDMS was used to calculate the KCRV.

Fig.2~ Fig.13 shows the distribution for the results of CCQM-K145 for each measurand respectively. Error bar represents the standard uncertainty (*u*), as reported.

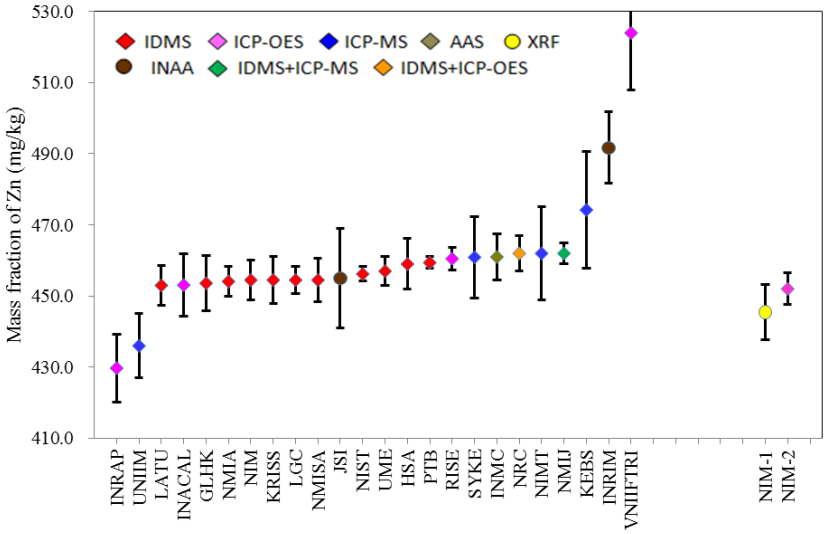

Fig.2 All results of Znic in CCQM-K145

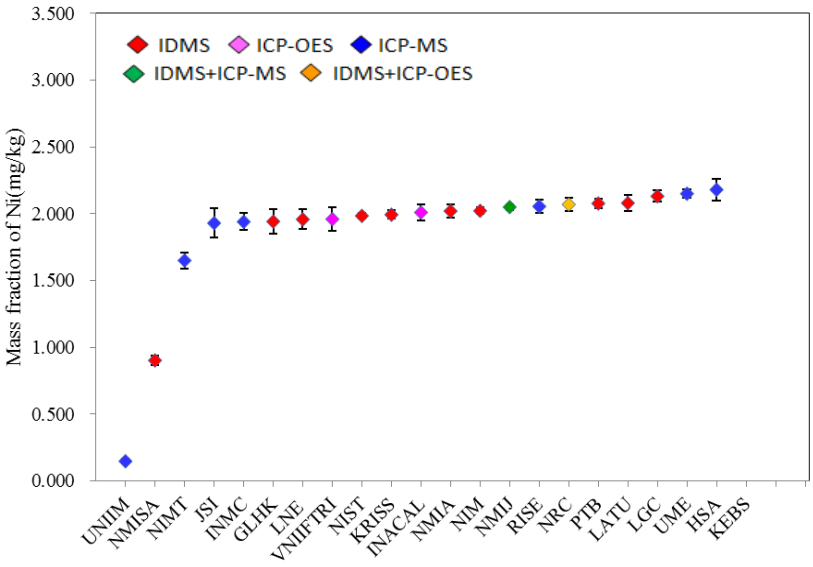

Fig.3 All results of Nickel in CCQM-K145

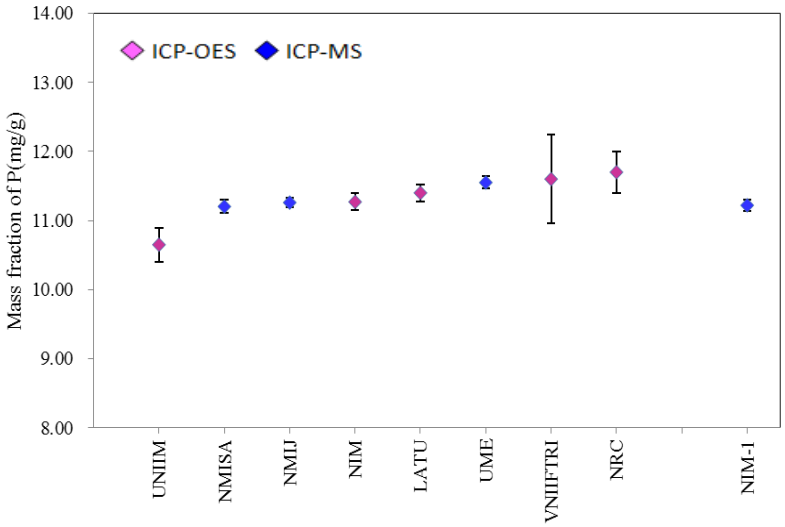

Fig.4 All results of Phosphorus in CCQM-K145

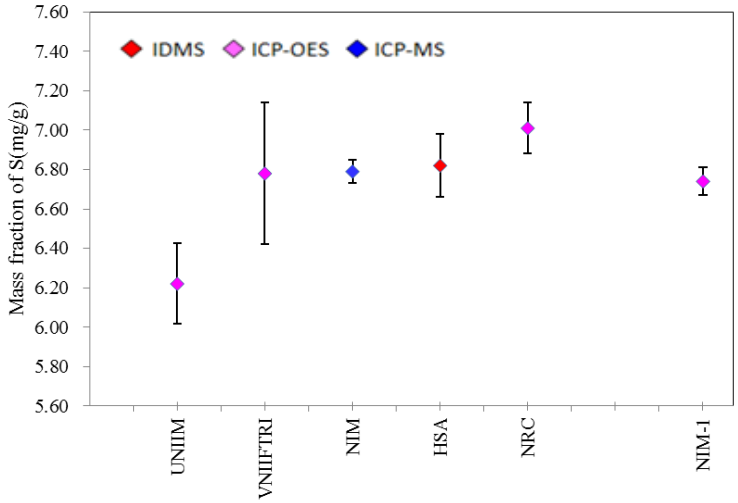

Fig.5 All results of Sulfur in CCQM-K145

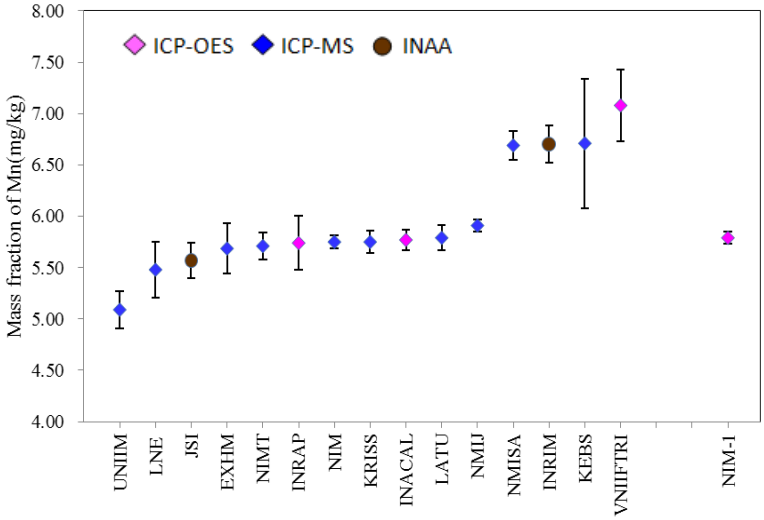

Fig.6 All results of Manganese in CCQM-K145

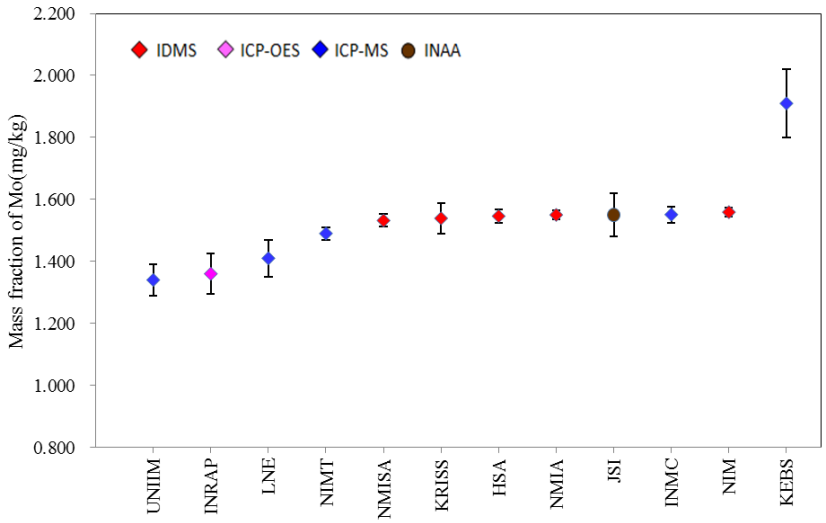

Fig.7 All results of Molybdenum in CCQM-K145

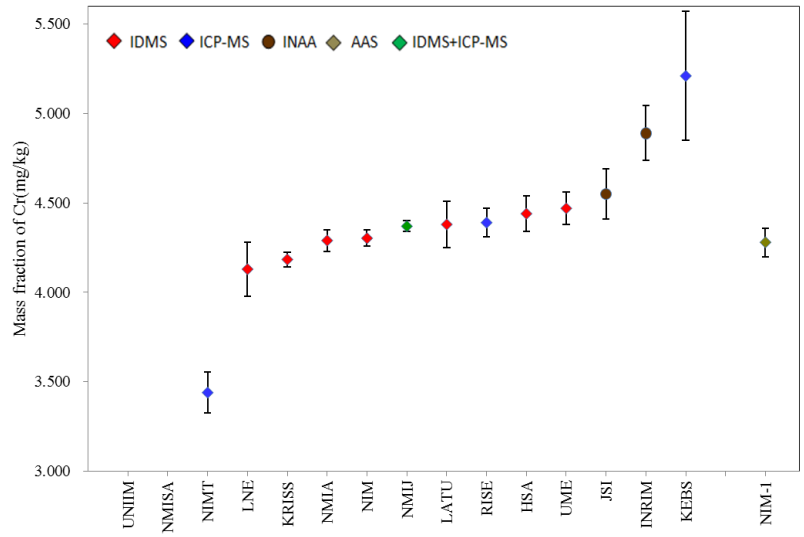

Fig.8 All results of Chromium in CCQM-K145

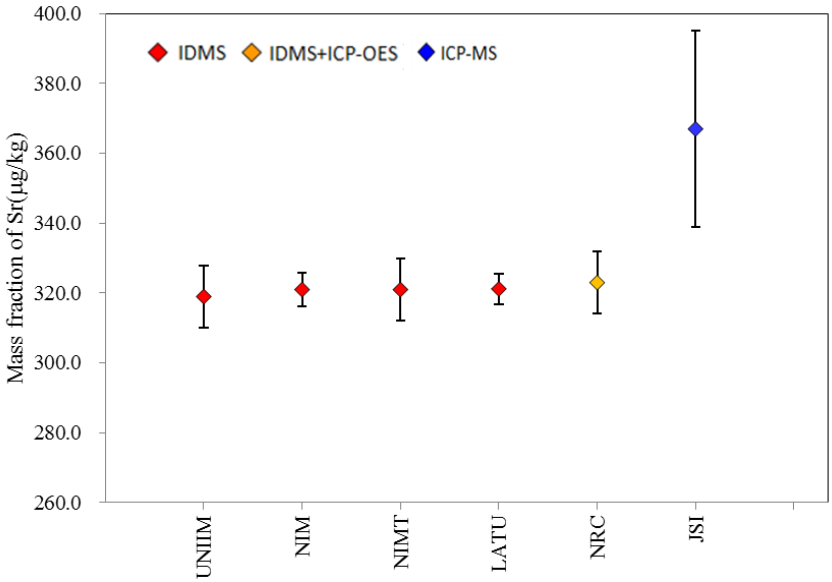

Fig.9 All results of Strontium in CCQM-K145

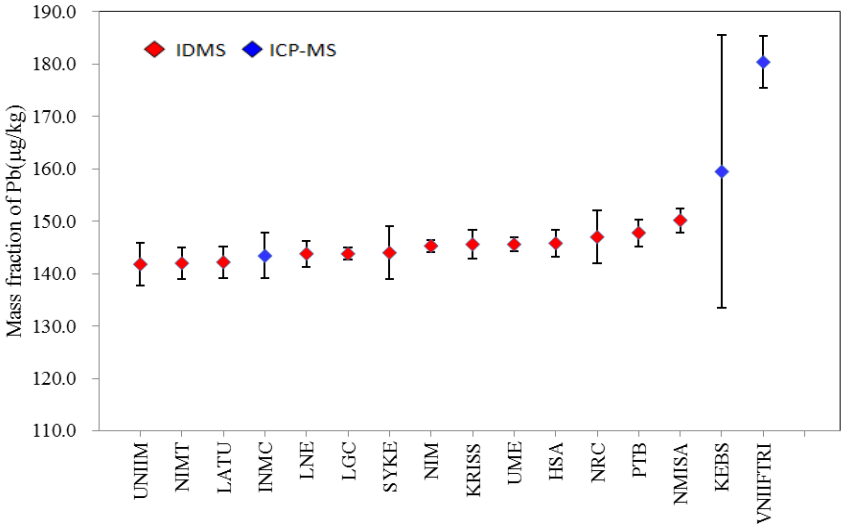

Fig.10 All results of Lead in CCQM-K145

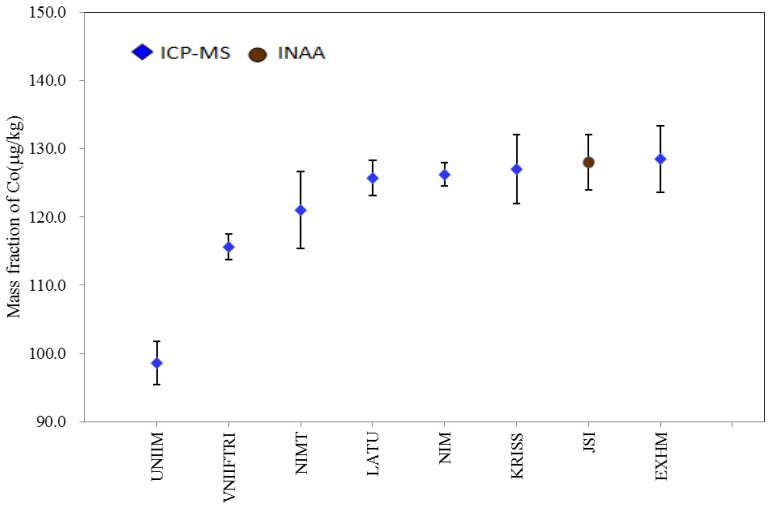

Fig.11 All results of Cobalt in CCQM-K145

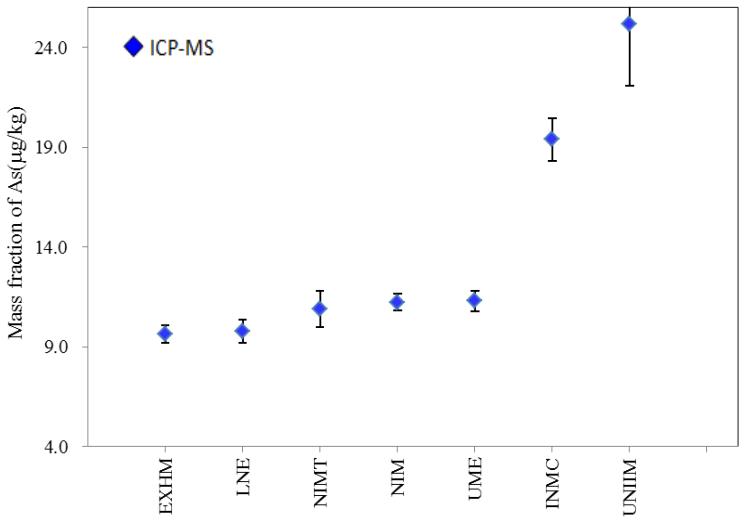

Fig.12 All results of Arsenic in CCQM-K145

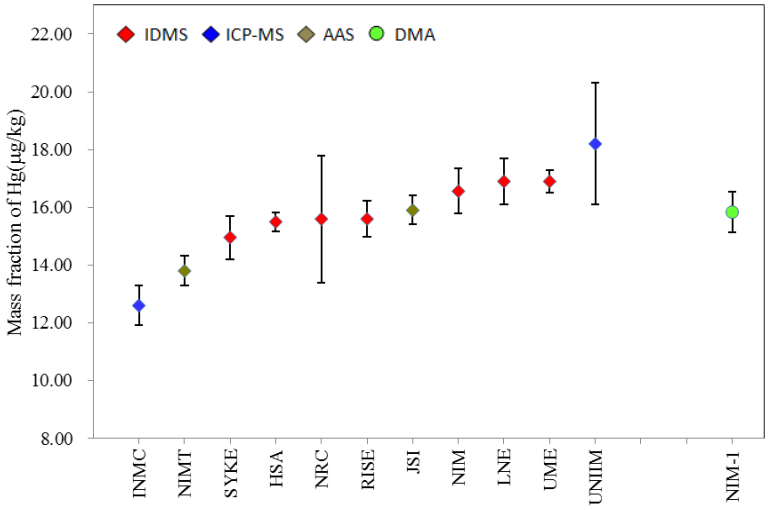

Fig.13 All results of Mercury in CCQM-K145

7.2 Screening the data for consistency and anomalous values

According to the CCQM Guidance Note [2], the result data reported by each participant were screened for the consistency and anomalous values. The robust estimate of location $\hat{\mu}$ and dispersion $\hat{\sigma}$ were hence used to detect possible outliers, i.e. values would be considered as extreme when outside $\hat{\mu} \pm 2\hat{\sigma}$ (corresponding to approximately 95 % confidence). The result data reported by each participant was detected according to the rule, and the outlier testing results are shown in Table 18.

Table 18. Summary of outlier testing results using robust estimates

Measurand	Robust mean $\hat{\mu}$	Robust SD dispersion $\hat{\sigma}$	$\hat{\mu} - 2\hat{\sigma}$	$\hat{\mu} \pm 2\hat{\sigma}$	Institutes found with suspected extreme results
Zn	457.03	4.92	447.18	466.87	INRAP, UNIIM, KEBS, INRIM
Ni	2.018	0.102	1.814	2.222	UNIIM, NMISA, NIMT, KEBS
P	11.318	0.232	10.853	11.782	UNIIM
S	6.795	0.209	6.377	7.213	UNIIM
Mn	5.763	0.192	5.378	6.147	UNIIM, NMISA, INRIM, KEBS
Mo	1.537	0.024	1.490	1.585	UNIIM, INRAP, LNE, KEBS
Cr	4.327	0.291	3.745	4.909	UNIIM, NMISA, NIMT, KEBS
Pb	145.10	2.75	139.61	150.59	KEBS
Co	125.68	2.91	119.86	131.51	UNIIM
As	11.68	2.26	7.15	16.21	INMC, UNIIM
Hg	15.73	1.47	12.79	18.66	INMC

Based on the IAWG meeting discussion and Dr. Sargent ‘s suggestion made in Paris on April 2018, also in order to present a more reasonable data processing for the comparison, the institutes found with suspected extreme results were asked to investigate reasons for their measurement results. Most of institutes found out some technical problems caused these results, which included the sample was not dissolved completely for sample preparation; parameter setting, instability, interference effect and blank correction for instrumental analysis. Hence, the outlier data reported by these institutes were excluded from the KCRV calculations. EXHM withdrew the results of Zn, Ni, Cr and Pb from their report. JSI removed data of Sr due to an unexpected contamination during the ICP-MS measurement.

7.3 Calculation of the reference mass fraction values and associated uncertainties

The report summarized the calculated consensus values and their respective standard deviation using different location estimators including arithmetic mean and median without the suspected extreme values being included in the calculation. Additionally, according to the information showed in Table 5, the measurement values used the commercial RM as calibrant cannot be use to calculate the KCRV. The calculated results are presented in Table 19.

Table 19. Results of calculation of consensus values and respective standard deviation by using arithmetic mean and median

Measurand	**n**	Arithmetic Mean	SD	**Median**	**MADe**
Zn (mg/kg)	19	457.20	3.40	456.20	4.15
Ni (mg/kg)	17	2.035	0.075	2.022	0.082
P (mg/g)	6	11.397	0.194	11.335	0.153
S (mg/g)	3	6.873	0.119	6.820	0.044
Mn (mg/kg)	10	5.716	0.119	5.745	0.059
Mo (mg/kg)	8	1.540	0.022	1.548	0.009
Cr (mg/kg)	11	4.400	0.203	4.380	0.133
Sr (μg/kg)	5	321.0	1.42	321.0	0.30
Pb (μg/kg)	14	144.9	2.38	144.7	1.78
Co (μg/kg)	6	126.1	2.70	126.6	1.71
As (μg/kg)	5	10.57	0.80	10.90	0.59
Hg (μg/kg)	10	15.99	1.21	15.75	1.19

7.4 KCRV and associated uncertainty

IAWG meeting hold in NRC in October 2018 made the decision for proposed KCRV calculation: the selection of mean or median should not be made on considerations other than the number of participants, and it was agreed that from this point forwards where number $\geqslant 8$, the median would be used as the KCRV, while where number $\leqslant 7$, the arithmetic mean would be applied for IAWG comparisons.

Based on the calculation results showed in Table 19 and mentioned above decision as well, the candidate estimators proposed for the KCRV and associated uncertainty of CCQM-K145 is as follows:

- **Arithmetic mean and associated uncertainty for P, S, Sr, Co, As**, the standard uncertainty is calculated using Equation (2).
- **Median and associated uncertainty for Zn, Ni, Mn, Mo, Cr, Pb, Hg,** the associated uncertainty is calculated using formulas (3).

The calculated KCRV and associated uncertainty of the all measurands are listed in Table 20.

$$u[x_{KCRV}] = \sqrt{\frac{1}{n}\left(\frac{1}{n-1}\sum_{i=1}^{n}(x_i - x_{KCRV})^2 + \frac{1}{n}\sum_{i=1}^{n}u^2(x_i)\right)} \quad (2)$$

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

Table 20. Calculated KCRV and associated uncertainty

Measurand	n	KCRV	*u* (KCRV)	Candidate estimator
Zn (mg/kg)	19	456.20	1.19	
Ni (mg/kg)	17	2.022	0.025	
Mn (mg/kg)	10	5.745	0.023	
Mo (mg/kg)	8	1.548	0.004	**Median**
Cr (mg/kg)	11	4.380	0.050	
Pb (μg/kg)	14	144.65	0.59	
Hg (μg/kg)	10	15.75	0.47	
P (mg/g)	6	11.40	0.10	
S (mg/g)	3	6.873	0.099	
Sr (μg/kg)	5	321.04	3.41	**Arithmetic mean**
Co (μg/kg)	6	126.07	2.04	
As (μg/kg)	5	10.57	0.45	

The results for 12 elements in the CCQM-K145 are graphically displayed in Fig.14 ~ Fig.25. Error bars depict standard uncertainties. The solid horizontal line is the suggested KCRV; the dashed lines show the standard uncertainty interval calculated with a coverage factor *k*=1.

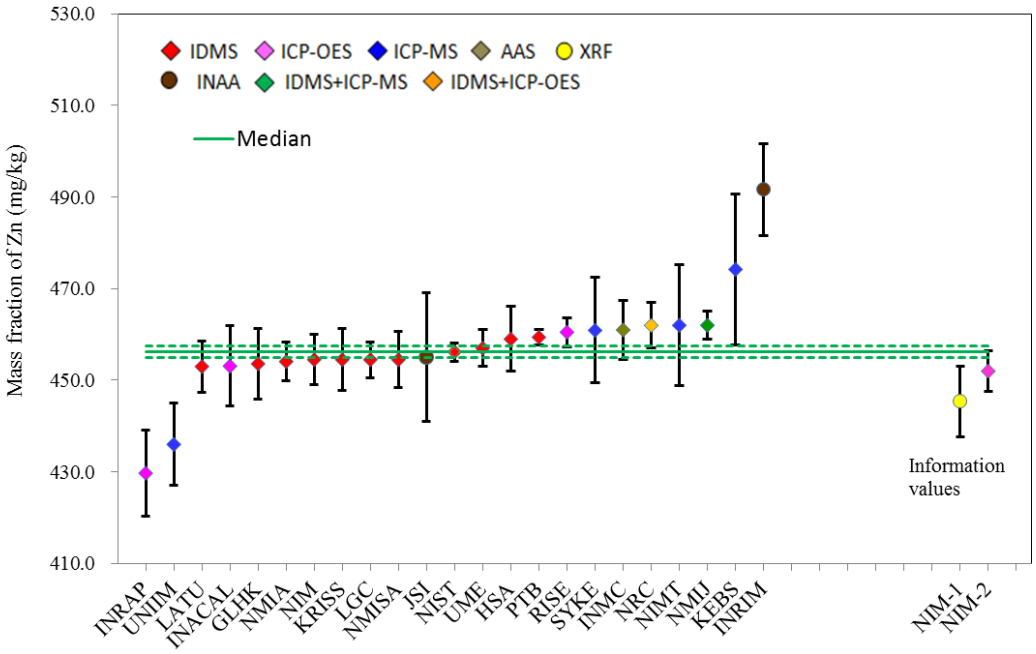

Fig.14 Results for Zinc in CCQM-K145 bovine liver sample

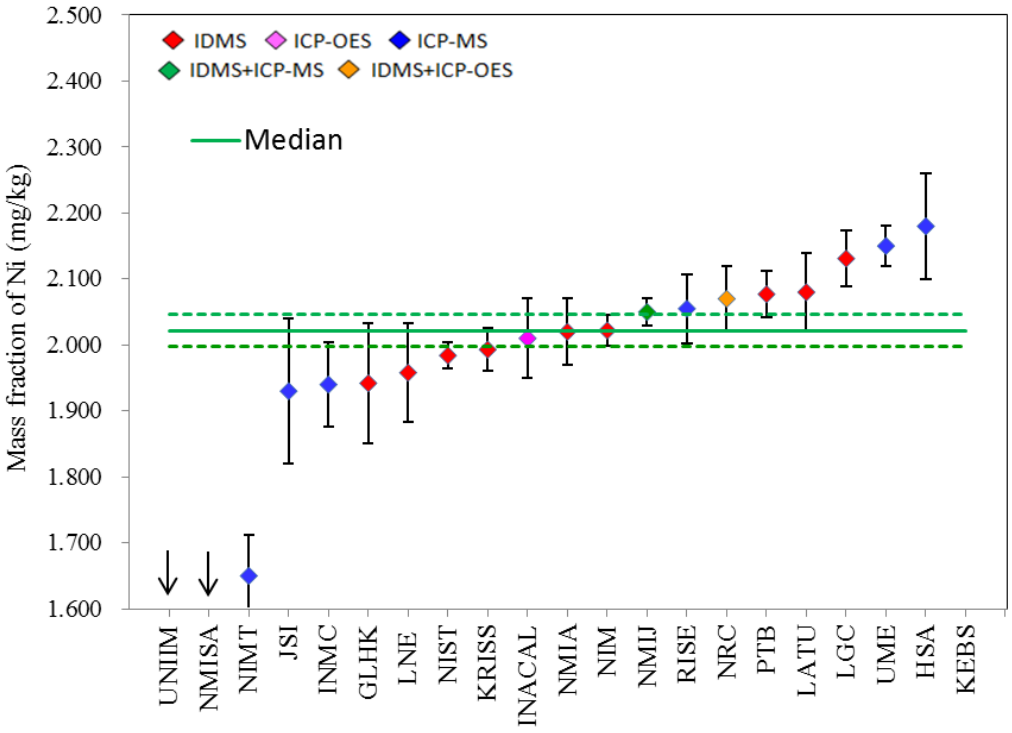

Fig.15 Results for Nickel in CCQM-K145 bovine liver sample

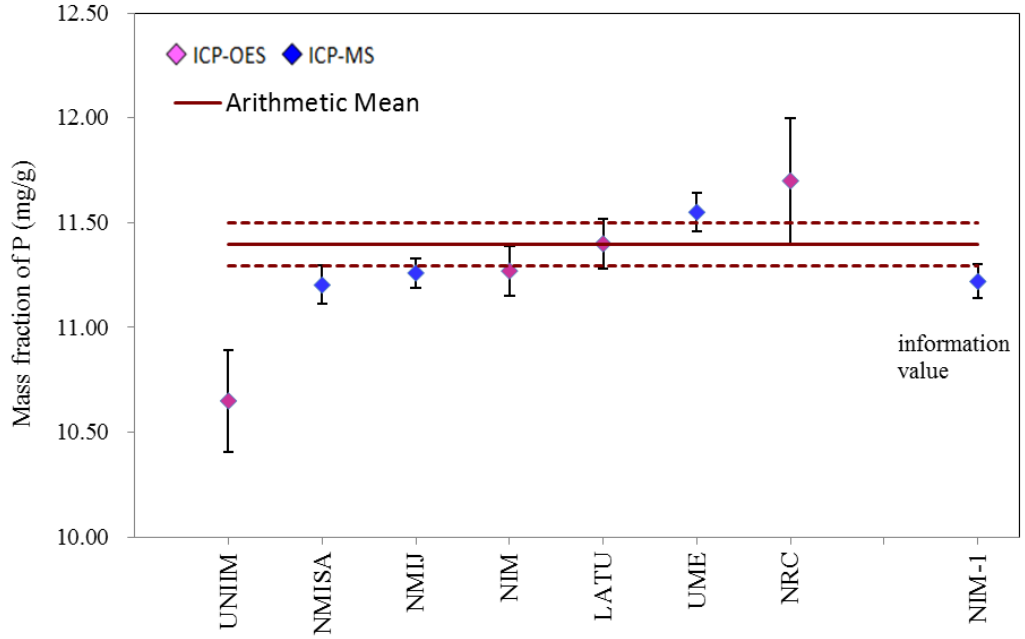

Fig.16 Results for Phosphorus in CCQM-K145 bovine liver sample

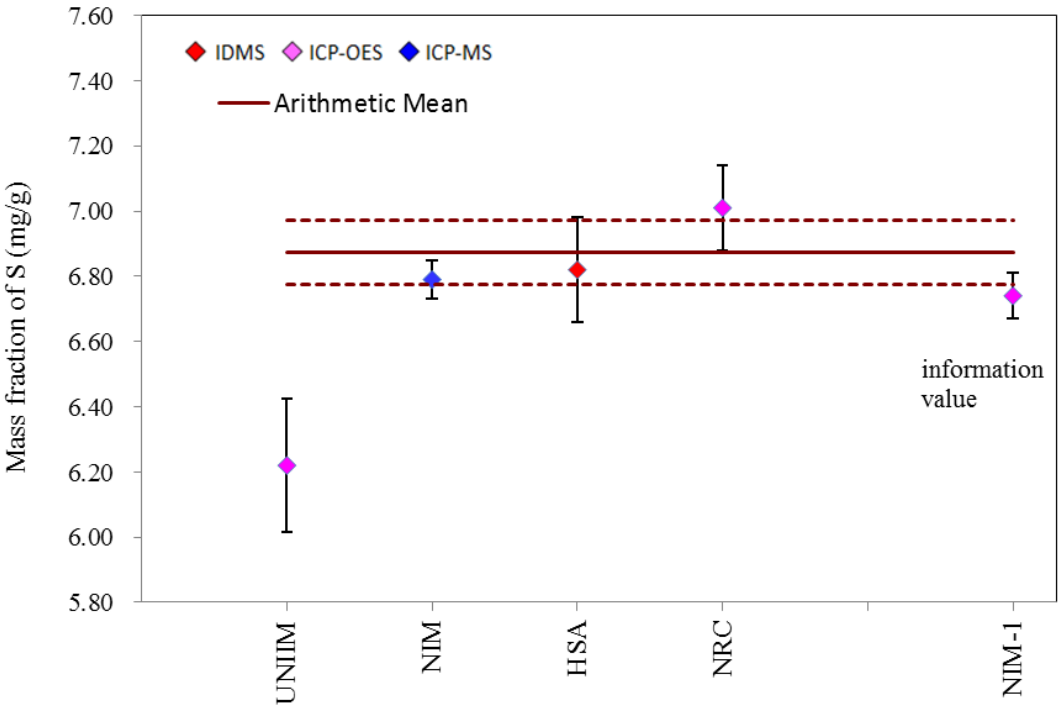

Fig.17 Results for Sulfur in CCQM-K145 bovine liver sample

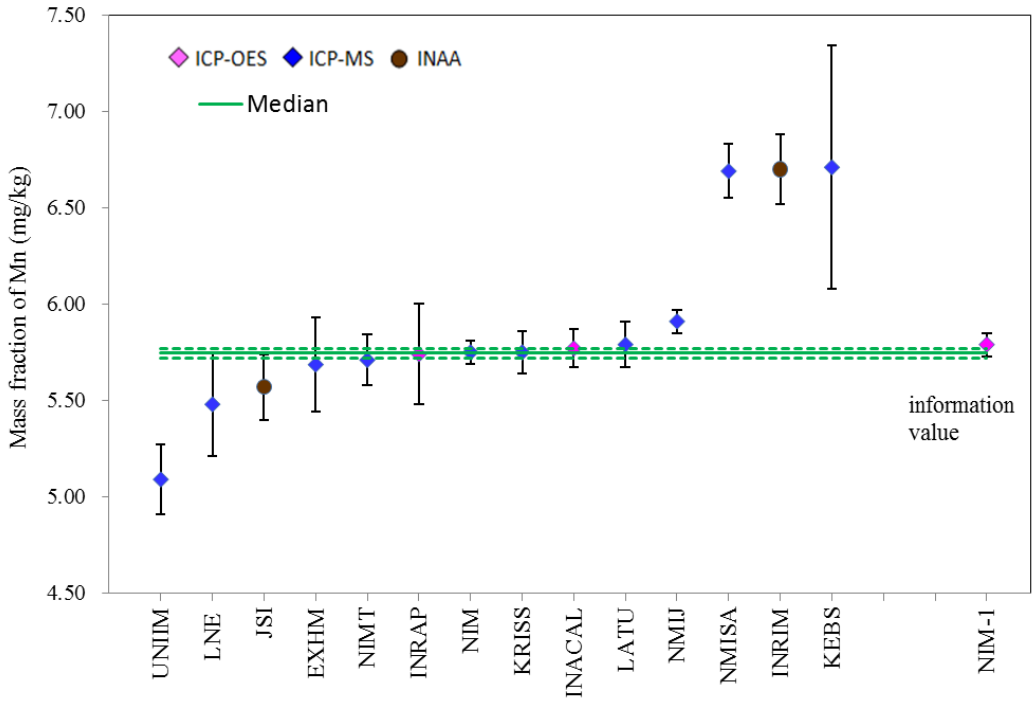

Fig.18 Results for Manganese in CCQM-K145 bovine liver sample

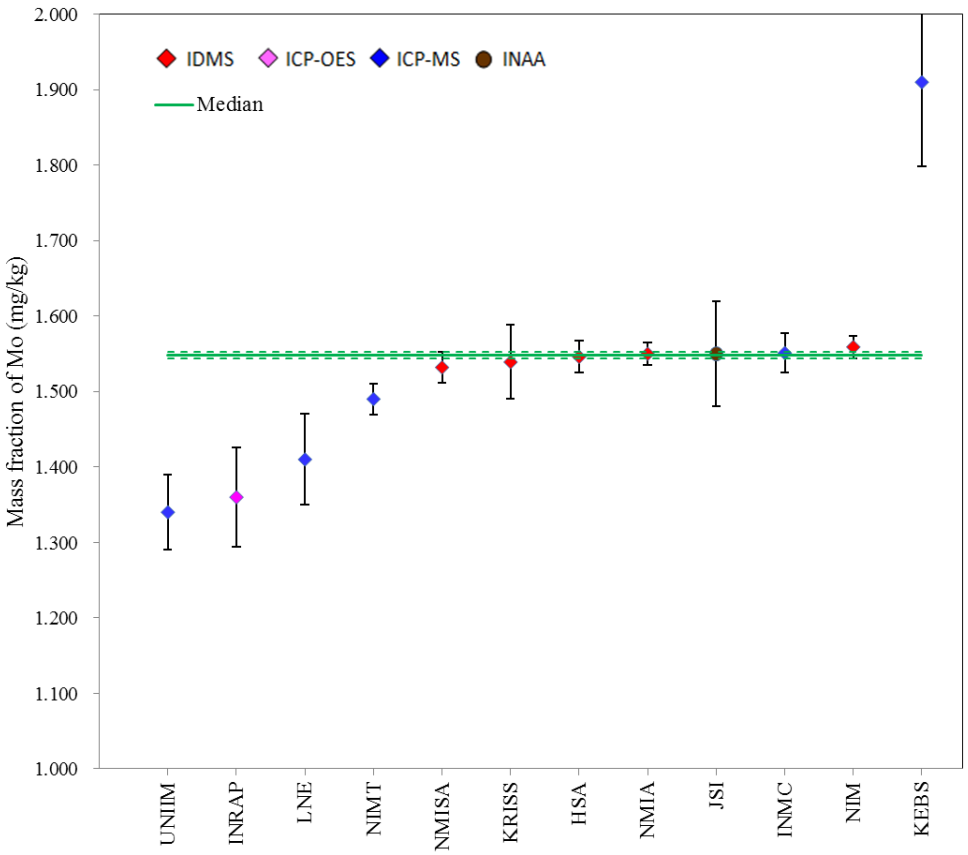

Fig.19 Results for Molybdenum in CCQM-K145 bovine liver sample

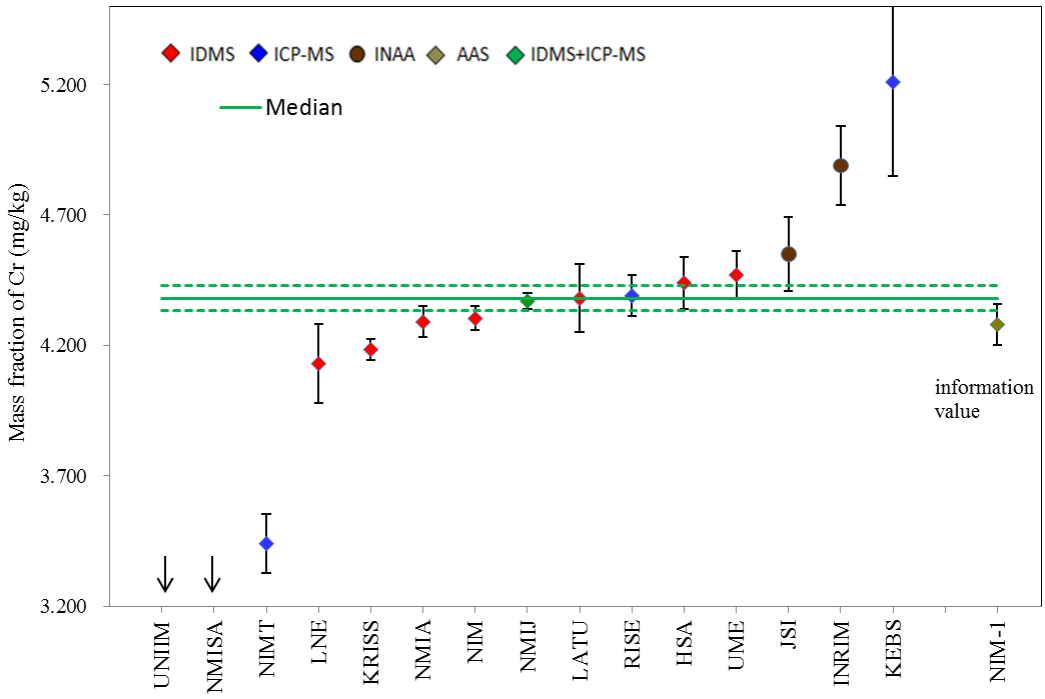

Fig.20 Results for Chromium in CCQM-K145 bovine liver sample

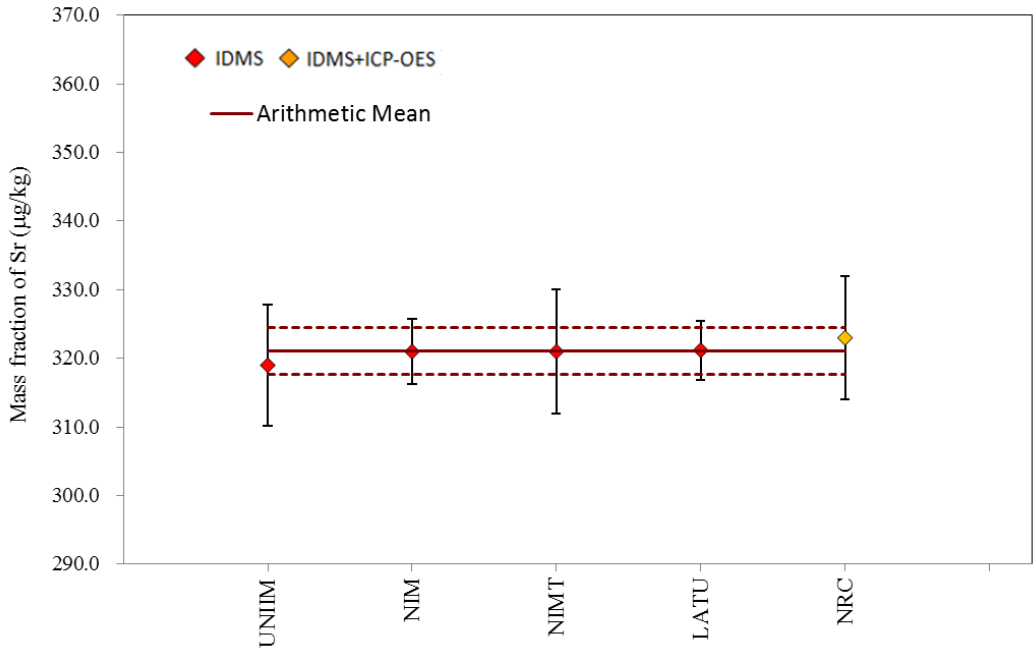

Fig.21 Results for Strontium in CCQM-K145 bovine liver sample

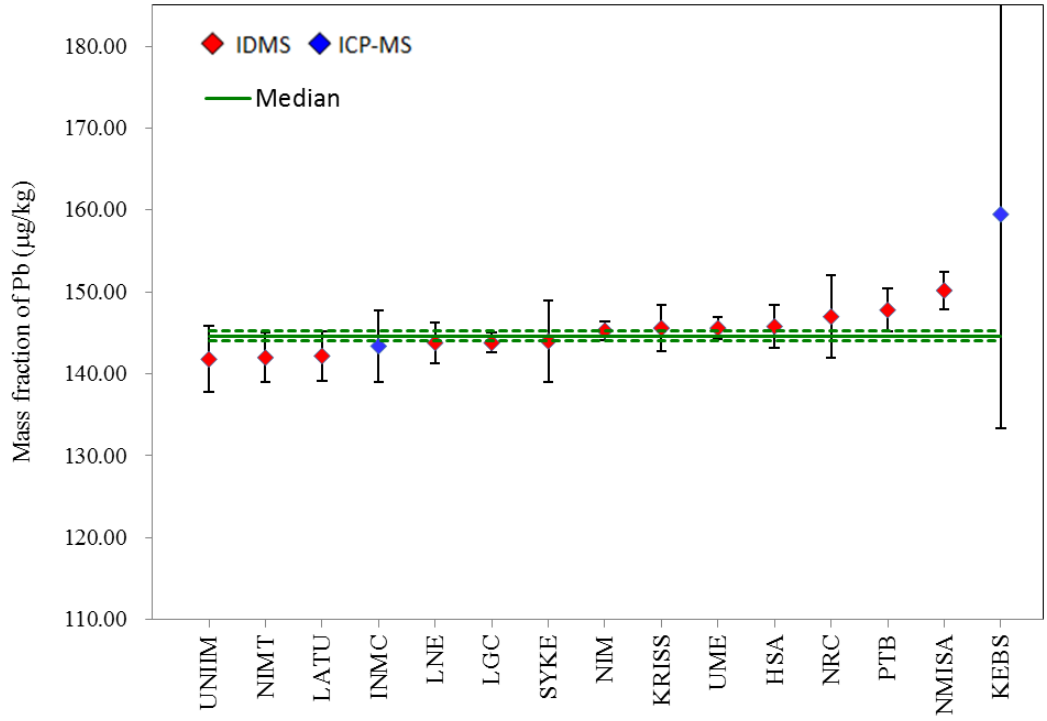

Fig.22 Results for Lead in CCQM-K145 bovine liver sample

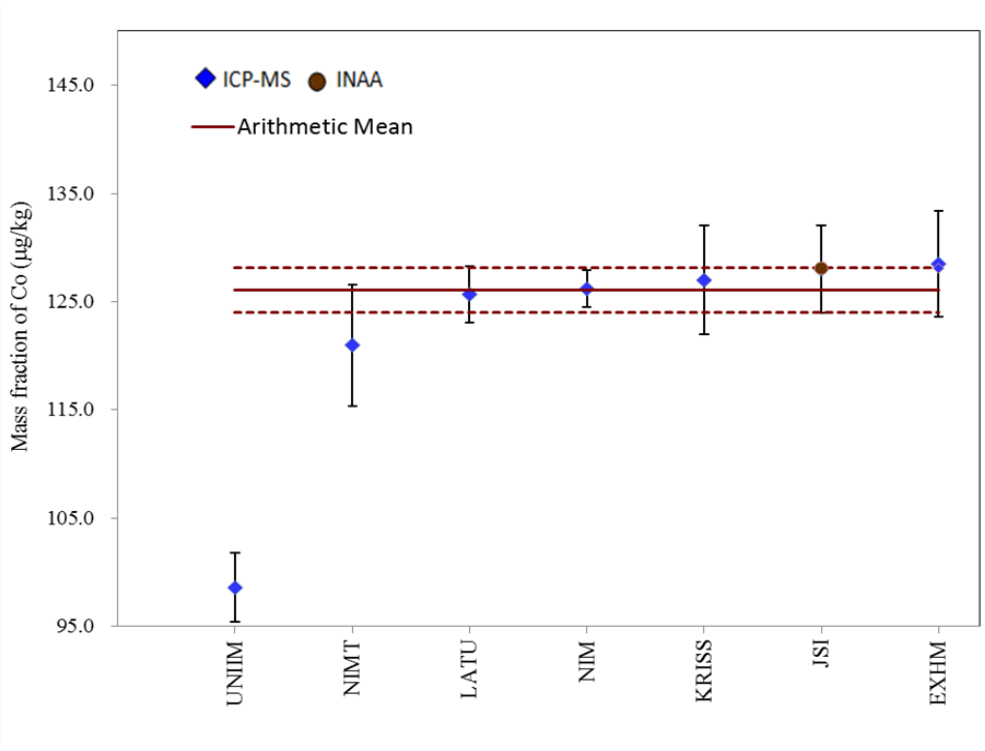

Fig.23 Results for Cobalt in CCQM-K145 bovine liver sample

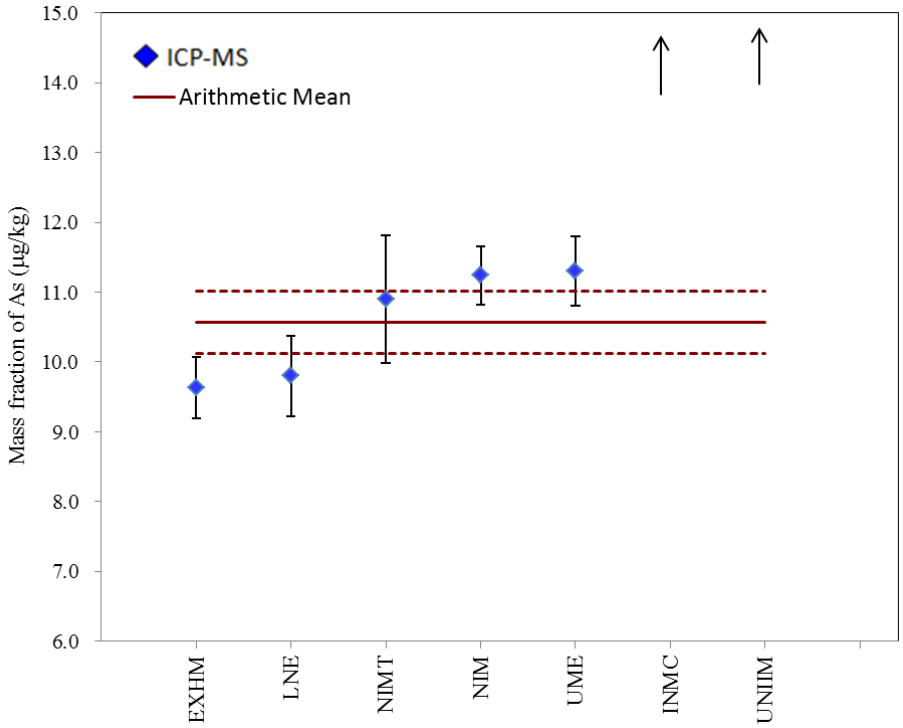

Fig.24 Results for Arsenic in CCQM-K145 bovine liver sample

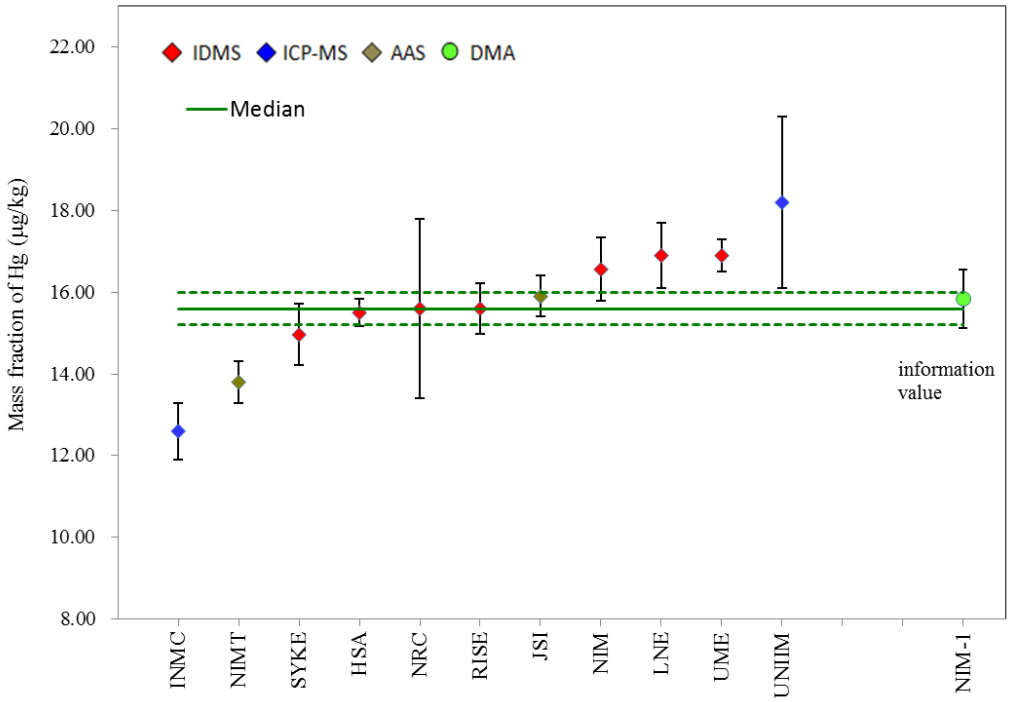

Fig.25 Results for Mercury in CCQM-K145 bovine liver sample

7.5 Equivalence statements

According to CCQM Guidance Note [2], the degree of equivalence of each national measurement standard is expressed quantitatively by two terms: its deviation from the key comparison reference value and the uncertainty of this deviation (at a 95 % level of confidence). The degree of equivalence or DoE (d_i, $U(d_i)$) are calculated using formulas (4) and (5).

$$d_i = (x_i - \mathrm{KCRV}) \tag{4}$$

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

Where:

x_i : reported value submitted by participant i (i = 1, …, n)

d_i : value component x_i – KCRV of the degree of equivalence (DoE) for participant i (i = 1, …, N)

$U(d_i)$: uncertainty component of the DoE for participant i (i = 1, …, N), this uncertainty is expressed at 95 % confidence.

Reported value x_i for measurand (Zn, Ni, P, S, Mn, Mo, Cr, Sr, Pb, As, Co, Hg) in the CCQM-K145 bovine liver sample with their associated combined standard uncertainties $u(x_i)$, together with the d_i, and the associated expanded combined uncertainties $U(d_i)$, are listed for each participant in Table21 ~ Table32. The equivalence statements for CCQM-K145 are shown graphically in Fig.26 ~ Fig.37.

Table 21. Equivalence statement of Zinc for CCQM-K145

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i/U(d_i)$
INRAP	429.71*	9.48	-26.5	19.1	-1.39
UNIIM	436*	9	-20	18	-1.1
LATU	453	5.6	-3	12	-0.3
INACAL	453.1	8.8	-3.1	18	-0.18
GLHK	453.6	7.7	-2.6	16	-0.17
NMIA	454.1	4.2	-2.1	8.7	-0.24
NIM	454.5	5.5	-1.7	11	-0.15
KRISS	454.5	6.7	-1.7	14	-0.13
LGC	454.5	3.9	-1.7	8.2	-0.21
NMISA	454.5	6.1	-1.7	12	-0.14
JSI	455	14	-1	28	-0.04
NIST	456.2	2.0	0.0	4.7	0.0
UME	457	4	1	8	0.1
HSA	459	7.1	3	14	0.2
PTB	459.4	1.7	3.2	4.2	0.77
RISE	460.5	3.2	4.3	6.8	0.63
SYKE	460.9	11.5	4.7	23.1	0.20
INMC	461	6.5	5	13.2	0.4
NRC	462	5	6	10	0.6
NIMT	462	13.2	6	26.4	0.2
NMIJ	462	3	6	6.5	0.9
KEBS	474.22*	16.46	18.0	33.0	0.55
INRIM	491.7*	10.0	35.5	20.2	1.76

Note: * reported value is not included in the calculation of KCRV.

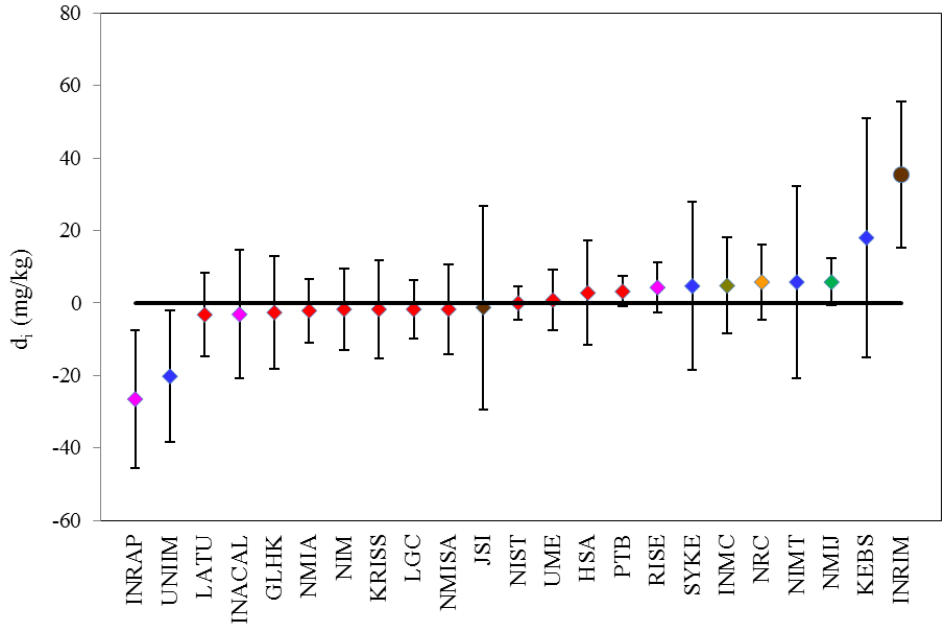

Fig.26 Equivalence statement of Zinc for CCQM-K145.
Points show the d_i, while the error bars denote the $U(d_i)$.

Table 22. Equivalence statement of Nickel for CCQM-K145

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i/U(d_i)$
UNIIM	0.147*	0.016	-1.88	0.059	-32
NMISA	0.902*	0.038	-1.12	0.090	-12
NIMT	1.65*	0.06	-0.37	0.13	-2.8
JSI	1.93	0.11	-0.09	0.23	-0.41
INMC	1.94	0.06387	-0.08	0.14	-0.60
GLHK	1.942	0.092	-0.080	0.19	-0.42
LNE	1.958	0.075	-0.064	0.16	-0.41
NIST	1.984	0.020	-0.038	0.064	-0.59
KRISS	1.993	0.033	-0.029	0.082	-0.35
INACAL	2.01	0.06	-0.01	0.13	-0.09
NMIA	2.02	0.05	-0.002	0.11	-0.02
NIM	2.022	0.023	0.000	0.068	0.00
NMIJ	2.05	0.02	0.03	0.06	0.5
RISE	2.055	0.052	0.033	0.12	0.29
NRC	2.07	0.05	0.05	0.11	0.45
PTB	2.077	0.035	0.055	0.086	0.64
LATU	2.08	0.059	0.06	0.13	0.45
LGC	2.131	0.042	0.109	0.097	1.1
UME	2.15	0.03	0.13	0.08	1.6
HSA	2.18	0.08	0.16	0.2	0.8
KEBS	4.63*	0.94	2.61	1.9	1.4

Note: * reported value is not included in the calculation of KCRV.

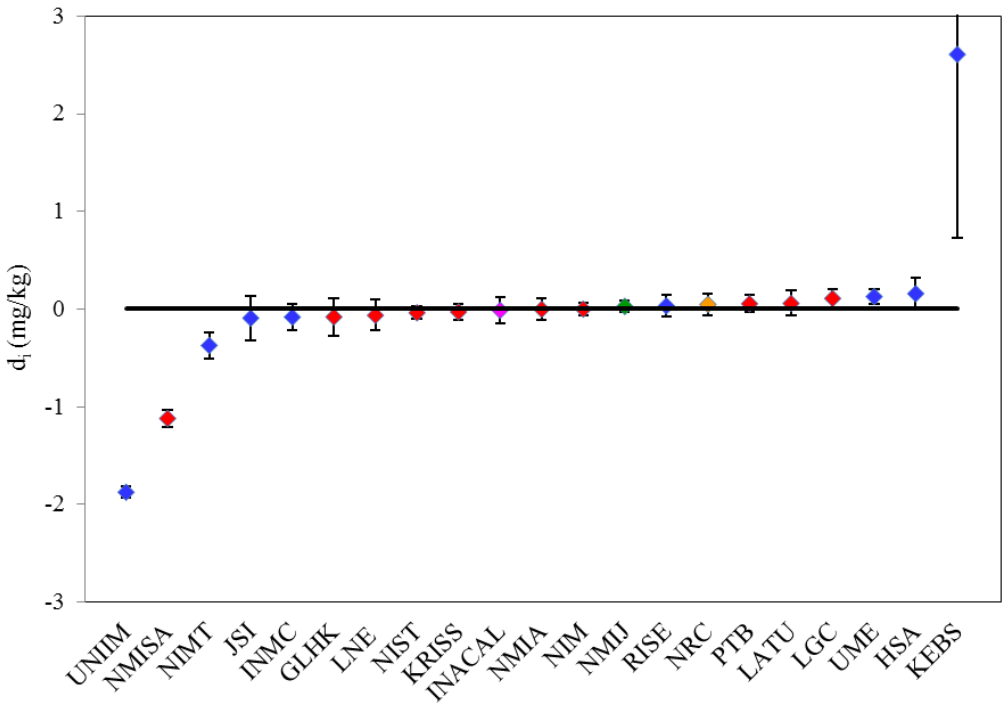

Fig.27 Equivalence statement of Nickel for CCQM-K145.
Points show the d_i, while the error bars denote the $U(d_i)$.

Table 23. Equivalence statement of Phosphorus for CCQM-K145

Institute	x_i (mg/g)	$u(x_i)$ (mg/g)	d_i (mg/g)	$U(d_i)$ (mg/g)	$d_i / U(d_i)$
UNIIM	10.65*	0.24	-0.75	0.53	-1.41
NMISA	11.203	0.092	-0.19	0.27	-0.71
NMIJ	11.26	0.07	-0.14	0.25	-0.56
NIM	11.27	0.12	-0.13	0.31	-0.41
LATU	11.40	0.12	0.00	0.31	0.00
UME	11.55	0.09	0.15	0.27	0.57
NRC	11.70	0.30	0.30	0.63	0.48

Note: * reported value is not included in the calculation of KCRV.

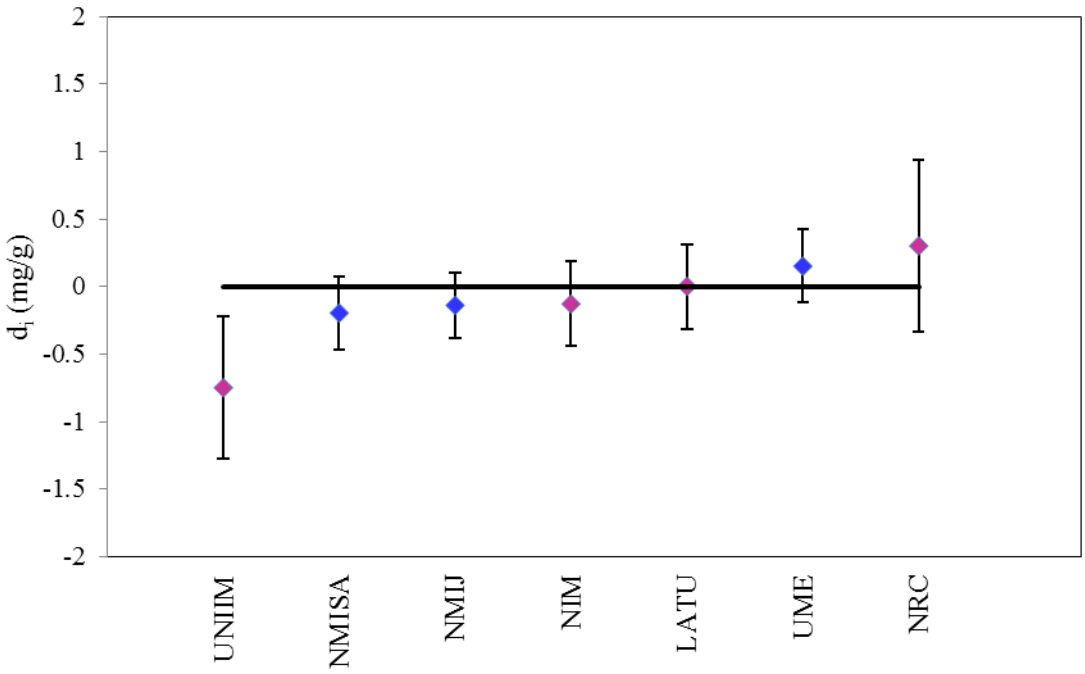

Fig.28 Equivalence statement of Phosphorus for CCQM-K145.
Points show the d_i, while the error bars denote the $U(d_i)$.

Table 24. Equivalence statement of Sulfur for CCQM-K145

Institute	x_i (mg/g)	$u(x_i)$ (mg/g)	d_i (mg/g)	$U(d_i)$ (mg/g)	$d_i / U(d_i)$
UNIIM	6.22*	0.21	-0.65	0.46	-1.43
NIM	6.79	0.06	-0.08	0.23	-0.36
HSA	6.82	0.16	-0.05	0.38	-0.14
NRC	7.01	0.13	0.14	0.33	0.42

Note: * reported value is not included in the calculation of KCRV

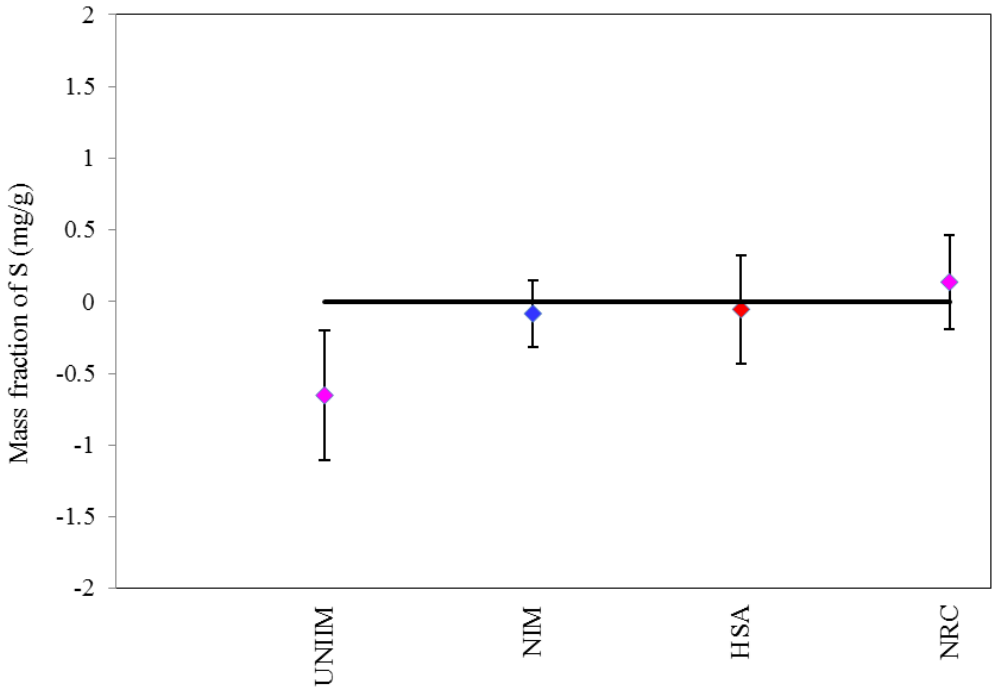

Fig.29 Equivalence statement of Sulfur for CCQM-K145.
Points show the d_i, while the error bars denote the $U(d_i)$.

Table 25. Equivalence statement of Manganese for CCQM-K145

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i / U(d_i)$
UNIIM	5.09*	0.18	-0.66	0.36	-1.8
LNE	5.48	0.27	-0.27	0.54	-0.49
JSI	5.57	0.17	-0.18	0.34	-0.51
EXHM	5.686	0.245	-0.059	0.49	-0.12
NIMT	5.71	0.13	-0.04	0.27	-0.15
INRAP	5.74	0.26	-0.01	0.52	-0.02
NIM	5.75	0.06	0.005	0.13	0.04
KRISS	5.75	0.11	0.005	0.23	0.02
INACAL	5.77	0.10	0.02	0.21	0.10
LATU	5.79	0.12	0.04	0.25	0.16
NMIJ	5.91	0.06	0.17	0.13	1.3
NMISA	6.69*	0.14	0.95	0.28	3.3
INRIM	6.70*	0.18	0.96	0.36	2.6
KEBS	6.71*	0.63	0.97	1.3	0.77

Note: * reported value is not included in the calculation of KCRV

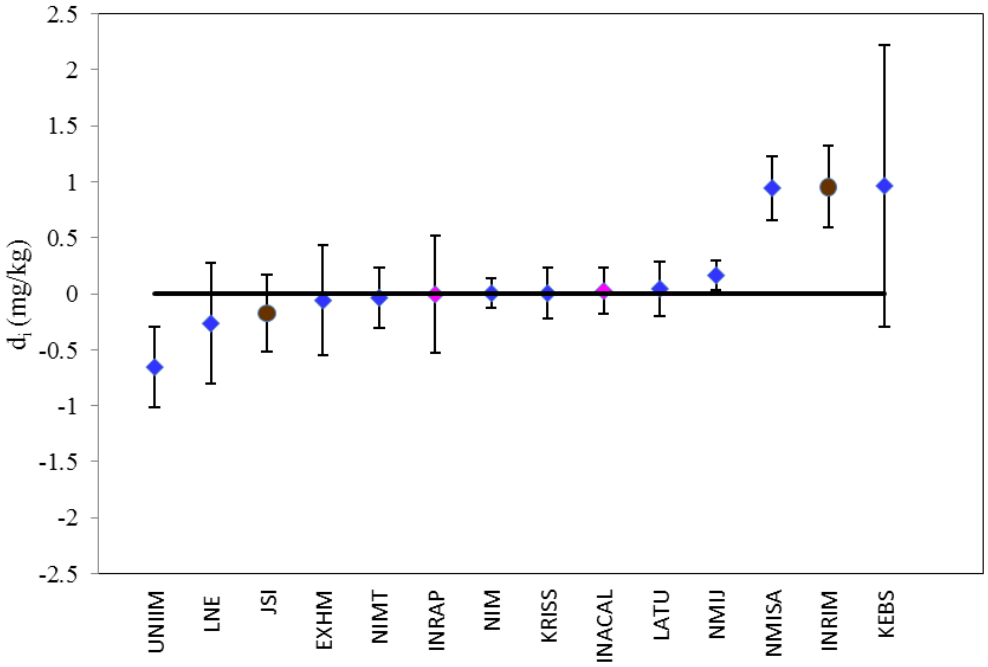

Fig.30 Equivalence statement of Manganese for CCQM-K145.
Points show the d_i, while the error bars denote the $U(d_i)$.

Table 26. Equivalence statement of Molybdenum for CCQM-K145

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i / U(d_i)$
UNIIM	1.34*	0.05	-0.21	0.1	-2
INRAP	1.36*	0.066	-0.19	0.13	-1.4
LNE	1.41*	0.06	-0.14	0.12	-1.2
NIMT	1.49	0.02	-0.058	0.04	-1.4
NMISA	1.532	0.021	-0.016	0.04	-0.4
KRISS	1.539	0.049	-0.009	0.10	-0.09
HSA	1.546	0.021	-0.002	0.04	-0.05
NMIA	1.550	0.015	0.002	0.03	0.06
JSI	1.55	0.07	0.002	0.14	0.014
INMC	1.551	0.026	0.003	0.05	0.06
NIM	1.559	0.015	0.011	0.03	0.36
KEBS	1.91*	0.11	0.36	0.22	1.6

Note: * reported value is not included in the calculation of KCRV

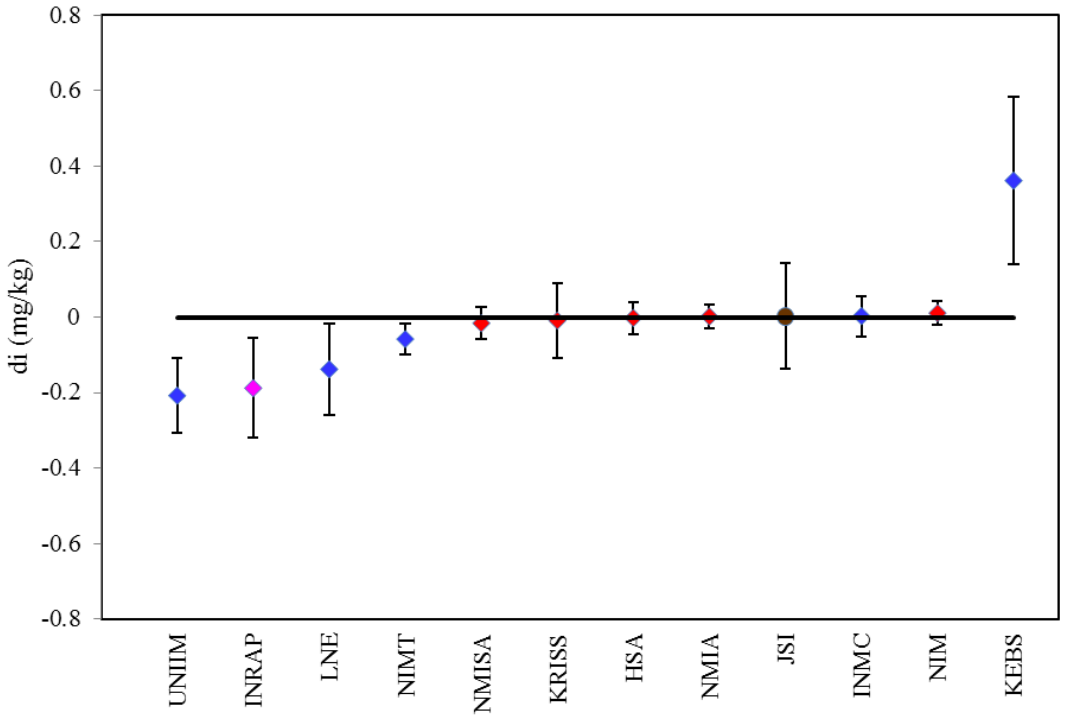

Fig.31 Equivalence statement of Molybdenum for CCQM-K145.
Points show the d_i, while the error bars denote the $U(d_i)$.

Table 27. Equivalence statement of Chromium for CCQM-K145

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d_i / U(d_i)$
UNIIM	0.345*	0.015	-4.04	0.10	-40
NMISA	1.816*	0.07	-2.56	0.17	-15
NIMT	3.44*	0.11	-0.94	0.25	-3.8
LNE	4.13	0.15	-0.25	0.32	-0.78
KRISS	4.184	0.041	-0.196	0.13	-1.5
NMIA	4.29	0.06	-0.09	0.16	-0.56
NIM	4.303	0.046	-0.080	0.14	-0.57
NMIJ	4.37	0.03	-0.01	0.12	-0.08
LATU	4.38	0.13	0.00	0.28	0.00
RISE	4.39	0.079	0.01	0.19	0.053
HSA	4.44	0.10	0.06	0.22	0.27
UME	4.47	0.09	0.09	0.2	0.4
JSI	4.55	0.14	0.17	0.30	0.57
INRIM	4.89	0.15	0.51	0.32	1.6
KEBS	5.21*	0.36	0.83	0.73	1.1

Note: * reported value is not included in the calculation of KCRV

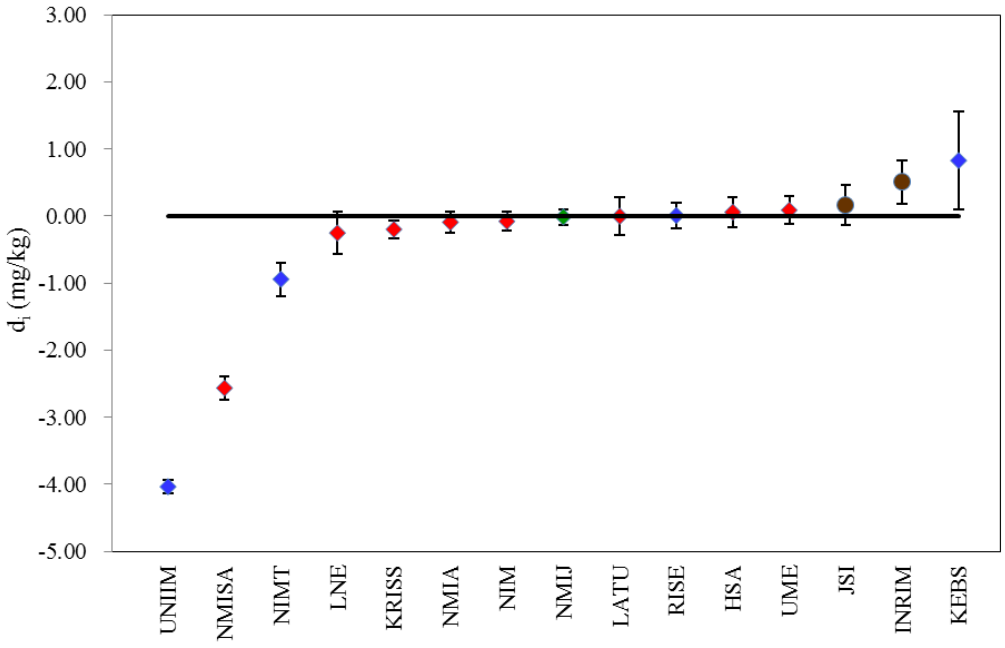

Fig.32 Equivalence statement of Chromium for CCQM-K145.
Points show the d_i, while the error bars denote the $U(d_i)$.

Table 28. Equivalence statement of Strontium for CCQM-K145

Institute	x_i (μg/kg)	$u(x_i)$ (μg/kg)	d_i (μg/kg)	$U(d_i)$ (μg/kg)	$d_i / U(d_i)$
UNIIM	319	9	-2	19	-0.1
NIM	321.0	4.7	-0.04	12	-0.003
NIMT	321	9	-0.04	19	-0.002
LATU	321.2	4.3	0.2	11	0.02
NRC	323	9	2	19	0.1

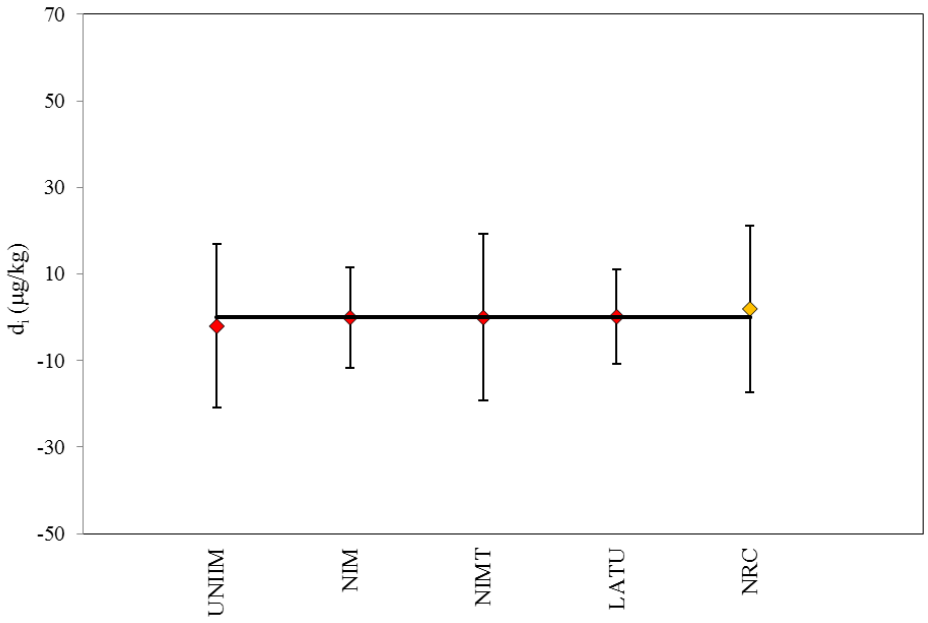

Fig.33 Equivalence statement of Strontium for CCQM-K145.
Points show the d_i, while the error bars denote the $U(d_i)$.

Table 29. Equivalence statement of Lead for CCQM-K145

Institute	x_i (μg/kg)	$u(x_i)$ (μg/kg)	d_i (μg/kg)	$U(d_i)$ (μg/kg)	$d_i/U(d_i)$
UNIIM	141.8	4	-2.9	8	-0.36
NIMT	142	3	-3	6	-0.5
LATU	142.2	3.0	-2.4	6	-0.4
INMC	143.4	4.3	-1.2	8.8	-0.14
LNE	143.8	2.5	-0.8	5.1	-0.16
LGC	143.8	1.2	-0.8	2.7	-0.3
SYKE	144.0	5.0	-0.6	10	-0.06
NIM	145.30	1.15	0.65	2.6	0.25
KRISS	145.6	2.8	0.9	5.7	0.2
UME	145.6	1.3	0.9	2.9	0.3
HSA	145.8	2.6	1.2	5.3	0.23
NRC	147	5	2	10	0.2
PTB	147.8	2.6	3.2	5.3	0.60
NMISA	150.2	2.3	5.6	4.8	1.2
KEBS	159.49*	26.09	14.8	52	0.28

Note: * reported value is not included in the calculation of KCRV

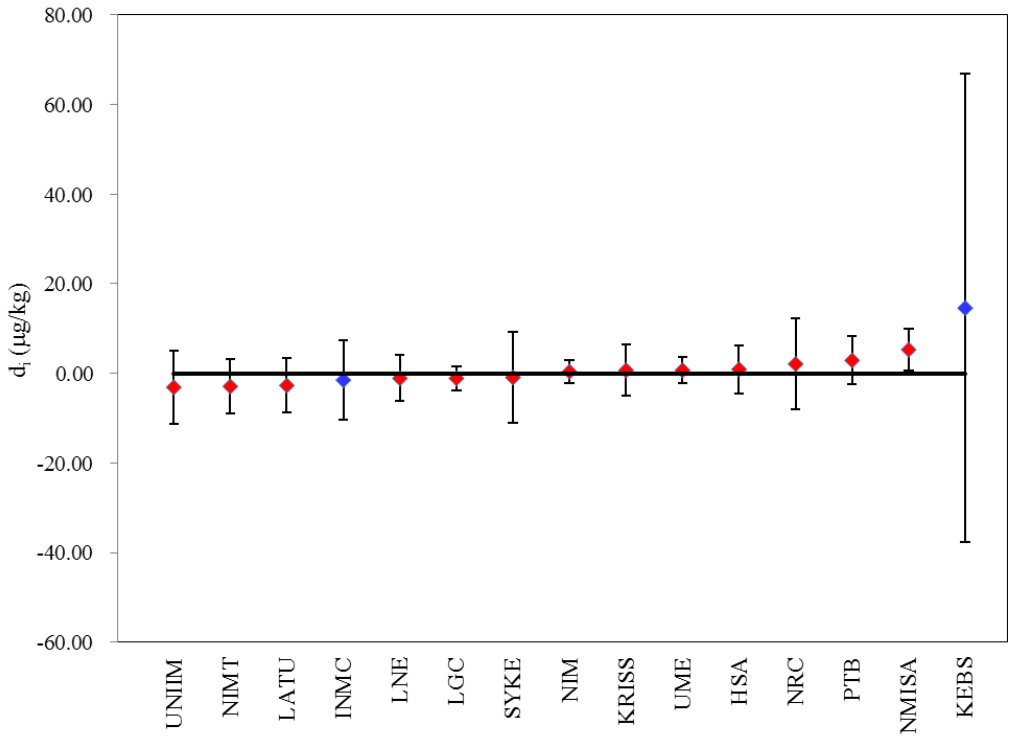

Fig.34 Equivalence statement of Lead for CCQM-K145.
Points show the d_i, while the error bars denote the $U(d_i)$.

Table 30. Equivalence statement of Cobalt for CCQM-K145

Institute	x_i (μg/kg)	$u(x_i)$ (μg/kg)	d_i (μg/kg)	$U(d_i)$ (μg/kg)	$d_i / U(d_i)$
UNIIM	98.6*	3.2	-27.5	7.6	-3.6
NIMT	121	5.6	-5	12	-0.4
LATU	125.7	2.6	-0.4	6.6	-0.06
NIM	126.2	1.7	0.1	5.3	0.02
KRISS	127	5	1	11	0.09
JSI	128	4	2	9	0.2
EXHM	128.5	4.9	2.4	11	0.22

Note: * reported value is not included in the calculation of KCRV

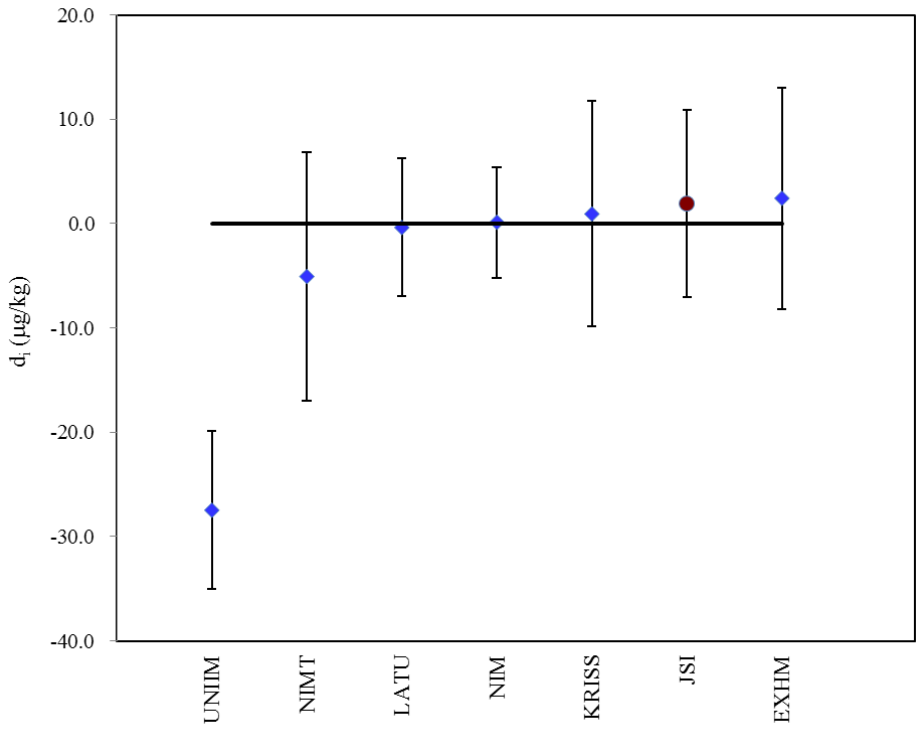

Fig.35 Equivalence statement of Cobalt for CCQM-K145.
Points show the d_i, while error bars denote $U(d_i)$.

Table 31. Equivalence statement of Arsenic for CCQM-K145

Institute	x_i (μg/kg)	$u(x_i)$ (μg/kg)	d_i (μg/kg)	$U(d_i)$ (μg/kg)	$d_i / U(d_i)$
EXHM	9.63	0.44	-0.94	1.2	-0.78
LNE	9.8	0.6	-0.8	1.5	-0.53
NIMT	10.9	0.91	0.3	2.0	0.15
NIM	11.24	0.42	0.67	1.2	0.56
UME	11.3	0.5	0.7	1.3	0.54
INMC	19.4*	1.1	8.8	2.3	3.8
UNIIM	25.2*	3.1	14.6	6.3	2.3

Note: * reported value is not included in the calculation of KCRV

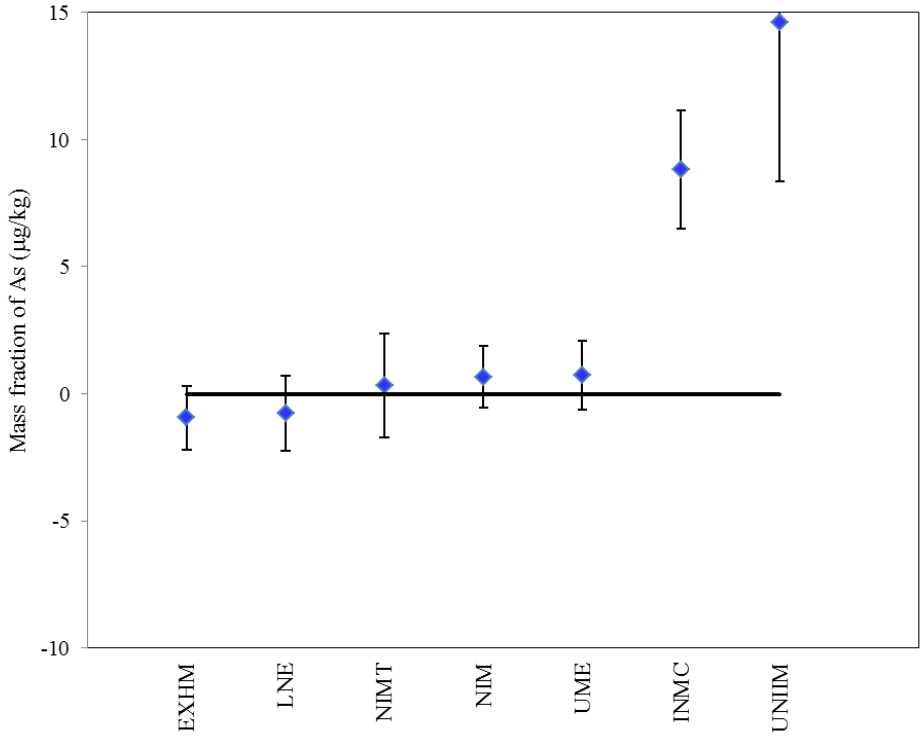

Fig.36 Equivalence statement of Arsenic for CCQM-K145.
Points show the d_i, while error bars denote $U(d_i)$.

Table 32. Equivalence statement of Mercury for CCQM-K145

Institute	x_i (μg/kg)	$u(x_i)$ (μg/kg)	d_i (μg/kg)	$U(d_i)$ (μg/kg)	$d_i / U(d_i)$
INMC	12.6*	0.69	-3.2	1.7	-1.9
NIMT	13.8	0.52	-2.0	1.4	-1.4
SYKE	14.96	0.75	-0.79	1.8	-0.44
HSA	15.50	0.33	-0.25	1.1	-0.23
NRC	15.6	2.2	-0.2	4.5	-0.04
RISE	15.6	0.62	-0.2	1.5	-0.13
JSI	15.9	0.5	0.1	1.4	0.07
NIM	16.56	0.78	0.81	1.8	0.45
LNE	16.9	0.8	1.1	1.8	0.61
UME	16.9	0.4	1.1	1.2	0.92
UNIIM	18.2	2.1	2.4	4.3	0.56

Note: * reported value is not included in the calculation of KCRV

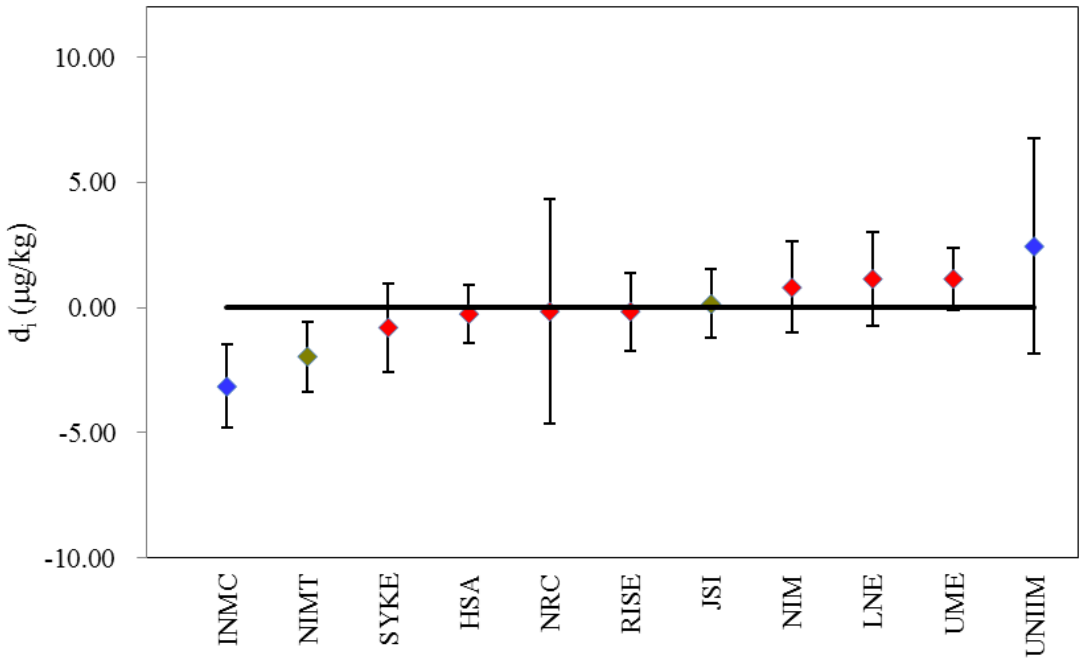

Fig.37 Equivalence statement of Mercury for CCQM-K145.
Points show the d_i, while error bars denote $U(d_i)$.

8. CONCLUSION

With respect to the methodology, most of the participants used microwave digestion methods for sample pretreatment. For the instrumental determination, a variety of techniques such as IDMS, ICP-OES, ICP-MS(non-ID), AAS and NAA were adopted by the participants. Some participants reported the measurement results by using a combined techniques, such as IDMS and ICP-MS(standard addition), IDMS and ICP-OES(standard addition). For Zn, Ni, Sr, Pb and Hg measurements, most participants chose ID-ICP-MS method, which showed the better performance in terms of consistency and reliability of the measruement results. According to the information of Table 6~Table 17, the measurement methods adopted by all participants in CCQM-K145 are summaried in Table 33.

Table 33. Measurement methods adopted in CCQM-K145

measurand	Measurement methods						
	IDMS	ICP-MS (non-ID)	ICP-OES	AAS	NAA	XRF	MDA
Zn	14	5	6	1	2	1	/
Ni	13	10	3	/	/	/	/
P	/	4	5	/	/	/	/
S	1	1	4	/	/	/	/
Mn	/	10	4	/	2	/	/
Mo	5	5	1	/	1	/	/
Cr	10	5	/	1	2	/	/
Sr	5	1	1	/	/	/	/
Pb	14	3	/	/	/	/	/
Co	/	7	/	/	1	/	/
As	/	8	/	/	/	/	/
Hg	7	2	/	2	/	/	1

Base on different statistic way to calculate the reference mass fraction values and associated uncertainties for each measurand, and removal of the suspected extreme values, the median values are proposed as the KCRV for Zn, Ni, Mn, Mo, Cr, Pb and Hg; the arithmetic mean values are proposed as the KCRV for P, S, Sr, Co and As. According to the CCQM Guidance Note[2], the expanded uncertainty of the reference value is calculated as $U = 2 \times u$.

In aspect of the traceability for the measurement results in CCQM-K145, most participants used their own (in house) CRMs or other NMI's CRMs to guarantee trace to SI unit. Most participants used similar matrix CRMs for quality control or method validation.

In general, the performances of the majority of CCQM-K145 participants are very good, illustrating their measurement capabilities for Zn, Ni, P, S, Mn, Mo, Sr, Cr, As, Co, Pb and Hg in a complex biological tissue matrix.

Measurement capability claims- How far the light shines

The purpose of CCQM-K145 is to ensure the comparable and traceable measurement results for essential and toxic elements such as P, S, Zn, Mn, Ni, Mo, Sr, Cr, Co, Pb, As and Hg in bovine liver among NMIs and other designated measurement bodies worldwide.

Bovine liver contains many kinds of nutrients and microelements, it can be regarded as a typical representative material of biological tissue and food. In CCQM-K145, the analytes involved alkali metals and transition elements, metalloids / semi-metals and non metals with a range of mass fraction from mg/g

to μg/kg. CCQM-K145 also tested the ability of NMIs/DIs to determine elements that were easy to be lost and polluted, and interfered significantly. The chemical pretreatment methods of samples used in the comparison is suitable for general food and biological matrix samples. A variety of measurement methods used in the comparison represent the main instrumental technology for elemental analysis.

Based on measurement of 12 elements in CCQM-K145, the CCQM IAWG Core Capability Table is shown in APPENDIX A. For supporting CMC claim, CCQM-K145 is readily applicable to measurement of more elements in a wide range of biological materials (including liquids and solids) and meat products.

9. ACKNOWLEDGEMENTS

The contact persons, analysts and institutes responded to this comparison and contributed their efforts to CCQM-K145 are highly appreciated and acknowledged. Many thanks for the support and advice from Dr. Mike Sargent and Dr. Michael Winchester.

10. REFERENCES

[1] International Standards Organization, ISO Guide 35: Reference materials – General and statistical principles for certification, Geneva, Switzerland, 2006.

[2] CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, Version: 10, 2013-04-12.

[3] The Core Capability approach in support of CMCs for Inorganic Analysis: guidelines for the use of the revised approach. 2018-10.

APPENDIX A: CCQM IAWG CORE CAPABILITY TABLE

CCQM IAWG Core Capability 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)						
				K145 (Sr)		
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)				**K145** (Hg)		
				K145 (Zn, Mn, Mo, Cr, Ni, Pb, Co)		
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)						
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)				**K145** (As)		
Non-metals (P, S, C, N, O)						
				K145 (P, S)		
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)

APPENDIX B: REGISTRATION FORM AND TECHNICAL PROTOCOL

CCQM-K145 & P183
Essential and Toxic Elements in Bovine Liver
Registration Form

Institute	Full Name:
	Abbreviative Name:
	☐ **NMI** ☐ **DI** ☐ **Expert institute**
City, Country	
Detail Address*	
Post Code	
Contact Person	
Fax	
Tel	
Email	

*** The sample will be dispatched directly to you according to this table, please fill in it in detail.**

Measurand	**CCQM-K145**	**CCQM-P183**	**Methods of analysis**
	Yes/No	**Yes/No**	
P			
S			
Zn*			
Ni*			
Mn			
Mo			
Cr			
Sr			
Pb			
Co			
As			
Hg			

*** Exemplary elements for the 6th IAWG Benchmarking Exercise.**

Other information:

a) Each participant will receive one numbered bottle containing 10g sample in each bottle. Based on the analyte and measurement methods chose by participant, if more sample is needed, please tell us at the time of registration.

b) A special requirement of customs entry for the sample dispatch should be described clearly, if needed.

Please send completed registration form to Wang Jun by e-mail no later than 10 June, 2017.

Coordinating laboratory and contact person
Dr. Wang Jun
National Institute of Metrology (NIM)
No. 18, Bei San Huan Dong Lu, Chaoyang District, Beijing, P.R.China
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CCQM-K145 & P183
Essential and Toxic Elements in Bovine Liver
Technical Protocol

1. Introduction

Liver plays a major role in metabolism and acts as a source of energy for the body by storing glycogen. Also, working with other systems and organs, it is responsible for several important functions such as storing iron, detoxifying harmful substances, maintaining the hormonal balance, and producing immune factors to fight infections. Cattle seemed to be the most sensitive animal species with respect to some metal toxicities resulting from ingestion of feed material. With the growing interest in the biological effects and also for the meet measurement quality, it is important and necessary to develop accurate and comparable analytical methods for elements in bio-samples. It has, however, been 10 years since the tissue sample (bovine liver) of CCQM-K49 key comparison. Therefore, the IAWG has included the need for such a key comparison to maintain, expand and improve core capabilities, and to support specific CMCs claim in bio-sample analysis as well.

The purpose of CCQM-K145&P183 is to ensure the comparable and traceable measurement results for essential and toxic elements such as P, S, Zn, Mn, Ni, Mo, Sr, Cr, Co, Pb, As and Hg in bovine liver among NMIs and other designated measurement bodies worldwide. The comparison has been agreed by IAWG as 6th IAWG Benchmarking Exercise with Zn and Ni as exemplary elements at the meeting in Korea in the early October 2016. The results of CCQM-K145 are expected to cover the measurement capability and support CMC claiming for inorganic elements in the similar biological tissue materials.

2. Sample

Liver tissues of new born healthy steers were collected and prepared under the strict protocols by the professional biological institutes. After the pretreatment of the raw materials, liver tissues were cut into portions of approximately 10 cm^3. Then, they were homogenized with a high speed mixer, frozen and lyophilized by a freeze dryer, ground with ball grinding mill. The bovine liver powder was subjected to a sieving process through 200 mesh sieve and thoroughly homogenized in a 3-dimensional mixer. The resulting final product was radiation sterilized, bottled and stored at room temperature.

The homogeneity was investigated by analyzing 25 bottles of the liver material and determined by ICP-OES, WD-XRF and ICP-MS, the sampling weight is about 300mg. The microwave digestion was used to the sample preparation for ICP-OES and ICP-MS analysis. The results based on the *F* test showed the homogeneity level can fit the objective of the comparison.

The stability of the liver material at room temperature was conducted by using ICP-OES and ICP-MS. The testing results show that no obvious change trend of quantity was observed for the typical level elements during the 6-month period. The long-term stability of the material will be continued until the deadline for submission of this comparison results.

3. Measurands

The measurands to be determined are the mass fractions of P, S, Zn, Mn, Mo, Cr, Ni, Pb, Sr, Co, As and Hg. The expected concentration ranges of the twelve elements are listed in Table 1.

Table 1. Measurands and expected concentration range

Elements	Expected concentration ranges
Phosphorus	(5~50)mg/g
Sulfur	(1~30)mg/g
Zinc*	(50~500) mg/kg
Nickel*	(0.1~10) mg/kg
Manganese	(0.1~10) mg/kg
Molybdenum	(0.1~10)mg/kg
Chromium	(0.1~10) mg/kg
Strontium	(50~500) μg/kg

Lead	(10~300) μg/kg
Cobalt	(10~300) μg/kg
Arsenic	(1~100) μg/kg
Mercury	(1~100) μg/kg

For the benchmarking purpose, participants should carry out the analysis of the two exemplary analyte Zinc and Nickel, and submit the analytical results for Zinc and Nickel accordingly.

4. Measurement method

Participants may use any appropriate method(s) of their choice. The sample should be mixed thoroughly before pretreatment, and the analysis should be conducted with a recommended sample size of at least 300mg. Sample digestion methods is not prescribed; however, for methods requiring sample digestion, participants are cautioned about potential analyte loss, especially with dry-ashing techniques. It is suggested that at least five replicate samples be analyzed in order to assess the impact of measurement replication on the overall analytical uncertainty.

5. Dry mass correction

Because lyophilized bovine liver tissues are somewhat hygroscopic, and its moisture content may be affected to change by the environmental conditions. So **it is recommended that moisture determinations should be made on separate test portions taken at the same time as the portions to be analyzed.** The recommended procedure is that the sample (size of 0.5~1g) is dried at 60℃ for 7 hours by using oven drying, then balanced in a desiccator to room temperature.

6. Distribution

Each participant will receive one numbered bottle containing 10g sample in each bottle. Based on elements and measurement methods chose by participants, if more sample is needed, please specify in the registration form. Participants will be informed the date of samples dispatching, also each participant is required to confirm the receipt of the sealed samples, to fill in the return receipt table and send it to the coordinator by e-mail. If there is any damage, please contact us immediately and NIM will mail out another one.

7. Handling and storing instructions

The sample should be stored at room temperature (18～22℃) in its original bottle, capped tightly and not exposed to intense direct light and ultraviolet radiation. The sample should be carefully opened for analysis in a short period of time to avoid contamination.

8. Time schedule

Call for Participation: May, 2017
Deadline for registration: 10 June, 2017
Dispatch of the samples: June-July, 2017
Deadline for receipt of the result report: 28 Feb., 2018
Discussing of the result: CCQM/ IAWG Paris meeting of 2018

9. Registration

Please complete the registration form and return it to wangjun@nim.ac.cn no later than 10 June 2017.

10. Reporting

A suggestion for a summary report table will be sent to the participants by email while the samples are dispatched. The report should be submitted before 20 December, 2017. NIM will confirm the receipt of each report. The report should include the following aspects:

✧ A final result and uncertainty evaluation. The results will be reported as mass faction [mg/g] for P and S, [mg/kg] for Zn, Mn, Mo, Cr and Ni, [μg/kg] for Pb, Sr, Co, As and Hg, respectively. At least five replicate

samples should be performed for each element.

- ✧ Please note that only one result from each institute will be considered for calculation of the KCRV of each element.
- ✧ A detail description of the applied method of measurement. If more than one method were applied, a detail description must be given for each method.
- ✧ Information about sample digestion and preparation.
- ✧ Information about the reference material used for calibration (origin, standard value, standard uncertainty and isotopic ratio if necessary) or other materials used in the analytical procedure.
- ✧ Information about the measurement uncertainty:
  - The complete specification of the measurement equation, including corrections, e.g. for blanks and interferences.
  - The identification and quantification of all uncertainty sources.
  - The combined standard uncertainty.
  - The value for the coverage factor and the expanded uncertainty.
- ✧ Filled core capability tables relating to the measurement methods used by participants.

11. Participation

National metrological institutes (NMIs), or an appropriate designated institute in accordance with the CIPM MRA, are welcome to participate in the key comparison CCQM-K145 or the pilot study CCQM-P183. Other expert institutes from countries that are members of the Metre Convention are also invited to participate in the pilot study.

Coordinating laboratory and contact person

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