CCQM-K124
Trace Elements and Chromium Speciation in Drinking Water

Part A: Trace Elements in Drinking Water
Part B: Chromium Speciation in Drinking Water

Final Report

Coordinated by

National Metrology Institute of Japan (NMIJ)

Government Laboratory, Hong Kong SAR (GLHK)

November 2016

CCQM-K124

Part A: Trace Elements in Drinking Water

Final Report

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Coordinated by NMIJ

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Abstract

CCQM-K124 was an activity of the Inorganic Analysis Working Group (IAWG) and was jointly coordinated by the National Metrology Institute of Japan (NMIJ) and the Government Laboratory, Hong Kong SAR (GLHK). The Part A of CCQM-K124 was organized by NMIJ and trace elements in drinking water were the measurands. The Part A of the key comparison was undertaken for NMIs and DIs to demonstrate their capabilities in measuring part-per-billion level (in µg/kg) or part-per-million level (in mg/kg) of trace elements in drinking water. It should also facilitate the acquisition of claims in Calibration and Measurement Capabilities (CMCs) as listed in Appendix C of Key Comparison Database (KCDB) under the Mutual Recognition Arrangement of the International Committee of Weights and Measures (CIPM MRA).

Results were submitted by 14 NMIs and nine DIs. The participants used different measurement methods, though most of them used direct measurement using inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS) and high resolution ICP-MS and isotope dilution technique with ICP-MS. Other methods were graphite furnace atomic absorption spectrophotometry (GFAAS) and flame atomic absorption spectrophotometry (FAAS).

The results of B, Ca, Cr, As and Cd show good agreement except some outliers.

Concerning Hg, instability was observed when the sample was stored in the light. And some participants observed instability of Mo. Therefore, it was agreed to abandon the Hg and Mo analysis as this sample was not satisfactory for KC.

Accounting for relative expanded uncertainty, comparability of measurement results for each of B, Ca, Cr, As and Cd was successfully demonstrated by the participating NMIs or DIs. Furthermore, the results of this key comparison can be utilized along with the IAWG core capability approach.

It is expected that arsenic, boron, cadmium, calcium and chromium at mass fractions greater than approximately 0.1 µg/kg, 1 µg/kg, 0.01 µg/kg, 1 mg/kg and 0.1 µg/kg respectively in drinking water and similar matrices (groundwater and river water etc.) can be determined by each participant using the same technique(s) employed for this key comparison to achieve similar uncertainties mentioned in the present report.

Table of Content

1. Introduction

Quality standards for drinking water, like WHO (World Health Organization) Guidelines, have been established in nations and regions around the world. Also, levels of many elements in drinking water are regulated for safety and health concerns.

In the IAWG's five-year plan, a comparison under the category of water analysis was recommended for the year 2014 and IAWG members were encouraged to attempt as the comparison would involve some basic and important analytical techniques. In this connection, NMIJ and GLHK proposed to coordinate this key comparison and an associated pilot study, CCQM-K124 and CCQM-P158 respectively at the IAWG meeting held November 5-6, 2013, for participating NMIs and DIs to demonstrate their analytical capabilities in determination of elements and chromium species in water by various analytical techniques so as to facilitate their claim on the Calibration and Measurement Capabilities (CMC). It was agreed to consider combining the two proposals as a study of water analysis. At the CCQM meeting following the IAWG meeting, the proposal was agreed as CCQM-K124, and NMIJ and GLHK were designated as the jointly coordinating laboratory.

CCQM-K124 is divided into two parts - Part A: Trace elements in drinking water, and Part B: Chromium speciation in drinking water. The Part A key comparison is coordinated by NMIJ. Drinking water is the test material, which was collected in NMIJ (Tsukuba, Ibaraki, Japan) and filtered (pore size: 0.45 μm), is a candidate material for a tap water certified reference material (CRM) of NMIJ. This study will investigate the core capabilities of participants to measure the contents of tested elements and chromium species in drinking water. Each participant could use the results of this study as evidence(s) not only for their CMC claims for elements and chromium species in drinking water but also their related CMC claims for them in similar matrices (groundwater and river water etc.) and/or others through a Core Capability Table.

The analytes in this key comparison were boron, calcium, chromium, arsenic, molybdenum, cadmium and mercury in tap water at mass fractions. Basically, the analytes to be measured were chosen with reference to existing guidelines or regulatory standards. Also, reference would be made to the analytical techniques to be involved. For the light elements, boron (B) is selected as there was no previous comparison on the determination of this element before. For the alkaline earth metals, calcium (Ca) is selected as the ICP-MS measurement involved would be challenging for participants. Chromium (Cr) is difficult to be measured by ICP-MS since the spectral interference of molecular ions resulting from argon occurs. Arsenic (As) is a mono-isotopic element, so isotope dilution mass spectrometry (IDMS) is not applicable. Molybdenum (Mo) is one of essential trace elements but no study for the measurement of molybdenum in water has been undertaken. Cadmium (Cd) is a representative of elements which can be measured by applying IDMS. Mercury (Hg) is a highly toxic element and its property on volatility would cast problem on the determination due to memory effect.

Each participant could use any suitable method(s) of measurement. Four measurements of each analyte had to be carried out by each participant. Results were submitted by 14 NMIs and nine DIs. The comparison results were discussed at the IAWG meetings held November 17-19, 2015, April 18-19 and October 4-6, 2016.

2. Participating Institutes

25 institutes were registered in the Key Comparison CCQM-K124 Part A. Table 1 depicts the list of the participating NMIs/DIs in alphabetic order of the countries' names.

Table 1. List of the Participating NMIs/DIs for CCQM-K124 Part A

No.	Institute	Country	Contact Person
1	**NMIA** National Measurement Institute Australia	Australia	David Saxby
2	**DRiCM*** Designated Reference Institute for Chemical Measurements	Bangladesh	Mala Khan
3	**INMETRO** National Institute of Metrology, Quality and Technology	Brazil	Marcelo Dominguez de Almeida
4	**BIM*** Bulgarian Institute of Metrology	Bulgaria	Boriana Kotzeva
5	**NRCC** National Research Council Canada	Canada	Lu Yang, Zoltan Mester
6	**ISPCH** Instituto de Salud Publica de Chile	Chile	Soraya Sandoval Riquelme

No.	Institute	Country	Contact Person
7	**NIM** National Institute of Metrology, P.R. China	P.R. China	Jingbo Chao, Jun Wang
8	**SYKE** Finnish environment institute, laboratory	Finland	Teemu Näykki
9	**LNE** Laboratoire national de métrologie et d'essais	France	Guillaume Labarraque
10	**PTB** Physikalisch-Technische Bundesanstalt	Germany	Olaf Rienitz
11	**EXHM/GCSL-EIM** National Laboratory of Chemical Metrology/ General Chemistry State Laboratories - Hellenic Institute of Metrology	Greece	Evgenia Lampi
12	**GLHK** Government Laboratory, Hong Kong	Hong Kong SAR, China	Wai-Hong Fung
13	**RCChem-LIPI** Research Center for Chemistry - LIPI	Indonesia	Rosi Ketrin
14	**NMIJ** National Metrology Institute of Japan	Japan	Takayoshi Kuroiwa, Yanbei Zhu
15	**KEBS** Kenya Bureau of Standards	Kenya	Tom Oduor Okumu
16	**KRISS** Korea Research Institute of Standards and Science	Republic of Korea	Yong-Hyeon Yim
17	**INACAL** (former name: INDECOPI) National Institute for Quality	Peru	Christian Uribe
18	**STD-ITDI** Standards & Testing Division, Industrial Technology Development Institute	Philippines	Natividad Mamplata
19	**VNIIM** D.I. Mendeleyev Institute for Metrology	Russia	L.A. Konopelko
20	**HSA** Health Sciences Authority	Singapore	Richard Shin
21	**JSI** Jožef Stefan Institute	Slovenia	Milena Horvat
22	**NIMT** National Institute of Metrology (Thailand)	Thailand	Sutthinun Taebunpakul, Charun Yafa
23	**TUBITAK UME** TÜBİTAK Ulusal Metroloji Enstitüsü	Turkey	Süleyman Z. Can
24	**LATU** Laboratorio Tecnológico del Uruguay	Uruguay	Ramiro Perez, Elizabeth Ferreira
25	**NIST** National Institute of Standards and Technology	USA	Stephen Long

*DRiCM and BIM did not submit their results for some reason.

3. Samples and Instructions to Participants

3.1 Material

The test material is a candidate material for a tap water certified reference material (CRM). The tap water was collected in NMIJ (Tsukuba, Ibaraki, Japan). The raw material was stored in a 200-L polyethylene tank after the filtration using cartridge filter with pore sizes of 0.45 µm and of 0.2 µm, sequentially. Elemental standards of Cd, Hg, As, Cr, Mn, and Se were added to elevate their concentrations because the concentrations of these elements were much lower than the target concentrations. Besides, nitric acid and hydrochloric acid were respectively added in the raw material to ensure the stability of the elements so that those final concentrations were adjusted to about 0.1 mol/L and 0.03 mol/L, respectively.

The 150 L raw material was stirred for one week using a magnetic stirrer for homogenization in a 200-L polypropylene tank. After that, the raw material was filtered (pore size: 0.20 µm) and bottled into 125-mL polyethylene bottles by 100 mL each. These bottles were washed with an aliquot of the raw material in advance. Each bottle of the candidate CRM was vacuum sealed in an individual transparent plastic bag for preservation and preventing contamination from the environment. The candidate CRM was stored at room temperature, i.e. 15 ˚C to 25 ˚C, and shielded from light. A part of the candidate CRM was used for this comparison as the test material.

3.2 Homogeneity and Stability Studies

The homogeneity of the material was investigated by analyzing 10 random bottles selected from the lot of 700 bottles. The test portions were analyzed using standard addition ICP-MS. The samples were analyzed without any further pretreatment except for the addition of standard. Each sample was analyzed at least five times.

ANOVA technique was applied to evaluate the between bottle homogeneity standard deviation (s_{bb}) for each element was calculated using the equation (1) given below in accordance with ISO Guide 35:2006 [1].

The results are shown in Table 2.

$$s_{\mathrm{bb}} = \sqrt{\frac{MS_{\mathrm{among}} - MS_{\mathrm{within}}}{n}} \qquad (1)$$

where

s_{bb} is the between bottle homogeneity standard deviation;

MS_{within} is the mean square of within bottles variance;

MS_{among} is the mean square of between bottles variance;

n is the number of replicates.

Table 2. Results of Homogeneity Study

Analyte	Between-bottle homogeneity standard deviation (s_{bb})
Arsenic	0.28 %
Boron	0.45 %
Cadmium	0.19 %
Calcium	0.43 %
Chromium	0.33 %
Mercury	0.62 %
Molybdenum	0.29 %

It can be seen from Table 2 that the values of s_{bb} for all measurand were less than 1 %. The homogeneity study indicated that there was no significant heterogeneity observed amount different bottles of test material, and therefore, the homogeneity is good enough to be used for this comparison.

The stability study was carried out for covering 20-month. Assessment of the results were carried out following ISO Guide 35:2006. The stability of the material was investigated by analyzing one bottle selected from the storing sample bottles by using standard addition with ICP-MS. The samples were analyzed without any further pretreatment except for the addition of standard. Each sample was analyzed at least five times. The results are shown in Figure 1 to 7. Based on the stability test, significant variation was not found for the concentration of all measurand. The trend-analysis technique proposed by ISO Guide 35:2006 was applied to assess the stability of the test material. ANOVA technique was applied to evaluate, the slope for each measurand was not significant. This material was assessed stable throughout this comparison.

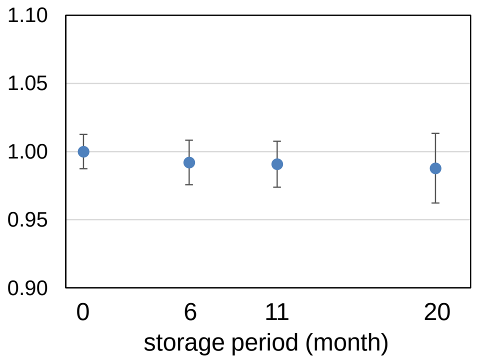

Figure 1. Stability study of arsenic

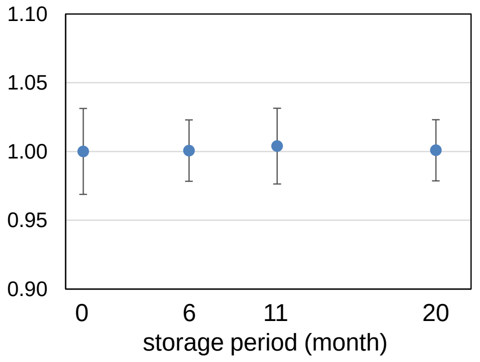

Figure 2. Stability study of boron

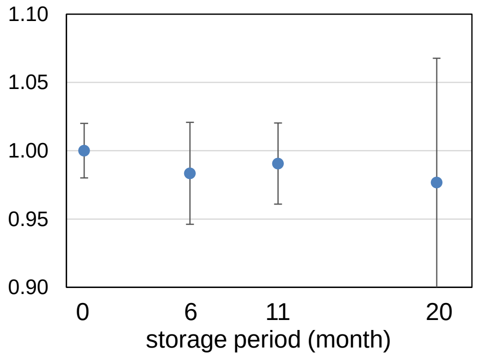

Figure 3. Stability study of cadmium

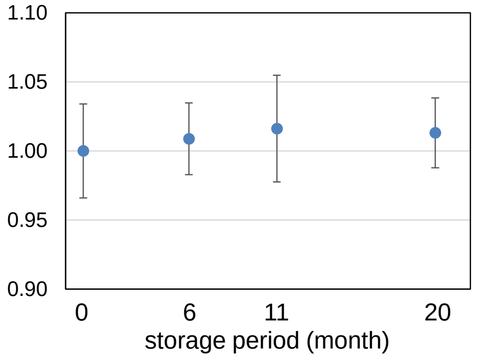

Figure 4. Stability study of calcium

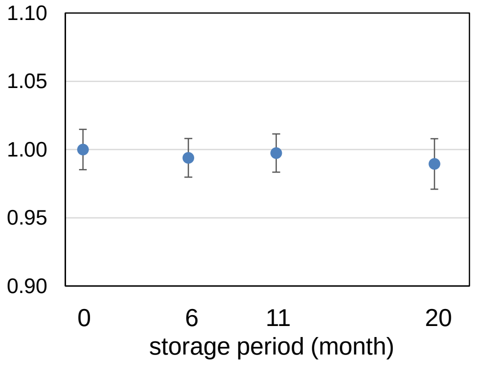

Figure 5. Stability study of chromium

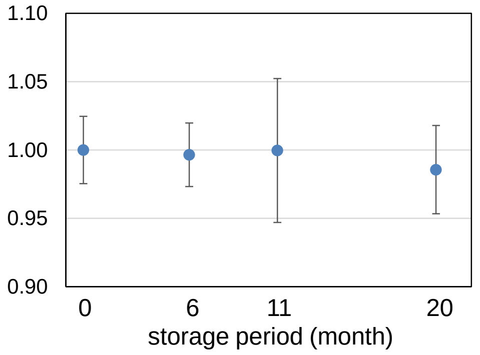

Figure 6. Stability study of mercury

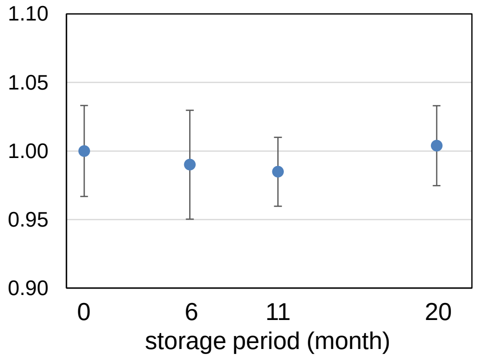

Figure 7. Stability study of molybdenum

3.3 Instructions to Participants

Each participant received two bottles of 100 mL water sample. The samples after receiving had to be kept at the laboratory temperature (15 ℃ to 25 ℃). Participants could use any analytical methods of measurement deemed appropriate, and was requested to perform at least four independent measurements in order to determine the mass fraction of each measurand and to use standards with metrological traceability for calibrations of analytical instruments.

To report the measurement results, the participants were requested to submit the mean value of four or more independent measurement data accompanying with the corresponding measurement uncertainty. The participants were requested to submit their results along with information on the sample preparation, analytical method, calculation of results, uncertainty estimation with a full measurement uncertainty budget and sources and standards used for calibration.

4. Methods of Measurement

Majority of the participants used measurement techniques are ICP-MS and isotope dilution ICP-MS. The method summary is shown in Table 3.

Table 3. Summary of Analytical Techniques Applied by the Participants

Institute	Analyte	Sample treatment	Analytical method	Instrumental technique
NMIA	As, Hg	None	As: Std. addition with internal standard (Y, Te) Hg: IDMS (enriched spike: ^{201}Hg)	As: ICP-MS (He mode) & ICP-SFMS Hg: ICP-MS & ICP-SFMS
INMETRO	Ca, Cr, As, Cd	None	Ca, Cr, As: external calibration Cd: ID-ICP-MS (enriched spike: ^{111}Cd)	Ca: ICP-OES Cr, As, Cd: ICP-MS
NRCC	Ca, Cr, As, Mo, Hg	None	Ca: Std. addition Cr, Mo, Hg: IDMS (^{52}Cr/^{53}Cr, ^{98}Mo/^{100}Mo, ^{202}Hg/^{201}Hg) As: Std. addition with internal standard (Ga)	Ca: ICP-OES Cr, As, Mo, Hg: HR-ICP-MS
ISPCH	Cr, As (Pilot study: Mo, Cd, Hg)	1M HNO_3 & 0.3M HCl	external calibration	ICP-MS

Institute	Analyte	Sample treatment	Analytical method	Instrumental technique
NIM	B, Ca, Cr, As, Mo, Cd, Hg	None	B, Cr, Mo, Cd, Hg: IDMS ($^{10}B/^{11}B$, $^{52}Cr/^{53}Cr$, $^{97}Mo/^{95}Mo$, $^{111}Cd/^{110}Cd$, $^{200}Hg/^{202}Hg$) As, Ca: external calibration	Ca: ICP-OES B, Cr, As, Mo, Cd, Hg: ICP-MS (Cr: H_2 mode, As: He mode)
SYKE	Hg	None	IDMS ($^{202}Hg/^{201}Hg$)	CV ICP-MS
LNE	As, Cd, Hg	Hg: all solutions / mixtures were stabilized with 0.5% $K_2Cr_2O_7$	Cd, Hg: IDMS ($^{112}Cd/^{111}Cd$ and $^{202}Hg/^{200}Hg$) As: Std. addition with internal standard (Mo; present in the sample is used)	ICP-MS (As: He mode)
PTB	Mo, Hg	None	Mo, Hg: IDMS ($^{98}Mo/^{97}Mo$, $^{202}Hg/^{201}Hg$)	HR-ICP-MS
EXHM	Cr, As, Cd (Pilot study: B, Ca, Mo, Hg)	None	Std. addition	HR-ICP-MS
GLHK	Ca, Cr, Cd	None	Ca: Std. addition with internal standard (Sc) Cr, Cd: IDMS (enriched spike: ^{50}Cr, ^{111}Cd)	Ca: ICP-OES Cr, Cd: ICPMS (He mode) and HR-ICPMS
RCChem-LIPI	Ca, Cd (Pilot study: Cr, As)	None	Ca: Std. addition with internal standard (Y) Cr, As: matrix matched calibration Cd: Std. addition	Ca: ICP-OES Cr, As: ICP-MS (As: He mode) Cd: GF-AAS
NMIJ	B, Ca, Cr, As, Mo, Cd, Hg	None	B, Ca, Cr, Mo, Cd, Hg: IDMS As: Std. addition with internal standard	B, Ca, Cr, As, Cd, Hg: ICP-MS (He mode) Mo: HR-ICP-MS
KEBS	B, Ca, Cr, As, Mo, Cd, Hg	None	external calibration	Ca: MP-AES B, Cr, As, Mo, Cd, Hg: ICP-MS
KRISS	Ca, Cr, As, Mo, Cd, Hg	None conc. HNO_3, final 5 %	Ca, Cr, Mo, Cd, Hg: IDMS (spike: ^{42}Ca, ^{53}Cr, ^{111}Cd, ^{100}Mo, ^{202}Hg) As: Std. addition with internal standard (Ge)	Ca, Cr, As: HR ICP-MS Mo, Cd, Hg: ICP-MS (Mo, Cd: He mode)
INACAL	Cr, As	None	Std. addition	GFAA
STD-ITDI	Ca	None	external calibration	Flame-AAS
VNIIM	B, Ca, Cr, As, Mo, Cd, Hg	None	external calibration	B, Ca, Cr, As, Mo, Cd: ICP-MS Hg: CV-AAS

Institute	**Analyte**	**Sample treatment**	**Analytical method**	**Instrumental technique**
HSA	Ca, Cr, As, Mo, Cd	None	Ca, As: Std. addition Cr, Mo, Cd: IDMS (^{53}Cr/^{52}Cr and ^{53}Cr/^{50}Cr, ^{100}Mo/^{98}Mo and ^{100}Mo/^{95}Mo, ^{111}Cd/^{114}Cd and ^{111}Cd/^{112}Cd)	Ca: ICP-OES As: ICP-HR-MS Cr, Mo, Cd: ICP-MS
JSI	Cr, As, Mo, Cd, Hg	Hg: BrCl/HCl digestion with UV irradiation	external calibration with internal standard (Y, Rh) except for Hg	Cr, As, Mo, Cd: ICP-MS (Cr, As, Mo: He mode) Hg: CV-AFS
NIMT	Ca, Cr, As, Cd, Hg	None	Ca, Cr, Cd: IDMS (^{44}Ca/^{42}Ca, ^{53}Cr/^{50}Cr, ^{112}Cd/^{106}Cd) As: Std. addition with internal standard (Rh) Hg: Std. addition	Ca, Cr, Cd, As: ICP-MS Hg: mercury analyzer (UV) in reduced vaporization mode
TÜBİTAK UME	B, Ca, Cr, As, Mo, Cd, Hg	None HNO_3 & HCl	Ca, B, Mo, As: matrix matched external calibration with internal standard (In) Cd, Cr, Hg: IDMS (spike: ^{111}Cd, ^{50}Cr, ^{202}Hg)	HR-ICP-MS
LATU	Ca, Cr, As	None	Ca: Std. addition with internal standard (Sc) Cr: IDMS (^{53}Cr/^{52}Cr) As: Std. addition with internal standard (Ge)	Ca: ICP-OES Cr, As: ICP-SFMS
NIST	B, Ca, Cr, As, Mo, Cd, Hg	None 2 % HNO_3	B, Ca, Cr, As, Mo: Std. addition with internal standard (In, Ca: Sc) Cd, Hg: IDMS (^{111}Cd/^{112}Cd, ^{111}Cd/^{113}Cd, ^{111}Cd/^{114}Cd, ^{202}Hg/^{201}Hg)	Ca: ICP-OES B, Cr, As, Mo, Cd: ICP-MS Hg: CV ICP-MS

5. Results and Discussion

5.1 General

All results which were reported from 23 NMIs/DIs for CCQM-K124 Part A were listed in Table 4 to 10 in ascending order.

Table 4. Reported Results of Arsenic

Institute	Reported mass fraction (µg/kg)	Reported std. uncertainty (µg/kg)	Reported expanded uncertainty (µg/kg)	Coverage factor, *k*
HSA	5.29	0.06	0.12	2
NIMT	5.32	0.10	0.20	2
NMIA	5.32	0.07	0.15	2.16
LATU	5.326	0.049	0.098	2
NMIJ	5.33	0.07	0.14	2
LNE	5.34	0.11	0.22	2
UME	5.34	0.14	0.27	2
NIM	5.346	0.051	0.102	2
INACAL	5.36	0.06	0.13	2
KRISS	5.45	0.13	0.29	2.31
EXHM	5.495	0.076	0.166	2.179
NRCC	5.54	0.18	0.36	2
ISPCH	5.60	0.23	0.46	2
JSI	5.80	0.08	0.15	2
INMETRO	5.88	0.1024	0.21	2.01
NIST	6.60	0.052	0.10	2
VNIIM	8.65	0.13	0.26	2
KEBS	9.1167	0.1521	0.4223	2.7764

Table 5. Reported Results of Boron

Institute	Reported mass fraction (µg/kg)	Reported std. uncertainty (µg/kg)	Reported expanded uncertainty (µg/kg)	Coverage factor, *k*
NIST	42.2	0.71	1.4	2
NMIJ	42.3	0.4	0.7	2
UME	42.8	0.8	1.6	2
NIM	43.38	0.56	1.11	2
VNIIM	43.66	0.545	1.09	2
KEBS	116.1349	1.4949	3.5279	2.4469

Table 6. Reported Results of Cadmium

Institute	Reported mass fraction (μg/kg)	Reported std. uncertainty (μg/kg)	Reported expanded uncertainty (μg/kg)	Coverage factor, *k*
NIMT	0.342	0.0078	0.016	2
NMIJ	0.345	0.005	0.009	2
HSA	0.3458	0.0043	0.0085	2
LNE	0.347	0.0032	0.0065	2
NIST	0.3499	0.0022	0.0044	2
UME	0.351	0.004	0.008	2
GLHK	0.352	0.0144	0.0289	2
NIM	0.353	0.003	0.007	2
KRISS	0.355	0.012	0.024	1.961
VNIIM	0.357	0.013	0.026	2
JSI	0.365	0.004	0.008	2
EXHM	0.373	0.006	0.012	2.179
INMETRO	0.378	0.0150	0.030	2.00
LIPI	0.820	0.075	0.15	2
KEBS	0.9410	0.2206	0.5399	2.4469

Table 7. Reported Results of Calcium

Institute	Reported mass fraction (mg/kg)	Reported std. uncertainty (mg/kg)	Reported expanded uncertainty (mg/kg)	Coverage factor, *k*
LIPI	8.00	0.32	0.65	2
STD-ITDI	15.6368	0.2523	0.5046	2
VNIIM	17.75	0.21	0.41	2
INMETRO	18.07	0.194	0.46	2.36
NMIJ	18.2	0.4	0.7	2
NIST	18.23	0.10	0.20	2
NIM	18.31	0.10	0.20	2
HSA	18.32	0.25	0.50	2
KRISS	18.40	0.41	0.80	1.962
LATU	18.43	0.15	0.30	2
UME	18.44	0.36	0.71	2
NRCC	18.49	0.093	0.19	2
GLHK	18.5	0.361	0.722	2
NIMT	19.9	0.51	1.1	2
KEBS	20.6705	0.3264	0.9063	2.7764

Table 8. Reported Results of Chromium

Institute	Reported mass fraction (µg/kg)	Reported std. uncertainty (µg/kg)	Reported expanded uncertainty (µg/kg)	Coverage factor, *k*
VNIIM	4.63	0.056	0.113	2
NIMT	4.74	0.15	0.30	2
ISPCH	4.879	0.059	0.118	2
HSA	4.96	0.06	0.13	2
LATU	5.041	0.031	0.062	2
KRISS	5.045	0.022	0.043	1.968
NMIJ	5.05	0.03	0.06	2
NRCC	5.07	0.114	0.23	2
UME	5.09	0.05	0.09	2
GLHK	5.10	0.0535	0.107	2
NIST	5.11	0.053	0.11	2
INMETRO	5.11	0.1220	0.26	2.16
NIM	5.118	0.046	0.092	2
INACAL	5.23	0.09	0.19	2
JSI	5.34	0.05	0.102	2
EXHM	5.491	0.111	0.242	2.179
KEBS	10.2138	0.2505	0.6129	2.4469

Table 9. Reported Results of Mercury

Institute	Reported mass fraction (µg/kg)	Reported std. uncertainty (µg/kg)	Reported expanded uncertainty (µg/kg)	Coverage factor, *k*
NIMT	0.334	0.013	0.026	2
JSI	0.334	0.019	0.038	2
NIST	0.3554	0.0047	0.0094	2
PTB	0.360	0.0064	0.014	2.05
UME	0.362	0.006	0.012	2
NMIA	0.363	0.015	0.031	2.04
SYKE	0.36388	0.00211	0.0042	2
KRISS	0.366	0.012	0.024	1.962
NIM	0.377	0.006	0.012	2
NMIJ	0.379	0.007	0.013	2
LNE	0.390	0.0060	0.0121	2
NRCC	0.404	0.016	0.032	2
VNIIM	0.438	0.014	0.028	2
KEBS	1.5009	0.4184	1.0251	2.7764

Table 10. Reported Results of Molybdenum

Institute	Reported mass fraction (μg/kg)	Reported std. uncertainty (μg/kg)	Reported expanded uncertainty (μg/kg)	Coverage factor, *k*
NIST	0.877	0.012	0.023	2
NRCC	0.937	0.0096	0.019	2
HSA	0.963	0.012	0.024	2
UME	0.971	0.018	0.036	2
KRISS	0.976	0.028	0.055	1.961
PTB	1.006	0.011	0.023	2.11
NMIJ	1.01	0.03	0.06	2
VNIIM	1.012	0.037	0.075	2
JSI	1.02	0.01	0.02	2
NIM	1.021	0.010	0.019	2
KEBS	2.2314	0.7567	1.6873	2.4469

The results of B, Ca, Cr, As and Cd show good agreement except some outliers. The submitted results from KEBS, VNIIM and NIST for As, from KEBS for B, from KEBS and LIPI for Cd, from LIPI for Ca, and from KEBS for Cr were considered as suspected outlying results. KEBS, VNIIM, NIST and LIPI agreed their outlying results should be excluded for the KCRV estimation. They tried to carry out the corrective action such as technical review and/or additional study for finding the reasons of their outlying results. The results and some comments sending from then are as follows:

KEBS: KEBS tried to find out what could have gone wrong during the measurements and was almost certain that the equipment had problems in the sampler and skimmer cones of ICP-MS which they overlooked.

NIST: NIST reported that their unsatisfactory result for As was due to an undetected interference.

VNIIM: VNIIM found an error, this was an operator`s mistake, As measurement using ICP-MS was done without use of He gas in collision reaction cell.

In this case preparation of the sample included addition of 0.03M HCl, what caused overlay polyatomic interference "ArCl" on "As". The results of As measurements in the both modes are shown in the following Table.

Run No.	^{75}As: Non gas Result (μg/kg)	RSD (%)	^{75}As: He mode Result (μg/kg)	RSD (%)
1	8.811	0.7	5.567	2.2
2	8.687	1.3	5.288	2.0
3	8.601	0.9	5.165	3.2
4	8.604	1.1	5.111	2.6
5	8.724	0.6	4.943	2.3

RCChem-LIPI: This is the first time for LIPI to participate in the IAWG-KC, therefore LIPI believed in the range given by the coordinating lab, but when LIPI got the result, felt that the obtained result through the direct measurement with external calibration method was wrong due to the improper range given for Ca (1 to 10 mg/kg) and Cd (0.5 to 4 μg/kg). Those results are shown in the following Table.

	Ca		Cd	
Method	External calibration	Std. addition	External calibration	Std. addition
Range conc. of calib. std.	10 - 30	5 - 10	0.5 - 2	0.3 – 1.1
Instrument	ICP-OES	ICP-OES	ICP-MS	GFAAS
Result	18.47	8.00	0.353	0.82
SD	0.60	0.31	0.04	0.04

There is a strange results obtained, that the standards addition results are always lower in the case of Ca and higher in the case of Cd than the external calibration results. The sample is drinking water which is classified has a simple matrices that is comparable to standard matrices. With this assumption, the standards addition method is unnecessary.

After got additional samples, LIPI carried out the re-measurement for Ca and Cd. The obtained results are shown in the following Table.

	Ca	Cd
Method	ICP-OES with external calibration	ICP-MS with bracketing calibration
Mean	18.51	0.35
Expanded uncertainty	1.61	0.06
Coverage factor	2	2

Though the stability testing, NMIJ found that the concentration of Hg decreased when the sample stored in the light. Hg instability was also reported from NMIA who had noticed significant differences in Hg concentration between all four of the bottles analyzed and changes in Hg concentration with time. It may be occurred that Hg ions became reduced to Hg (0) by a photo-reaction. In NMIJ's homogeneity and stability testing, the sample bottles were stored in a dark place at room temperature, and Hg was measured just after open the bottles. NMIJ did not noticed regarding a light reaction when the sample was sent, because we found this phenomena at the last stability testing (October, 2015). It was agreed to abandon the Hg analysis as it was not satisfactory for a KC.

NRCC suggested instability of Mo in the sample. NRCC reported that the repeat analysis of Mo concentration of solution remaining in the two sample bottles showed a significant Mo loss since previous analyses but more importantly, significantly different losses in Mo between the two bottles.

NMIJ had re-analyzed by ICP-MS a number of different bottles of solution, some were remaining samples had been previously analyzed, others were unopened new bottles. All of these bottles had been stored at room temperature and exposed to light. But no significant loss of Mo from any of these bottles was observed. Long term stability test for Mo by NMIJ are shown in Figure 8.

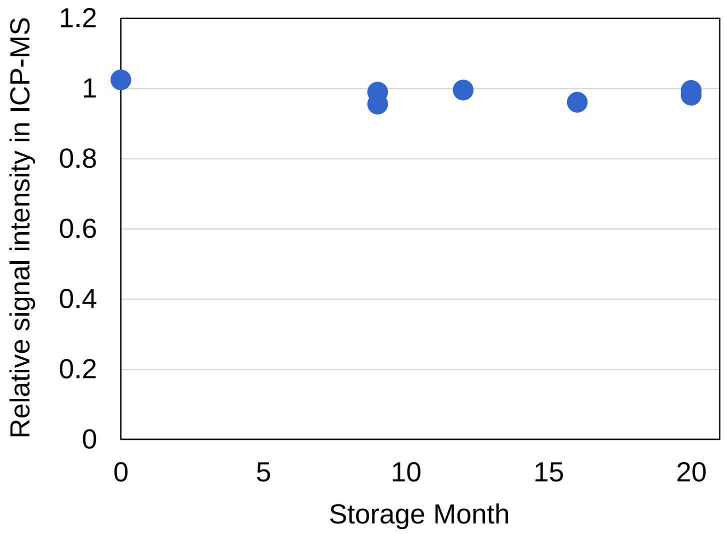

Figure 8. Long term stability test for Mo by NMIJ

Note: All the samples has been stored in a room under a room light.

NMIJ asked the participants for who measured Mo to provide a information regarding storage and handling of samples. In addition, NMIJ asked all participants if they had any remaining sample solution to request a re-analyzing of Mo concentration to check for loss.

Nine participants provided additional information regarding storage and handling of samples. Those information and already reported information are summarized in Table 11.

Table 11. Information regarding sample handling for Mo measurement

Lab.	Submitted result, μg/kg	Date of opening	Storage condition (RT: room temp.)	Dilution	Addition of acid	Other information
NIST	0.877	Feb. 10, 2015	RT under light	○	○ 2 % HNO_3	addition of diluent and internal standard only.
NRCC	0.937	Dec. 9, 2014	RT under light	×	× (from spike: 1 % HNO_3)	samples were spiked and left for 2 days prior to measurements
HSA	0.963	Oct. 8 & 14, 2014	RT under light	×	× (from spike: 5 % HNO_3)	addition of IDMS spike only
UME	0.971	Jan. 19, 2015	refrigerator at 4 ℃	○	○ HNO_3 & HCl	matrix matched external caliblation
KRISS	0.976	Mar. 24, 2015	RT under light	×	○ conc. HNO_3, final 5 %	IDMS
PTB	1.006	Jan. 14 & Mar. 5, 2015	RT	×	× (from spike: 0.08 mol/kg HNO_3)	approx. diluted 1:1 by spike
VNIIM	1.012	Apr. 21, 2015	RT under light	×	×	external calibration
JSI	1.02	Mar. 26, 2015	refrigerator at 4 ℃	×	×	external calibration
NIM	1.021	Nov. 3, 2014	refrigerator at 4 ℃	×	×	addition of IDMS spike only
INRAP	1.059	not reported	not reported	×	×	addition method by the use of NIST 1640a
EXHM	1.076	May 18, 2015	RT	×	×	standard additions
ISPCH	1.30	not reported	not reported	×	○ 1M HNO_3 & 0.3M HCl	external calibration

Seven participants provided re-analyzed values, other participants could not re-analyze because they did not have any remaining sample.

Table 12. Re-analyze the remaining sample for Mo concentration

Lab.	Submitted result (mg/kg)	Re-checked (mg/kg)		Storage condition	Sample preparation & Measurement
PTB	1.006	1.012	-	room temperature shielded from light	IDMS spike addition acid from spike, HNO_3: 0.08 mol/kg
NMIJ	1.01	1.02	-	room temperature under light	standard addition
VNIIM	1.012	0.95	1.02	room temperature under light	No preparation ICP-MS: external standard
NRCC	0.937	0.57	0.21	clean room at room temperature under lights	no preparation Intensities of ^{97}Mo, ^{98}Mo, ^{100}Mo were measured directly from the bottles and 1 ppb Mo standard was used to estimate analyte concentration
HSA	0.963	0.69	-	room temperature under light	addition of IDMS spike only 5% HNO_3
NMIA	Not reported	0.8	0.7		
UME	1.01	0.905, 0.932	0.839, 1.248	refrigerator at 4 ℃ shielded from light	matrix matched standard additions method

Three participants observed no significant loss of Mo, but three participants observed significant loss of Mo.

One potentially reason for the instability of Mo is the transportation of the sample. NMIJ carried out the additional stability study under the condition that assumed the condition of transportation, high (50℃) and low (-20℃) temperature. Two bottles were kept in a drying oven at 50℃ for 5 hours and another two bottles were kept in a freezer at -20˚ for 5 hours. After having returned them to room temperature, Mo in each bottle was measured. Furthermore, Mo was measured again after having kept those bottles at room temperature for two months. The results are summarized in Figure 9 and 10.

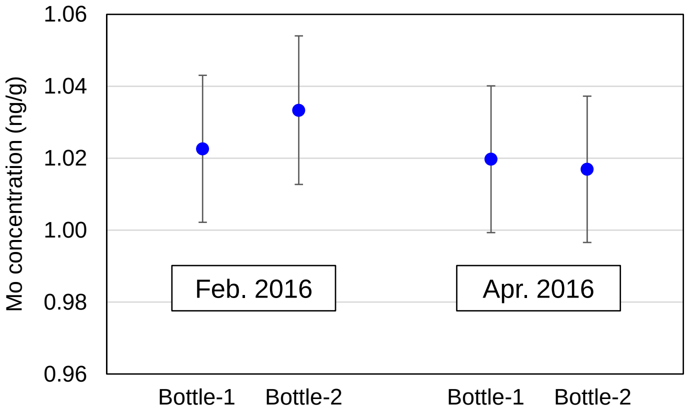

Figure 9. Additional stability study for Mo: keep in a freezer at -20℃ for 5 h

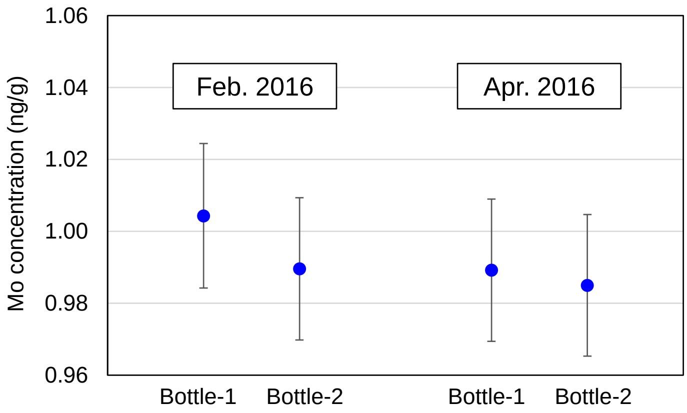

Figure 10. Additional stability study for Mo: keep in a drying oven at 50℃ for 5 h

In this accelerating stability test, no significant loss of Mo was observed.

The Mo instability issue could not be clearly solved through the additional investigation. It is not able to deny the possibility of a decrease of Mo concentration. Two potentially triggers to be concerned, precipitation with small particles or core crystals and effect of the transportation condition, higher temperature in transportation. It was agreed that this sample solution was not satisfactory for a KC for Mo analysis.

Based on the results of those additional studies, NMIJ suggested that all participants add higher concentration nitric acid to any remaining sample that they might have and re-analyze for Mo to see if adsorbed Mo could be released. NRCC have re-analyzed the Mo in two bottles. The first bottle was used as control, no concentrate acid was added. To the second bottle, 0.5ml concentrate HNO_3 was added, bottle was shaking for a few minutes and left to stand for 30 minutes prior to the measurements. Then 1 ml HCl was added to this bottle, shaking and stand prior to the measurements again. The results are shown in the following Table.

	Nov. 10-12, 2015 external check	June 2, 2016 external check	treatment
Bottle-1	0.57 ppb	0.57 ppb	without adding HNO_3
Bottle-2	0.21 ppb	0.13 ppb	Added 0.5 mL HNO_3
		0.11 ppb	Added 0.5 mL HNO_3 and 1 mL HCl

Mo is not recovered even if added higher concentration acid. The additional investigations had not uncovered the source of Mo instability.

5.2 Traceability of Calibrants used by Participants

Participants were required to provide the information about the traceability of the reference materials/calibrants they used in this comparison. This information is summarized in Appendix AI.

5.3 Calculation of the Reference Mass Fraction Value and Associated Uncertainties

In this report, the calculated consensus values and their respective dispersions estimate using two different location estimators, arithmetic mean and median, were summarized in Table 14 to 18.

MAD_E = median absolute deviation (MAD) ×1.483

Table 14. Results of the Calculated Consensus Values and the Respective Dispersion for Arsenic (excluding the results of NIST, VNIIM and KEBS); unit = µg/kg

Measurand	Arithmetic mean	Standard deviation	Median	MAD_E
Arsenic	5.449	0.184	5.346	0.039

Table 15. Results of the Calculated Consensus Values and the Respective Dispersion for Boron (excluding the result of KEBS); unit = µg/kg

Measurand	Arithmetic mean	Standard deviation	Median	MAD_E
Boron	42.87	0.64	42.80	0.86

Table 16. Results of the Calculated Consensus Values and the Respective Dispersion for Cadmium (excluding the results of RCChem-LIPI and KEBS); unit = µg/kg

Measurand	Arithmetic mean	Standard deviation	Median	MAD_E
Cadmium	0.355	0.011	0.352	0.007

Table 17. Results of the Calculated Consensus Values and the Respective Dispersion for Calcium (excluding the result of RCChem-LIPI); unit = mg/kg

Measurand	Arithmetic mean	Standard deviation	Median	MAD_E
Calcium	18.38	1.10	18.36	0.20

Table 18. Results of the Calculated Consensus Values and the Respective Dispersion for Chromium (excluding the result of KEBS); unit = µg/kg

Measurand	Arithmetic mean	Standard deviation	Median	$\mathrm{MAD_E}$
Chromium	5.063	0.206	5.080	0.057

As shown in Table 14 to 18, the significant difference is not found between the consensus values of the arithmetic mean and the median was observed. According to the CCQM Guidance Note [2] and the results of the discussions at the IAWG meeting, they were decided that the arithmetic mean for B, and the median for As, Cd, Ca and Cr should be used as the KCRV for CCQM-K124 Part A.

According to the CCQM Guidance Note, the *u*(KCRV) with the arithmetic mean and median approach can be calculated using equation (2) and (3) respectively, and the KCRU can then be calculated by multiplying *u*(KCRV) by two. The KCRV and KCRU were shown in Table 19 to 23.

$$u(\mathrm{KCRV}) = \frac{s(x)}{\sqrt{m}} \qquad (2)$$

$$u(\mathrm{KCRV}) = \mathrm{MAD_E} \times \sqrt{\frac{\pi}{2m}} \qquad (3)$$

where $s(x)$ is standard deviation of qualified results and m is number of qualified participants.

Table 19. The Calculated KCRV and KCRU using the Median Approach

Measurand	KCRV (µg/kg)	*u*(KCRV) (µg/kg)	KCRU (µg/kg)	KCRU (%)
Arsenic	5.346	0.012	0.025	0.5 %

Table 20. The Calculated KCRV and KCRU using the Mean Approach

Measurand	KCRV (µg/kg)	*u*(KCRV) (µg/kg)	KCRU (µg/kg)	KCRU (%)
Boron	42.87	0.29	0.58	1.3 %

Table 21. The Calculated KCRV and KCRU using the Median Approach

Measurand	KCRV (µg/kg)	*u*(KCRV) (µg/kg)	KCRU (µg/kg)	KCRU (%)
Cadmium	0.352	0.003	0.005	1.5 %

Table 22. The Calculated KCRV and KCRU using the Median Approach

Measurand	KCRV (mg/kg)	*u*(KCRV) (mg/kg)	KCRU (mg/kg)	KCRU (%)
Calcium	18.36	0.07	0.134	0.7 %

Table 23. The Calculated KCRV and KCRU using the Median Approach

Measurand	KCRV (µg/kg)	*u*(KCRV) (µg/kg)	KCRU (µg/kg)	KCRU (%)
Chromium	5.080	0.018	0.036	0.7 %

For a more convenient review, a graphical presentation of the KCRV, *u*(KCRV) and the participants' results for CCQM-K124 Part A is given in Figure 11 to 15. The error bars represent the combined standard uncertainties for the individual participant's results. The horizontal solid red line represents the KCRV, and the red dashed lines represent KCRV ± *u*(KCRV). (*the results were not included in the calculation of the KCRVs)

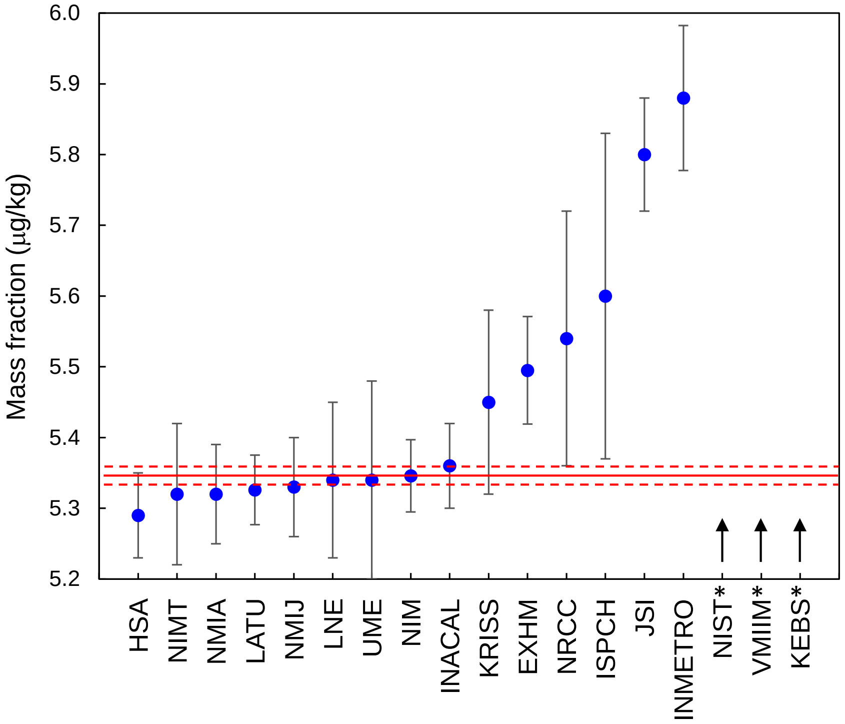

Figure 11. CCQM-K124 Part A: Participants' Results and Measurement Uncertainties for arsenic; unit = µg/kg

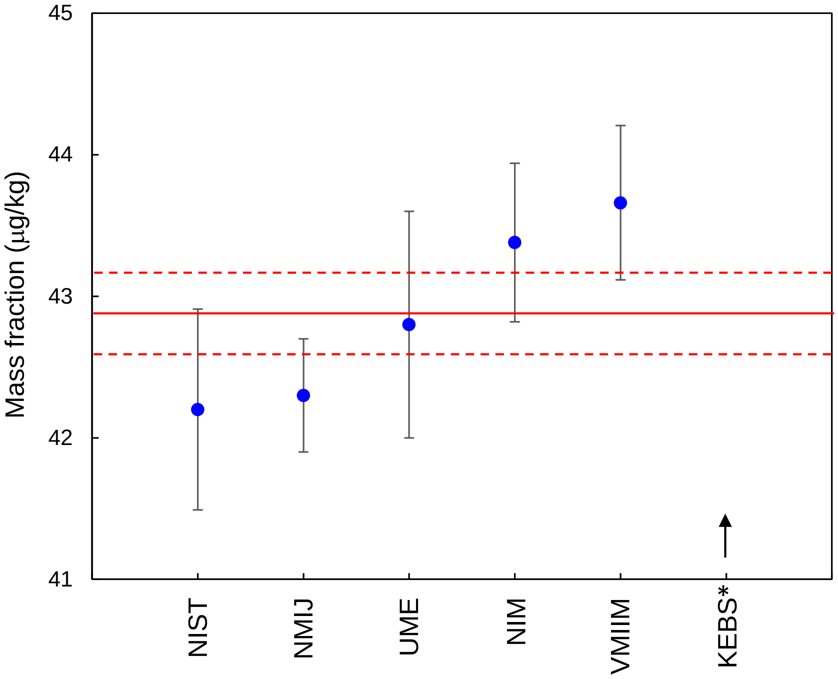

Figure 12. CCQM-K124 Part A: Participants' Results and Measurement Uncertainties for boron; unit = µg/kg

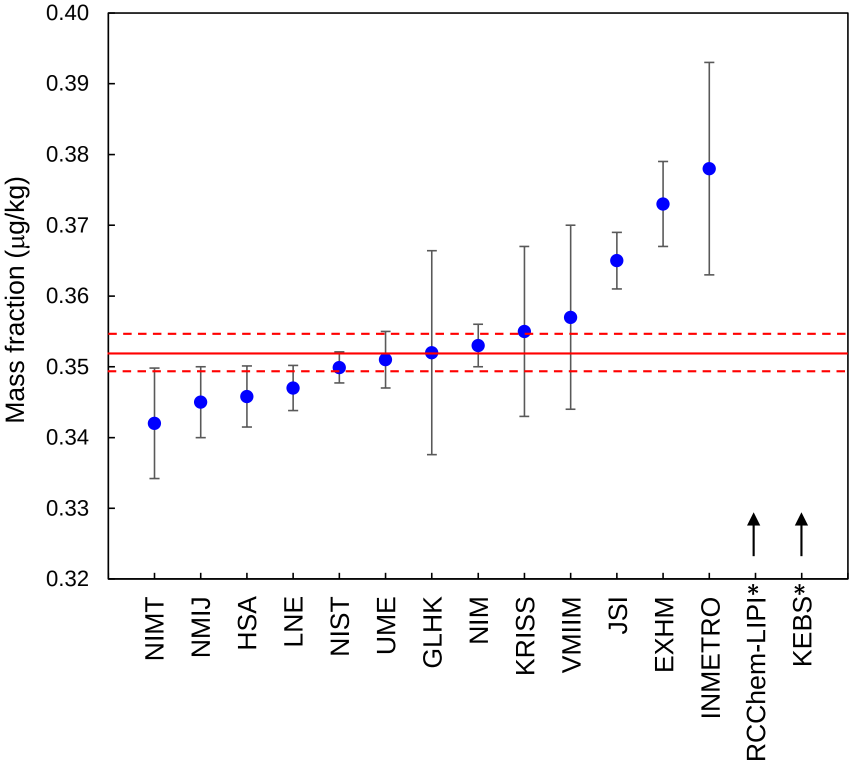

Figure 13. CCQM-K124 Part A: Participants' Results and Measurement Uncertainties for Cadmium; unit = µg/kg

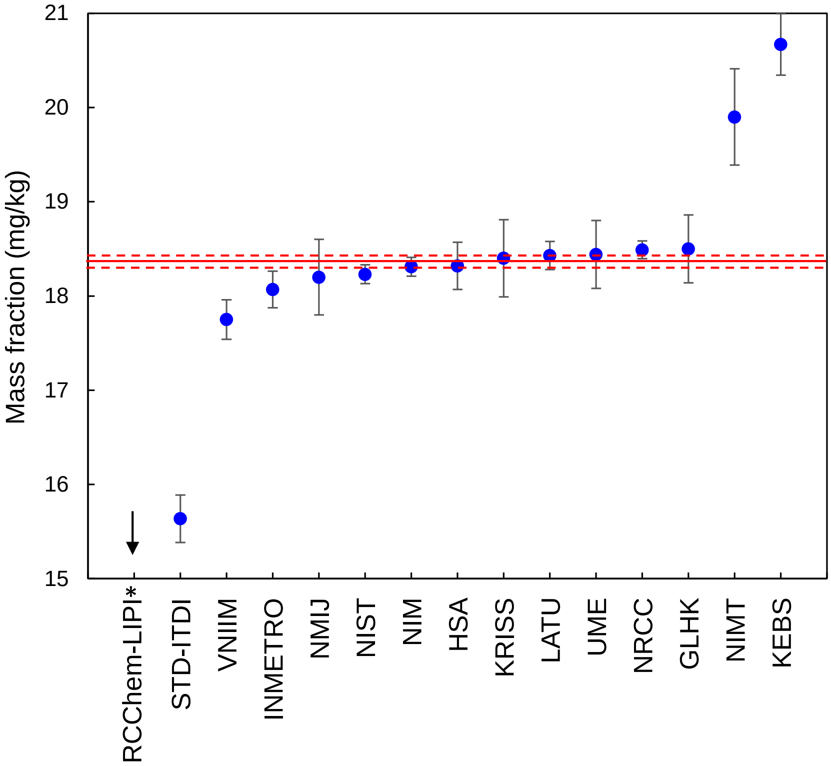

Figure 14. CCQM-K124 Part A: Participants' Results and Measurement Uncertainties for Calcium; unit = mg/kg

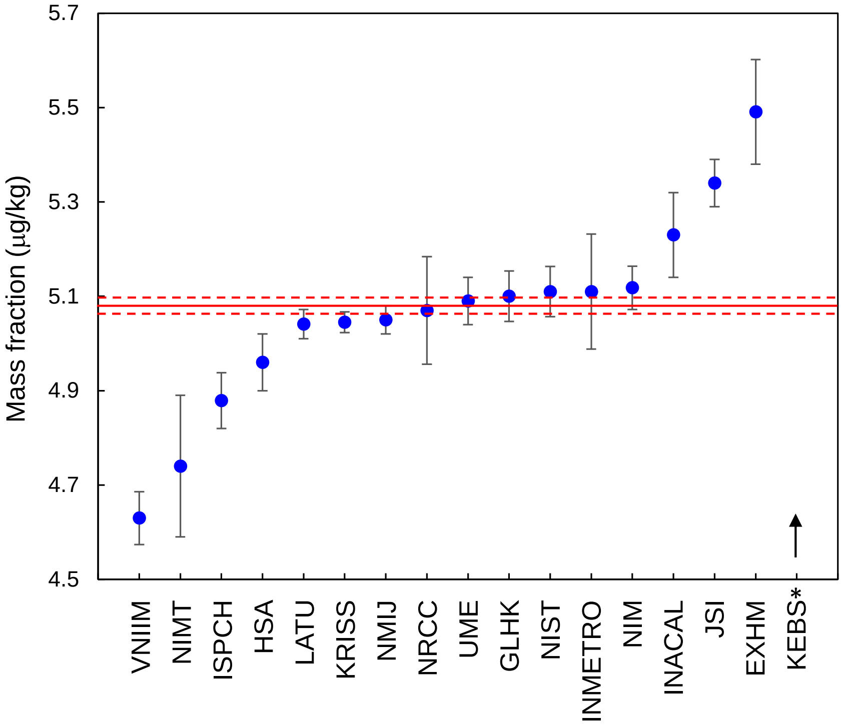

Figure 15. CCQM-K124 Part A: Participants' Results and Measurement Uncertainties for Chromium; unit = µg/kg

5.4 Equivalence Statements

The degree of equivalence and its uncertainty of a reported result by a participant compared to the KCRV were calculated using equations (4) to (5) as follows:

$$D_i = (x_i - x_R) \qquad (4)$$

$$U_i^2 = (k^2 u_i^2 + 2^2 u_R^2) \qquad (5)$$

where D_i is the degree of equivalence (DoE) between the result x_i and the KCRV x_R, and U_i is the expanded uncertainty (k = 2; declared ones of some participants were not used.) of D_i calculated by both the combined standard uncertainty u_i of x_i and the standard uncertainty u_R of x_R.

The equivalence statements for CCQM- K124 Part A based on the calculated KCRV are listed in Table 24 to 28, and the graphical presentation is given in Figure 16 to 20.

Table 24. Equivalence Statements of arsenic for CCQM-K124 Part A

Institute	Reported value, x_i, µg/kg	Reported std. uncertainty, $u(x_i)$, µg/kg	D_i	U_i
HSA	5.29	0.06	-0.056	0.123
NIMT	5.32	0.10	-0.026	0.202
NMIA	5.32	0.07	-0.026	0.142
LATU	5.326	0.049	-0.020	0.101
NMIJ	5.33	0.07	-0.016	0.142
LNE	5.34	0.11	-0.006	0.221
UME	5.34	0.14	-0.006	0.281
NIM	5.346	0.051	0.000	0.105
INACAL	5.36	0.06	0.014	0.123
KRISS	5.45	0.13	0.104	0.261
EXHM	5.495	0.076	0.149	0.154
NRCC	5.54	0.18	0.194	0.361
ISPCH	5.60	0.23	0.254	0.461
JSI	5.80	0.08	0.454	0.162
INMETRO	5.88	0.1024	0.534	0.206
NIST*	6.60	0.052	1.254	0.107
VNIIM*	8.65	0.13	3.304	0.261
KEBS*	9.1167	0.1521	3.771	0.305

*The results from NIST, VNIIM and KEBS were not included in the calculations of the KCRV.

Table 25. Equivalence Statements of boron for CCQM-K124 Part A

Institute	Reported value, x_i, µg/kg	Reported std. uncertainty, $u(x_i)$, µg/kg	D_i	U_i
NIST	42.2	0.71	-0.668	1.533
NMIJ	42.3	0.4	-0.568	0.986
UME	42.8	0.8	-0.068	1.701
NIM	43.38	0.56	0.512	1.260
VNIIM	43.66	0.545	0.792	1.233
KEBS*	116.1349	1.4949	73.267	3.045

*The result from KEBS was not included in the calculations of the KCRV.

Table 26. Equivalence Statements of cadmium for CCQM-K124 Part A

Institute	Reported value, x_i, µg/kg	Reported std. uncertainty, $u(x_i)$, µg/kg	D_i	U_i
NIMT	0.342	0.0078	-0.010	0.016
NMIJ	0.345	0.005	-0.007	0.011
HSA	0.3458	0.0043	-0.006	0.010
LNE	0.347	0.0032	-0.005	0.008
NIST	0.3499	0.0022	-0.002	0.007
UME	0.351	0.004	-0.001	0.010
GLHK	0.352	0.0144	0.000	0.029
NIM	0.353	0.003	0.001	0.008
KRISS	0.355	0.012	0.003	0.025
VNIIM	0.357	0.013	0.005	0.027
JSI	0.365	0.004	0.013	0.010
EXHM	0.373	0.006	0.021	0.013
INMETRO	0.378	0.0150	0.026	0.030
LIPI*	0.820	0.075	0.468	0.150
KEBS*	0.9410	0.2206	0.589	0.441

*The result from RCChem-LIPI and KEBS were not included in the calculations of the KCRV.

Table 27. Equivalence Statements of calcium for CCQM-K124 Part A

Institute	Reported value, x_i, mg/kg	Reported std. uncertainty, $u(x_i)$, mg/kg	D_i	U_i
LIPI*	8.00	0.32	-10.360	0.654
STD-ITDI	15.6368	0.2523	-2.723	0.522
VNIIM	17.75	0.21	-0.610	0.441
INMETRO	18.07	0.194	-0.290	0.411
NMIJ	18.2	0.4	-0.160	0.811
NIST	18.23	0.10	-0.130	0.241
NIM	18.31	0.10	-0.050	0.241
HSA	18.32	0.25	-0.040	0.518
KRISS	18.40	0.41	0.040	0.831
LATU	18.43	0.15	0.070	0.329
UME	18.44	0.36	0.080	0.732
NRCC	18.49	0.093	0.130	0.229
GLHK	18.5	0.361	0.140	0.734

Institute	Reported value, x_i, mg/kg	Reported std. uncertainty, $u(x_i)$, mg/kg	D_i	U_i
NIMT	19.9	0.51	1.540	1.029
KEBS	20.6705	0.3264	2.311	0.666

*The result from RCChem-LIPI was not included in the calculations of the KCRV.

Table 28. Equivalence Statements of chromium for CCQM-K124 Part A

Institute	Reported value, x_i, µg/kg	Reported std. uncertainty, $u(x_i)$, µg/kg	D_i	U_i
VNIIM	4.63	0.056	-0.450	0.118
NIMT	4.74	0.15	-0.340	0.302
ISPCH	4.879	0.059	-0.201	0.123
HSA	4.96	0.06	-0.120	0.125
LATU	5.041	0.031	-0.039	0.072
KRISS	5.045	0.022	-0.035	0.057
NMIJ	5.05	0.03	-0.030	0.070
NRCC	5.07	0.114	-0.010	0.231
UME	5.09	0.05	0.010	0.106
GLHK	5.10	0.0535	0.020	0.113
NIST	5.11	0.053	0.030	0.112
INMETRO	5.11	0.1220	0.030	0.247
NIM	5.118	0.046	0.038	0.099
INACAL	5.23	0.09	0.150	0.184
JSI	5.34	0.05	0.260	0.106
EXHM	5.491	0.111	0.411	0.225
KEBS*	10.2138	0.2505	5.134	0.502

*The result from KEBS was not included in the calculations of the KCRV.

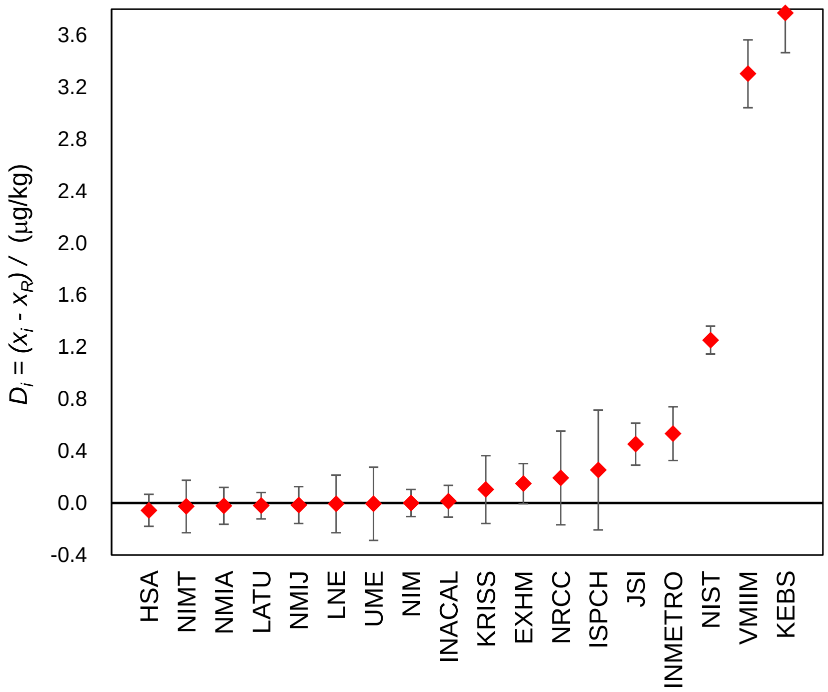

Figure 16. Equivalence Statements of arsenic for CCQM-K124 Part A

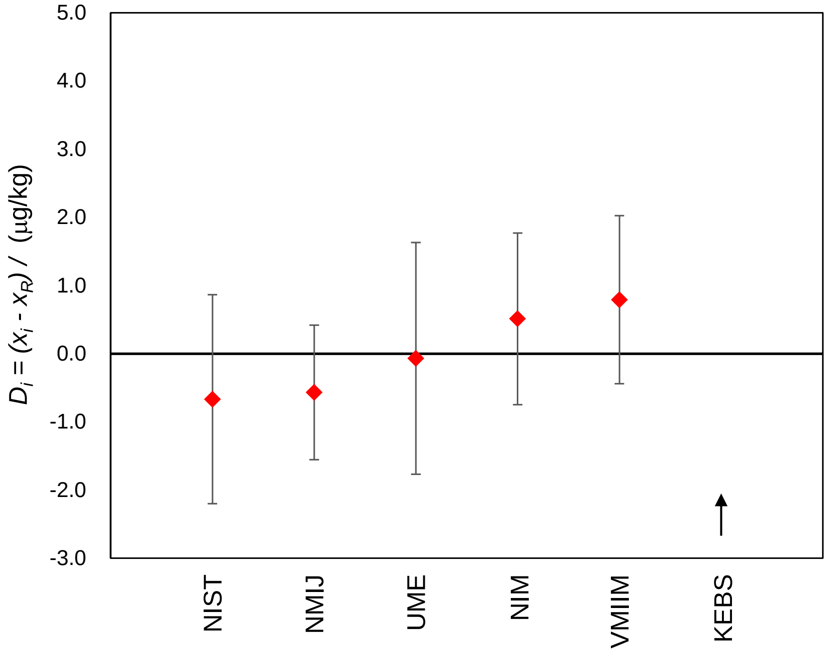

Figure 17. Equivalence Statements of boron for CCQM-K124 Part A

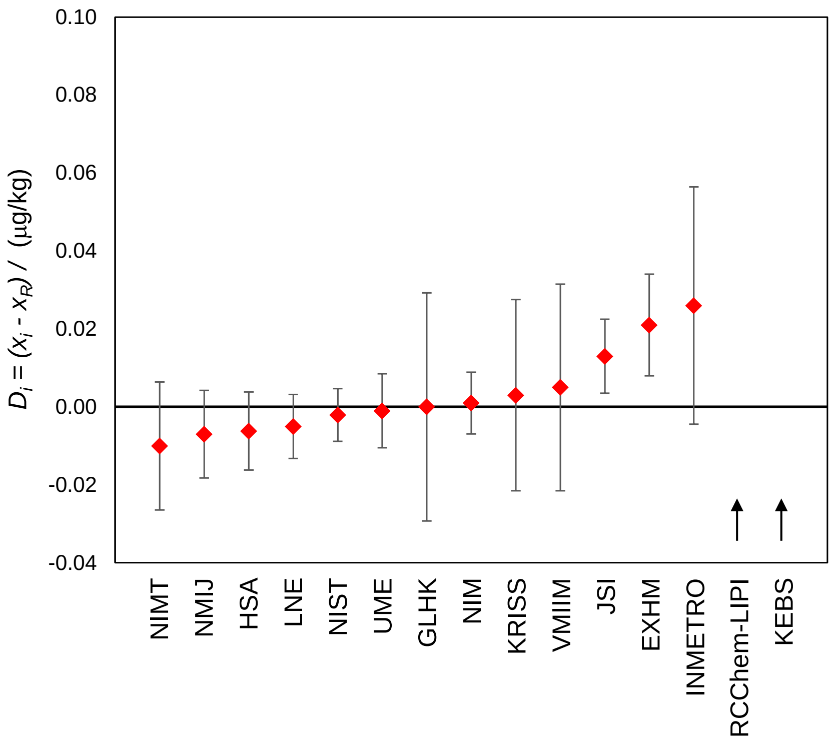

Figure 18. Equivalence Statements of cadmium for CCQM-K124 Part A

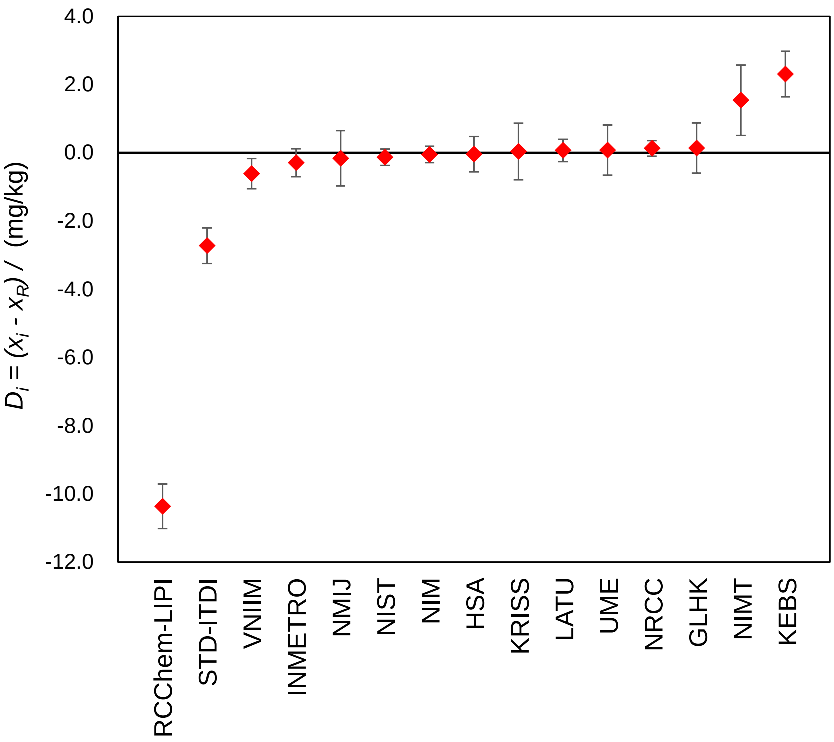

Figure 19. Equivalence Statements of calcium for CCQM-K124 Part A

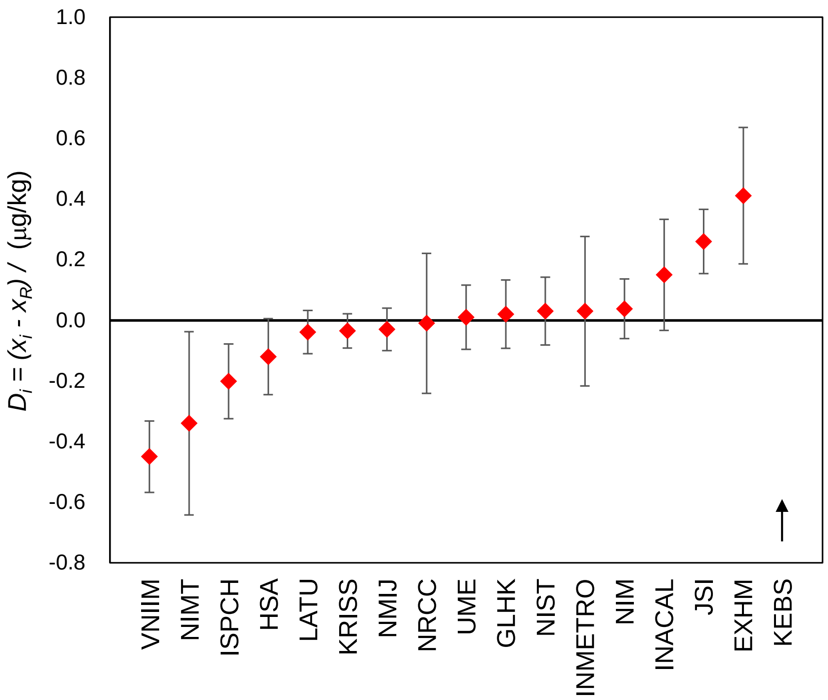

Figure 20. Equivalence Statements of chromium for CCQM-K124 Part A

6. Demonstration of Core Capabilities

As agreed by the CCQM IAWG meetings, a system of Core Capabilities (CC) for inorganic analysis will be employed to improve the efficiency and effectiveness of key comparisons to support CMC claims. With the use of this system, new CMC claims can be supported by describing CC that are required to provide the claimed measurement service and by referencing CC that were successfully demonstrated by participation in relevant key/supplementary comparisons. In this connection, all participants submitted their Inorganic CC Tables to the coordinator for compilation, and they are summarized five Summary Tables in the Appendix AII.

It is expected that arsenic, boron, cadmium, calcium and chromium at mass fractions greater than approximately 0.1 µg/kg, 1 µg/kg, 0.01 µg/kg, 1 mg/kg and 0.1 µg/kg respectively in drinking water and similar matrices (groundwater and river water etc.) can be determined by each participant using the same technique(s) employed for this key comparison to achieve similar uncertainties mentioned in the present report.

7. Conclusions

The KCRVs and DoEs were approved for As, B, Cd, Ca and Cr (except Mo and Hg) at the IAWG meetings held at Paris and Daejeon (Korea) in 2016.

Results were submitted by 14 NMIs and nine DIs. The participants used different measurement methods, though most of them used direct measurement using inductively coupled plasma-optical emission spectrometry (ICP-OES) for Ca, inductively coupled plasma-mass spectrometry (ICP-MS) and high resolution ICP-MS and isotope dilution technique with ICP-MS for other elements.

The results of B, Ca, Cr, As and Cd show good agreement except some outliers.

Concerning Hg, instability was observed when the sample stored in the light. And some participants observed instability of Mo. Therefore, it was agreed to abandon the Hg and Mo analysis as this sample was not satisfactory for KC.

Accounting for relative expanded uncertainty, comparability of measurement results for each of B, Ca, Cr, As and Cd was successfully demonstrated by the participating NMIs or DIs. Furthermore, the results of this key comparison can be utilized along with the IAWG core capability approach.

Acknowledgement

The coordinating laboratory would like to express the most sincere gratitude for the effort and supports from the contact persons and/or analysts of the participating NMIs/DIs.

Institute	Contact person and/or analysts
NMIA	David Saxby, Ian White, Jeffrey Merrick
DRiCM	Mala Khan
INMETRO	Thiago Araujo, Marcelo Almeida, Jefferson Rodrigues
BIM	Boriana Kotzeva
NRCC	Lu Yang, Indu Gedara Pihillagawa, Juris Meija, Zoltan Mester
ISPCH	Soraya Sandoval Riquelme, Leonardo Pérez, Rodrigo Barriga, Claudia Núñez
NIM	Jingbo Chao, Jun Wang, Qian Wang, Naijie Shi, Hai Lu, Panshu Song
SYKE	Teemu Näykki, Timo Sara-Aho
LNE	Guillaume LABARRAQUE, Caroline OSTER
PTB	Olaf Rienitz, Reinhard Jährling, Carola Pape
EXHM/GCSL-EIM	Evgenia Lampi, Elias Kakoulides
GLHK	W H Fung, H S Chu
RCChem-LIPI	Rosi Ketrin, Eka Mardika, Isna Komalasari
NMIJ	Yanbei Zhu, Kazumi Inagaki
KEBS	TOM ODUOR OKUMU, JACQUELINE NJERI KANG’IRI
KRISS	Yong-Hyeon Yim, Sung Woo Heo, Kyoung-Seok Lee, Jung Ki Suh, Youngran Lim
INACAL	Christian Uribe, Elmer Carrasco
STD-ITDI	Emma D. Tayag, Admer Rey C. Dablio, Elyson Keith P. Encarnacion Ruth L. Damian
VNIIM	Leonid Konopelko, Anatoli Krylov, Smirnov Vadim
HSA	Richard Shin, Sim Lay Peng, Wang Juan, Xu Chang, Fransiska Dewi
JSI	Milena Horvat, Tea Zuliani
NIMT	Sutthinun Taebunpakul, Charun Yafa, Nattikarn Kaewkhomdee, Usana Thiengmanee
TÜBİTAK UME	Süleyman Z. CAN, Betül ARI, Oktay CANKUR
LATU	Elizabeth Ferreira, Ramiro Pérez
NIST	Stephen E. Long, Brittany L. Kassim, Karen E. Murphy, John L. Molloy, Therese A. Butler

We would like to thank Dr. Mike Sargent for supporting throughout the course of this KC.

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.

Appendix AI

Traceability of Calibrants/Reference Materials used by Participants

Participant	Calibrants/Reference Materials
NMIA	As: NIST SRM 3103a Hg: NIST SRM 3133
INMETRO	Ca: NIST SRM 3109a Cr: NIST SRM 3112a As: NIST SRM 3103a Cd: IRMM 621 and NIST SRM 3108
NRCC	NRC Primary Standard Cr: Cr-29143 As: As-28858 Mo: Mo-28967 Hg: Hg-24877 Ca: NIST SRM 9819
ISPCH	Cr: NIST SRM 3112a Cd: NIST SRM 3108 As: NIST SRM 3103a Mo: NIST SRM 3134 Hg: NIST SRM 3133
NIM	B: GBW(E) 080217 Cr: GBW 08614 As: GBW (E) 080117 Ca: GBW (E) 080118 Mo: GBW(E) 080218 ^{111}Cd: GBW 04441 ^{202}Hg: GBW 04443
SYKE	Hg: NIST SRM 3133
LNE	Enriched spikes Cd: ^{111}Cd (IRMM) Hg: ^{202}Hg, ERM-AE640 Mass bias control solutions Cd: high purity standard (LNE) Hg: ERM 639 As: High purity standard As_2O_5 (99.9 %, Alfa Aesar)
PTB	Mo: NIST SRM 3134 and in-house prepared primary solution Hg: NIST SRM 3133 and in-house prepared primary solution
EXHM	B: NIST SRM 3107 Mo: NIST SRM 3134 Cd: NIST SRM 3108 Hg: NIST SRM 3133 Ca: NIST SRM 3109a Cr: NIST SRM 3112a As: NIST SRM 3103a
GLHK	Cd: NIST SRM 3108 Cr: NIST SRM 3112a Ca: NIST SRM 3109a ^{111}Cd isotope spike: IRMM 622 ^{50}Cr isotopic spike: IRMM 624
RCChem-LIPI	Ca: NIST SRM 3109a Cr: NIST SRM 3112a As: NIST SRM 83d Cd: KRISS RM No 105-02-006
NMIJ	JCSS (Japanese Calibration Service System) guaranteed single element standard solutions which are traceable to SI.
KEBS	Agilent Calibration Standard traceable to NIST SRMs
KRISS	KRISS standard solution (Ca, Cr, Cd, Mo, Hg and As) ^{111}Cd (US Services, Inc.) ^{42}Ca, ^{53}Cr, ^{100}Mo and ^{202}Hg (Oak Ridge National Lab.)
INACAL	As: NIST SRM 3103a Cr: NIST SRM 3112a
STD-ITDI	Ca: NIST SRM 3109a
VNIIM	ICP multi-element standard solution IV (Merck) Environmental calibration standard (Agilent Technologies) Hg standard solution (Merck)

Participant	Calibrants/Reference Materials
HSA	Ca: NIST SRM 3109a Cr: NIST SRM 3112a As: NIST SRM 3103a Cd: NIST SRM 3108 Mo: NIST SRM 3134
JSI	Cr: NIST SRM 3112a As: NIST SRM 3103a Cd: NIST SRM 3108 Mo: TraceCERT 68780 (Fluka) Hg : NIST SRM 3133
NIMT	Cd: NIST SRM 3108 Ca: NIST SRM 3109a Cr: NIST SRM 3112a As : NIST SRM 3103a Hg : NIST SRM 3177
TÜBİTAK UME	Ca: NIST SRM 3109a B: NIST SRM 3107 As: NIST SRM 3103a Cr: NIST SRM 3112a Mo: NIST SRM 3134 Hg: NIST SRM 3133 ^{111}Cd: IRMM 622 ^{50}Cr: IRMM 624 ^{202}Hg: ERM-AE 639 and ERM-AE 640
LATU	Ca : NIST SRM 3109a Cr : NIST SRM 3112a As : NIST SRM 3103a
NIST	As: NIST SRM 3103a B: NIST SRM 3107 Ca: NIST SRM 3109a Cr: NIST SRM 3112a Cd: archived NIST SRM 746 and NIST SRM 3108 Mo: NIST SRM 3134 Hg : NIST SRM 1641d

Inorganic Core Capabilities
Summary Table

CCQM Study: K124 Part A Trace Elements in Drinking Water

Institute(s): INMETRO, NRCC, NIM, LNE, GLHK, NMIJ, KRISS, HSA, NIMT, TÜBİTAK UME,

Method: ID-ICP-MS

Analyte(s): B, Cd, Ca, Cr

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 (Cd, Ca, Cr)	INMETRO (Cd) NRCC (Cr) NIM (B, Cd, Cr) LNE (Cd) GLHK (Cd, Cr) KRISS (Cd, Ca, Cr) HSA (Cd, Cr) UME (Cd, Cr) LATU (Cr) NIST (Cd)	Adopted procedures to avoid contamination include, use of type 1 water, in-house distilled acid for purification and blank control. (INMETRO) Blank correction (NIM) High purity reagents needed (LNE) Blank samples involved in the sample preparation, and the concentration is insignificant. (GLHK) All sample preparations were performed using ultrapure grade HNO_3 in ISO Class 6 laboratory to avoid contamination. (UME) Cd was present in the sample at a mass fraction in the sub part per billion range; thus contamination control was necessary. Techniques and procedures employed to reduce contamination and accurately correct for the procedure blank included the following: Test portions were processed in HEPA-filtered clean room and chemical fume hood, all labware was rigorously cleaned prior to use, ultra-pure reagents were used, sample processing and reagent use was minimized, four procedure blanks were processed via the method of isotope dilution analysis concurrent and in identical manner to the test portions and used to correct the test portions for contamination, and lastly the accuracy of the procedure blank correction was verified by comparison to a linear regression approach in which the Cd mass fraction was derived from the slope of the regression line formed from a plot of the measured mass of Cd vs. test portion mass (test portion

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
			masses ranged from 2 g to 3.5 g) and the procedure blank was derived from the *y*-intercept. (NIST)
Digestion/dissolution of organic matrices *All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.*	All		
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.*	All		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	All		
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	All		
Vapor generation *Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.*	All		
Matrix separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	All		
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample.*	NIMT (Cd, Ca, Cr)	INMETRO (Cd) NRCC (Cr) NIM (B, Cd, Cr) LNE (Cd) GLHK (Cd, Cr) KRISS (Cd, Ca, Cr) HSA (Cd, Cr) UME (Cd, Cr)	Spike was allowed to equilibrate for 24h. (INMETRO) Samples were left for 24 h prior to ICPMS measurements (NRCC) Necessity of inorganic spikes (LNE) Measurements of blend solutions were performed at least 48 hours after preparation for isotopic

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
		LATU (Cr) NIST (Cd)	equilibration. (UME) A simple dilution procedure was used which involved acidification to 2 % v/v HNO_3 followed by physical mixing of the test portion and added enriched ^{111}Cd isotopic spike. This was found to be comparable to a wet digestion procedure in which spiked test portions were heated with concentrated HNO_3. The data reported by NIST was acquired using the simple dilution procedure. (NIST)
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 (Ca)	INMETRO (Cd) NRCC (Cr) NIM (B, Cd, Cr) LNE (Cd) GLHK (Cd, Cr) KRISS (Cd, Ca, Cr) HSA (Cd, Cr) NIMT (Cd, Cr) UME (Cd, Cr) LATU (Cr) NIST (Cd)	The low concentration of the analyte was addressed with the use of an ultrasound nebulizer (USN) which provided a better signal to noise ratio, although it degraded the standard deviation of the measured ratio, consequently increasing the uncertainty associated to the measurement. (INMETRO) CRC-ICP-MS (He mode) and HR-ICPMS are employed for the analysis. Signal is relatively low for Cd. (GLHK) Cd level were too low (KRISS) Low levels of Cd and Cr present in sample. (NIMT) Since the signals were very low, the uncertainty contribution from relative standard deviation on ratios increased the measurement uncertainty. (UME) Samples were analyzed in both standard mode and collision cell kinetic energy discrimination mode (CC/KED mode). In comparison to standard mode, CC/KED mode has the advantage of lower molecular ion formation, but the disadvantage of lower sensitivity. For both modes, parameters were optimized using a tune solution containing indium (In) and cerium (Ce). The operating parameters were first adjusted to obtain maximum sensitivity for ^{115}In and then further adjusted until the minimum achievable ^{156}CeO+/^{140}Ce+ ratio was obtained. A resulting sensitivity of 17 Kcps and 6 Kcps ^{114}Cd per μgkg^{-1} Cd (Cd standard solution) was obtained for standard mode and CC/KED mode respectively. (NIST)
Memory effect *Any techniques used to avoid,*	INMETRO (Cd),	NIM (B, Cd, Cr)	Samples are separated by blanks in

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.	HSA (Cd, Cr), NIMT (Cd, Ca, Cr)	GLHK (Cd, Cr) NMIJ (B) KRISS (Cd, Ca, Cr) UME (Cd, Cr) LATU (Cr) NIST (Cd)	the injection sequence (GLHK) In order to remove the memory effect, 10% ammonia solution was applied as a washing solution. (NMIJ) For Cd and Cr measurements, background check (memory effect) was performed between each run. (UME) Cones were cleaned and new sample introduction tubing was used to mitigate Cd carryover and reduce Cd background coming from the instrument. (NIST)
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.*	NIM (B) NIMT (Cd)	INMETRO (Cd) NRCC (Cr, As) NIM (Cd, Cr) LNE (Cd) GLHK (Cd, Cr) NMIJ (Ca) KRISS (Cd, Ca, Cr) HSA (Cd, Cr) NIMT (Ca, Cr) UME (Cd, Cr) LATU (Cr) NIST (Cd)	Optimization of the equipment for the lowest oxide generation was important to minimize the possible interference due to Mo presence. For this purpose a solution of Mo was used as “setup” solution keeping the MoO level <0.6%. The use of USN was useful for this objective also. (INMETRO) Used medium resolution to resolve polyatomic interferences for Cr and used high resolution to resolve polyatomic interferences for As. (NRCC) Adopted He and NH_3 reaction gas to reduce interference of $^{40}Ar^{13}C$ to ^{53}Cr. Evaluated $^{95}Mo^{16}O$, $^{94}Mo^{16}O$ interference to ^{111}Cd and ^{110}Cd. (NIM) Subtraction of a closed matrix matching (LNE) CRC-ICP-MS (He mode) and HR-ICPMS (medium resolution) are employed for remove interferences from polyatomic species. Isobaric elements are monitored and found to be insignificant. (GLHK) Cold plasma condition was applied to remove spectral interferences by ^{40}Ar. (NMIJ) Ca, Cr: medium resolution was used to remove interferences. Cd: ICP-QQQ in MS/MS mode was used to remove interferences. (KRISS) Use H_2 and He as collision/reaction gases for minimizing polyatomic/isobaric interferences (NIMT) Cd and Cr measurements were performed at medium resolution mode of HR-ICPMS. Isobaric interferences on Cr for V were corrected mathematically. Possible polyatomic interferences on Cd

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
			were checked at higher interfering element concentration but no significant contribution was observed from oxide formation of Mo. (UME) Medium resolution (R>4000) was used to resolve interferences. (LATU) The potential effect of spectral interference on the accurate measurement of Cd was studied and found to be minimal for this material. Nonetheless, correction algorithms and instrumental methods of interference reduction (collision cell/kinetic energy discrimination mode) were additionally employed. (NIST)
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	NIM (B, Cd, Cr), KRISS (Cd, Ca, Cr) NIMT (Cd, Ca, Cr)	INMETRO (Cd) NRCC (Cr) LNE (Cd) GLHK (Cd, Cr) HSA (Cd, Cr) UME (Cd, Cr) LATU (Cr) NIST (Cd)	The detector dead time was corrected automatically by the software (INMETRO) Use of the calculated value by the producer of the ICP/MS (LNE) ID-MS methodologies can compensate for this effect when exact matching approach is used. (GLHK) Sample and calibration blends intensities were matched to reduce the significance of this effect. (HSA) Dead time correction was measured before measurements. (UME) Detector dead-time was experimentally determined using natural gadolinium solutions with mass fractions that resulted in count rates spanning the count rate range from 1 x 105 counts per second (cps) to 9 x 105 cps. The measured dead-time was 37 ns. (NIST)
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*		All	A natural abundance standard in a concentration close to the sample (NIST 3108) was measured and results used to correct mass bias using the sample-spike bracketing model. (INMETRO) Used natural abundance standard solution for mass bias correction (NRCC) Use of high purity standard solutions (LNE) Standard solutions with known isotope compositions are used to correct for mass bias. (GLHK) Mass bias/fractionation was corrected for by bracketing

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
			correction using an isotope ratio standard (KRISS) Sample and calibration blends were bracketed with a standard solution with known isotopic composition to correct for mass bias. (HSA) Use standard solution to monitor mass bias (NIMT) Mass bias correction factors were determined between runs and included in the calculations. Bracketing technique was used for mass bias correction. (UME) A solution of pure Cd with natural isotopic composition was used to measure the mass bias correction factor. The mass bias correction factor was measured at the beginning of the analysis sequence and then used to correct the ratio of a spike calibration sample measured immediately afterward. The spike calibration sample had an isotopic ratio similar to the spiked test portions and was re-measured throughout the analysis. It was used to correct the blanks, remaining calibration samples, test portions and controls for mass bias and any subsequent instrument drift. Drift was assessed every three samples and a correction applied by assuming it to be linear with time. (NIST)
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*	INMETRO (Cd), LATU (Cr)	NRCC (Cr) NIM (B, Cd, Cr) LNE (Cd) NMIJ (B, Cd, Ca, Cr) KRISS (Cd, Ca, Cr) HSA (Cd, Cr) NIMT (Cd, Ca, Cr) UME (Cd, Cr) NIST (Cd)	Used double ID method (NRCC) In house accurate preparation of the high purity standard solution for Cd. (LNE) Double ID-ICP-MS was applied. (NMIJ) Double isotope dilution technique was used (KRISS) Exact-matching IDMS was used. (HSA) Reverse IDMS to calibrate the isotopic spike (NIMT) Reverse IDMS was used, employing two calibration solutions, which were SRM 3108 Cd Standard Solution, Lot No. 130116, and a solution prepared in-house from SRM 746 Cadmium-Vapor Pressure. (NIST)

Inorganic Core Capabilities
Summary Table

CCQM Study: K124 Part A Trace Elements in Drinking Water

Institute(s): NMIA, INMETRO, NRCC, ISPCH, NIM, LNE, EXHM/GCSL-EIM, NMIJ, KRISS, VNIIM, HSA, JSI, NIMT, TÜBİTAK UME, LATU, NIST

Method: ICP-MS (without Isotope Dilution)

Analyte(s): As, B, Cd, Ca, Cr

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.*	NMIA (As) EXHM (As, Cd, Cr) VNIIM (As, B, Cd, Ca, Cr)	INMETRO (As, Cr) NRCC (As) NIM (As) LNE (As) NMIJ (As) KRISS (As) HSA (As) JSI (As, Cd, Cr) NIMT (As) UME (As, B, Ca) LATU (As) NIST (As, B, Cr)	Method blanks used for contamination control (NMIA) Adopted procedures to avoid contamination include, use of type 1 water, in-house distilled acid for purification and blank control. (INMETRO) Blank correction (NIM) High purity reagents needed (LNE) The blank values were under the limits of detection. (JSI) Clean room and low As level in acid used are required (NIMT) In order to minimize the possible contamination of sample, ultrapure reagents and pre-cleaned PFA labwares were used during the analysis and the samples were prepared in ISO Class 6 level clean laboratory environment. (UME) Blanks were prepared for each element measured, for each sample prepared so that the run order was sample/blank/sample with each measured solution having a blank run right after it for correction. An initial run showed bad precision due to contamination within the instrument. This was solved by cleaning sampling/skimmer cones and replacing pump tubing. (NIST)
Digestion/dissolution of organic matrices *All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.*	All		
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.*	All		

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	All		
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	All		
Vapor generation *Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.*	All		
Matrix separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	All		
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		All	Standard Addition calibration (NMIA) Standards were prepared from a commercial certified reference material (NIST 3103a and 3112a). Dilutions were performed daily in a calibrated and balance with 0.00001 g of resolution using 2% nitric acid solution. (INMETRO) Standard addition method with internal standard was used. (NIM) Accurate gravimetric preparation of high purity standard solutions for Standard addition method (LNE) Standard additions at exact matching (EXHM) Gravimetric standard addition method with internal standard was used. (KRISS) Calibration standards were prepared from multielement standard solutions by weighing in 2 or 3 steps. Calibration method-bracketing. Internal standard (Y: 10 mg/kg) was used, but it was not used for correction of final results (recovery over 99%) (VNIIM)

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
			Standard addition was used. (HSA) External calibration. The standards were prepared gravimetrically. (JSI) Matrix matched standard addition method was used for the calibration. In order to monitor and minimize the drift on the signal, internal standard was used. (UME) Performed standard additions using spike solutions prepared from NIST 3100 series SRMs (NIST)
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.*	INMETRO (As, Cr) VNIIM (As, B, Cd, Ca, Cr) JSI (As, Cd, Cr) NIMT (As) UME (As, B, Ca)	NMIA (As) NRCC (As) NIM (As) LNE (As) EXHM (As, Cd, Cr) KRISS (As) HSA (As) LATU (As) NIST (As, B, Cr)	As high first ionization potential (NMIA) As is difficulty to measure due to polyatomic interferences, thus high resolution mode was used but sensitivity was significantly reduced. (NRCC) Measurements were performed at high resolution (R≅10000) causing poor sensitivity, decreasing precision. (LATU) For B the signals for ^{10}B and ^{11}B were added together to improve precision. (NIST)
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	NMIA (As) INMETRO (As, Cr) EXHM (As, Cd, Cr) VNIIM (As, B, Cd, Ca, Cr) HSA (As) LATU (As)	NIM (As) LNE (As) KRISS (As) JSI (As, Cd, Cr) NIMT (As) UME (As, B, Ca) NIST (As, B, Cr)	Washing procedures with 5% HNO_3 were inserted between every sample measurements. (NIM) Necessity of cleaning step between sample solutions analysis (LNE) Washing procedures with 5% and 1% HNO_3, and MilliQ water were inserted between every sample measurement. (JSI) Reagent blank needed to be measured prior to follow-up measurement. (NIMT) The significant memory effect was observed for B. For the elimination of this effect, the duration for cleaning of introduction system was increased. (UME) Blanks were run between each sample solution analysis and were monitored for elevated signal levels. Replicates of each blank solution were measured over the course of the run and monitored for changes from one replicate to the next. (NIST)
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*	EXHM (Cd) VNIIM (As, B, Cd, Ca, Cr)	NMIA (As) INMETRO (As, Cr) NRCC (As) NIM (As) LNE (As) EXHM (As, Cr) NMIJ (As) KRISS (As)	High resolution or collision/reaction cell required for ArCl and other interferences. CoO interference not fully resolved with high resolution MS. Only 1 isotope available for ICPMS measurement. (NMIA) The high Cl amount in the sample favor the formation of polyatomic interfering species to both analytes.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.		HSA (As) JSI (As, Cd, Cr) NIMT (As) UME (As, B, Ca) LATU (As) NIST (Cr)	The dynamic reaction cell was used with ammonia to remove these interferences. (INMETRO) Used high resolution to resolve polyatomic interferences (NRCC) Adopted He reaction gas to reduce interference of ^{40}Ar^{35}Cl to ^{75}As. (NIM) Use of the collision cell with He (3mL/min) to remove ArCl isobaric interference on ^{75}As (LNE) Measurement at medium and high resolution (EXHM) High energy collision condition (collision cell) was applied to get rid of spectral interferences in the measurement. (NMIJ) ICP/MS at high resolution (R≥9000) was used to avoid polyatomic interferences. (KRISS) High resolution mass spectrometry was used to remove interferences. (HSA) Reaction-collision cell was used for the removal of interferences. (JSI) Oxygen mode was employed to shift the m/z of arsenic from 75 to 91 and to also avoid overlapping polyatomic interferences from ^{40}Ar^{35}Cl^{+} (NIMT) HR-ICPMS was operated at medium resolution mode for the isotopes used in measurements. The signals for the internal standard were also corrected for isobaric interferences. (UME) High resolution (R≅10000) was used to resolve interferences. (LATU) For Cr, polyatomic/isobaric interferences could be present. While the data used for value assignment were collected with the collision cell turned off, an additional run was performed to test for the presence of interferences and noticed such an occurrence for ^{53}Cr, but not for ^{52}Cr (NIST)
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.*	LNE (As) KRISS (As) VNIIM (As, B, Cd, Ca, Cr) NIMT (As)	NMIA (As) INMETRO (As, Cr) NIM (As) EXHM (As, Cd, Cr) NMIJ (As) HSA (As) JSI (As, Cd, Cr) UME (As, B, Ca) LATU (As) NIST (As, B, Cr)	Standard addition used to remove the effect of matrix effects (NMIA) Indium was used as internal standard to evaluate the incidence of non-spectral interferences. (INMETRO) Adopted standard addition to correct possible bias of matrix effect. (NIM) Standard additions at exact matching (EXHM) Standard addition was applied to get rid of the matrix effect. (NMIJ) Standard addition was used. (HSA) Internal standards (Y and Rh) were

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
			used. (JSI) Matrix matched standard additions method was applied during the measurements. (UME) Gravimetric standard addition with ^{73}Ge as internal standard (LATU) The method of standard additions was used in conjunction with an internal standard to correct for such issues. (NIST)
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	NMIA (As) INMETRO (As, Cr) NIM (As) EXHM (As, Cd, Cr) KRISS (As) VNIIM (As, B, Cd, Ca, Cr) HSA (As) JSI (As, Cd, Cr) NIMT (As) UME (As, B, Ca) NIST (As, B, Cr)	NRCC (As) LNE (As) LATU (As)	Deadtime correction by ICPMS software (NMIA) Use of the calculated value by the producer of the ICP/MS (LNE)
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	All		Sample bracketing used (NMIA)

Appendix AII

Inorganic Core Capabilities
Summary Table

CCQM Study: K124 Part A Trace Elements in Drinking Water

Institute(s): INMETRO, NRCC, NIM, GLHK, RCChem-LIPI, HSA, LATU, NIST

Method: ICP-OES

Analyte(s): Ca

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.*		All	Adopted procedures to avoid contamination include, use of type 1 water, in-house distilled acid for purification and blank control. (INMETRO) Blank correction. (NIM) Blank samples involved in the sample preparation and corrected for sample concentration. (GLHK) Prepared and measured the blank of sample and reagents (LIPI) Blanks were prepared for each sample prepared so that the run order was sample/blank/sample with each measured solution having a blank run right after it for correction. (NIST)
Digestion/dissolution of organic matrices *All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ICP.*	All		
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ICP.*	All		Challenge from low level of analyte. Digestion was not employed to reduce the need for excessive dilution and potential contamination from added reagents/handling. (NIST)
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	INMETRO NIM GLHK HSA LATU NIST	LIPI	Store the sample at room temperature (<25 °C) and maintain the solution from any evaporation by maintain the weight of sample solution. (LIPI)
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ICP. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	All		
Vapor generation *Techniques such as hydride generation and cold vapor generation used to remove the analyte from the sample as a gas for introduction into the ICP.*	All		
Matrix separation *Techniques and procedures used to isolate*	All		

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
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.			
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		All	Standards were prepared from a commercial certified reference material (NIST 3109a). Dilutions were performed daily in a calibrated and balance with 0.00001 g of resolution using 2% nitric acid solution. (INMETRO) Used external calibration method, and QC solution was used during determination. (NIM) Gravimetric standard addition technique is employed. (GLHK) Used standard additions procedure to minimize the effect of sample matrix interference. (LIPI) Standard addition was used. (HSA) Performed standard additions using spike solution prepared from NIST SRM 3109a. (NIST)
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..*	INMETRO HSA	NRC NIM GLHK LIPI LATU NIST	ICP-OES is employed for the analysis, the signal sensitivity is enough. (GLHK) Used several wavelengths (LIPI) For Ca sample had to be diluted to get signal intensity to working range of instrument. (NIST)
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	INMETRO NIM LIPI HSA LATU	GLHK NIST	Samples are separated by blanks in the injection sequence (GLHK) Blanks were run between each sample solution analysis and were monitored for elevated signal levels. Replicates of each blank solution were measured over the course of the run and monitored for changes from one replicate to the next. (NIST)
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.*	INMETRO LIPI HSA NIST	NRCC NIM LATU	Choose wave line without significant interference, inter element correction was applied (NRCC)
Correction or removal of matrix-induced signal suppression or enhancement *Chemical or instrumental procedures used*	INMETRO	NRCC NIM GLHK LIPI	Standard additions calibration was applied (NRCC) Evaluated matrix and acid effect to signal during determination. (NIM)

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
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.		HSA LATU NIST	Gravimetric standard addition technique can compensate for this effect. (GLHK) Used Yttrium as an internal standard and correct the signal with the signal of Y in order to remove the signal suppression or enhancement. (LIPI) Standard addition was used. (HSA) The method of standard additions was used in conjunction with an internal standard to correct for such issues. (NIST)

Inorganic Core Capabilities
Summary Table

CCQM Study: K124 Part A Trace Elements in Drinking Water

Institute(s): RCChem-LIPI, INACAL,

Method: ETA-AAS (or GF-AAS)

Analyte(s): Cd (RCChem-LIPI), As and Cr (INACAL)

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.*		All	Prepared and measured the blank of sample and reagents (LIPI) Use of blanks for contamination control and correction (INACAL)
Digestion/dissolution of organic matrices *All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ETA-AAS.*	All		
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ETA-AAS.*	All		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	INACAL	LIPI	Store the sample at room temperature (<25 ℃) and maintain the solution from any evaporation by maintain the weight of sample solution. (LIPI)
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the ETA-AAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	All		
Matrix separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	All		
Hydride preconcentration/matrix separation of volatile species. *Coupling of a hydride system to the ETA-AAS and optimization of conditions.*	All		
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures. Also use of matrix-matched standards to minimize effect of interferences.*		All	Used standard additions procedure to minimize the effect of sample matrix interference. (LIPI) Standard addition measurement optimization (INACAL)
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*		All	Used Zeeman background correction. (LIPI) Optimization of operating conditions for low concentration of

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
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).			analytes (INACAL)
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	LIPI	INACAL	Use of blanks for evaluation of memory effect (INACAL)
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.*	All		
Correction or removal of matrix effects or interferences *Chemical or instrumental procedures used to avoid or correct for spectral and non-spectral interferences. Includes effects of differences in viscosity and chemical equilibrium states of analyte between the standard and sample. Selection of matrix modifier to adjust volatility of analyte and/or matrix to eliminate these effects is also included. Addition of reactive gases (eg oxygen) to the carrier gas to improve matrix separation. Also included is Zeeman or other background correction techniques to remove interference due to absorption and scattering from coexisting molecules/atoms in the sample.*		All	Selection of matrix modifier to adjust volatility of analyte. (LIPI) Selection of matrix modifier (INACAL)

Appendix AII

Inorganic Core Capabilities
Summary Table

CCQM Study: K124 Part A Trace Elements in Drinking Water

Institute(s): STD-ITDI

Method: Flame-AAS

Analyte(s): Ca

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.*		X	The laboratory does not use yet acid steam cleaning system for cleaning of glassware and acids used for analysis are not purified using an acid distillation system.
Digestion/dissolution of organic matrices *All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the ETA-AAS.*		X	The laboratory still uses wet digestion by hotplate method with the use of suprapure grade acids. This does not ensure complete digestion of the sample. The laboratory has requested the purchase of a microwave-assisted digestor as an answer to this problem.
Digestion/dissolution of inorganic matrices *All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the ETA-AAS.*		X	The laboratory still uses wet digestion by hotplate method with the use of suprapure grade acids. This does not ensure complete digestion of the sample. The laboratory has requested the purchase of a microwave-assisted digestor as an answer to this problem.
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*		X	The digestion method used by the laboratory is just an open system which can lead to loss of volatile elements and there is no control of temperature.
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.*		X	The laboratory only performs evaporation of sample to concentrate the analyte.
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.*		X	The laboratory does not perform any separation techniques for various matrices of samples.
Hydride preconcentration/matrix separation of volatile species. *Coupling of a hydride system to the ETA-AAS and optimization of conditions.*		X	The laboratory conducts hydride preconcentration for Arsenic analyte only. The laboratory did not perform As analysis for this key comparison due to a discrepancy encountered in a previous test.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
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.*		X	The laboratory performs gravimetric preparation of NIST traceable standard solutions, which accuracy is also traceable to a reference value from a reference material analyzed by a metrological institute. The laboratory aims to purchase balances that are more sensitive and has high resolution.
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).*		X	Since the laboratory cannot yet have a contamination control, there is a limitation in terms of the detection and recording of the absorption signals of analytes.
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		X	The laboratory performs quality control procedures like inclusion of reagent blanks, calibration drift check every after 10 sample measurements, and good (95-105%) recovery of certified reference materials. The laboratory is experiencing difficulty in the purchase of CRMs and SRMs.
Optimization of the flame conditions *Optimization of flame stoichiometry and composition.* *Certain elements present a greater challenge.*		X	The laboratory ensures that before analytical measurements the instrument has been optimized for all the instrumental parameters in the quantitation of specific analytes. The laboratory is experiencing regular drifts in the readings of the analytical instrument.
Correction or removal of matrix effects or interferences *Chemical or instrumental procedures used to avoid or correct for spectral and non-spectral interferences. Includes effects of differences in viscosity and chemical equilibrium states of analyte between the standard and sample. Selection of matrix modifier to adjust volatility of analyte and/or matrix to eliminate these effects is also included. Addition of reactive gases (eg oxygen) to the carrier gas to improve matrix separation. Also included is Zeeman or other background correction techniques to remove interference due to absorption and scattering from coexisting molecules/atoms in the sample.*		X	The laboratory uses modifiers to correct or minimize the effects of various interferences and it also uses reagent blanks and standard additions to correct for the matrix effects. Standard addition was not performed for this key comparison. Standard addition is not fully explored by the laboratory as an alternative option to correct for matrix effects and interferences.

CCQM-K124

Part B: Chromium Speciation in Drinking Water

Final Report

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Coordinated by GLHK

November 2016

Abstract

CCQM-K124 was an activity of the Inorganic Analysis Working Group (IAWG) and was jointly coordinated by the National Metrology Institute of Japan (NMIJ) and the Government Laboratory, Hong Kong SAR (GLHK). The Part B of CCQM-K124 was organised by GLHK and hexavalent chromium (Cr(VI)) in drinking water was the measurand.

The Part B of the key comparison was undertaken for NMIs and DIs to demonstrate their capabilities in measuring part-per-billion level (in µg/kg) of hexavalent chromium in drinking water. It should also facilitate the acquisition of claims in Calibration and Measurement Capabilities (CMCs) as listed in Appendix C of Key Comparison Database (KCDB) under the Mutual Recognition Arrangement of the International Committee of Weights and Measures (CIPM MRA).

Results were summited by six NMIs and one DI. The methods applied were direct measurement using 1,5-diphenylcarbazide (DPC) derivatisation UV-visible spectrophotometry, standard addition using ion chromatography—UV-visible spectrophotometry or HPLC—inductively coupled plasma-mass spectrometry (ICP-MS) and isotope dilution technique with ion chromatography—ICP-MS.

Table of Content

1. **Introduction**

CCQM-K124 is divided into two parts — Part A: Trace elements in drinking water, and Part B: Chromium speciation in drinking water. The Part B key comparison is coordinated by the Government Laboratory of Hong Kong SAR (GLHK). Drinking water, which was purchased from local markets in Hong Kong, fortified with various chromium species was prepared as the test material.

Chromium exhibits a wide range of possible oxidation states. Elemental metal, trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] are the most commonly observed chromium species in environment. Chromium in water supplies can be either from naturally occurring sources or as the result of industrial activities. Because of the widespread use of Cr in many industrial activities, industrial wastes and effluents become the dominant source of Cr releasing to surface water and groundwater.

WHO has established a guideline value of 0.05 mg/L for total Cr in drinking water. Many governments and safety regulatory agencies have also set maximum allowable limit for total Cr in drinking water to ensure safe consumption. However, toxicity, mobility and bioavailability are largely different for different Cr species. Trivalent chromium is an essential micronutrient which plays a vital role in releasing energy from fats and sugars. Hexavalent chromium, in contrast, is highly toxic and is known to be carcinogenic. Therefore, a thorough study on Cr species in drinking water is crucial for evaluating potential hazards and safeguarding the public health.

Key comparison exercises involving speciation such as methylmercury in fish (CCQM-K43 & CCQM-K43.1), selenium speciation in wheat flour (CCQM-K60), arsenobetaine in tuna fish (CCQM-K97) and arsenic speciation in brown rice flour (CCQM-K108 & CCQM-K108.2014) have been conducted. Although total chromium content in various matrices had been studied in previous key comparisons, hexavalent chromium in the presence of other chromium species in drinking water remained a challenging project as comparison exercise.

The aim of this study is to demonstrate the capability of participating NMIs and DIs in measuring the content of hexavalent chromium in drinking water in the presence of other chromium species in a μg/kg level. The exercise could also facilitate the participating laboratories to acquire claims on Calibration and Measurement Capabilities (CMC) 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). “Core Capabilities” tables were also distributed so that participants could provide evidence for the CMC claims on their selected technique.

In the IAWG meeting held in Teddington (UK), November 2015, it was agreed that the median approach is suitable for the calculation of KCRV for CCQM-K124 Part B.

2. Participating Institutes

Seven institutes registered in the Key Comparison CCQM-K124 Part B and Table 1 depicts the list of the participating NMIs/DIs in alphabetic order of the countries' names.

Table 1. List of the Participating NMIs/DI for CCQM-K124 Part B

No.	Institute	Country	Contact Person
1	NIM National Institute of Metrology	China	Jingbo Chao, Jun Wang
2	EXHM/GCSL-EIM General Chemical State Laboratory	Greece	Elias Kakoulides
3	GLHK Government Laboratory, Hong Kong	Hong Kong SAR, China	Della Wai-Mei Sin, Alvin Wai-Hong Fung
4	CENAM Centro Nacional de Metrologia	Mexico	Judith Velina Lara Manzano
5	INRAP National Institute of Research and Physical Chemical Analysis	Tunisia	Hanen Klich
6	TUBITAK UME Ulusal Metroloji Enstitüsü	Turkey	Süleyman Z. Can
7	LGC	UK	Heidi Goenaga Infante

3. Samples and Instructions to Participants

3.1 Material

Bottles of 4-L distilled drinking water were purchased from a local market in Hong Kong, and the water samples were tested using ion chromatography-inductively coupled plasma-mass spectrometry (IC-ICP-MS) to confirm not containing any detectable Cr(III) or Cr(VI) species. In a Class 1000 cleanroom, the distilled drinking water was transferred to a pre-cleaned and dried 10-L polypropylene bottle, and appropriate amounts of the Cr(VI) solution (prepared from NIST SRM 136f, $K_2Cr_2O_7$, certified purity = 99.9954%) and the chromium(III) acetylacetonate solution ($[Cr(C_5H_7O_2)_3]$, purity > 99%) were added. A solution of potassium peroxodisulfate (prepared from Fluka, $K_2S_2O_8$, purity ≥ 99%) was also added for preservation purpose. The water material was thoroughly homogenised in a 3D-mixer at 12 rpm for 30 minutes. To a pre-cleaned and dried 125-mL high density polyethylene (HDPE) bottle, 50 g of the water material were transferred, and the bottle was closed tightly and the bottle neck was wrapped with a strip of Parafilm®. Each bottle of water sample was sealed with an aluminum bag under atmospheric pressure. The samples were stored in a Class 1000 cleanroom at room temperature (20 ± 5 ˚C) before distribution.

3.2 **Homogeneity and Stability Studies**

The homogeneity study was conducted after the samples of the test material were bottled and sealed in an aluminum bag. Ten random bottles of the test material were selected out of about 80 bottles. Two test portions of 5.5 g were drawn from each bottle for analysis.

Quantification of hexavalent chromium (Cr(VI)) was accomplished by gravimetric standard addition technique. The test portions were made up to 10 g with a solution of 25 mM ethylenediaminetetraacetate (EDTA) at pH 7.1, and 2.5 g of the resulting solutions were spiked with a suitable amount of Cr(VI) standard calibration solution and then made up to 5 g using Mili-Q water. The analytical solutions and method blanks were analysed using ICP-qMS with prior anion-exchange column separation.

ANOVA technique was applied to evaluate the between bottle heterogeneity, and its standard uncertainty (u_{bb}) was calculated using the equation (1) given below in accordance with ISO Guide 35:2006 [1]. The result was shown in Table 2.

$$u_{\mathrm{bb}} = \sqrt{\frac{\mathrm{MS}_{within}}{n} \times \sqrt{\frac{2}{v_{MSwithin}}}} \qquad (1)$$

where

u_{bb} is the standard uncertainty due to between bottles heterogeneity;

$\mathrm{MS}_{\mathrm{within}}$ is the mean square of within bottles variance;

$v_{MS\mathrm{within}}$ is the degree of freedom of MS_{within};

n is the number of replicates.

Table 2. Results of Homogeneity Study

Analyte	ANOVA test on heterogeneity		Relative standard uncertainty due to between bottle heterogeneity (u_{bb})
	F-value	F-test Critical value	
Hexavalent chromium	0.863	3.020	1.28%

The homogeneity study indicated that there was no significant heterogeneity observed amount different bottles of test material, and therefore, its quality is fit for the comparison programme.

Long-term and short-term stability studies were conducted for the test material using the same analytical procedure as for the homogeneity study. The long-term stability study was intended to examine the behavior of the test material throughout the complete comparison exercise to ensure that there was no significant change in the analyte mass fraction, while the short-term stability study mimicked the conditions during sample transport to evaluate the possible change in stability of the test material. The long-term stability study was carried out at room temperature (20 ± 5 ˚C) throughout the period from test material preparation to the deadline of result submission. The short-term stability studies were conducted at room temperature and 40 ˚C, respectively, over a 1-month period (sampling points: 0 day, 7 days, 15 days, 29 days).

The trend-analysis technique proposed by ISO Guide 35:2006 [1] was applied to assess the stability of the test material at room temperature and 40 ˚C. The basic model for the stability study is expressed as

$$Y = \beta_0 + \beta_1 X + \varepsilon \tag{2}$$

Where

β_0 and β_1 are the regression coefficients

ε is the random error component

Using the appropriate *t*-factor, β_1 can be tested for significance of deviation from zero.

Table 3 depicts the stability test results for 20 ˚C and 40 ˚C, respectively.

Table 3. Summary of Stability Test Results

Analyte	p-value for significance test for β_1		
	Short-term Room temperature	Short-term 40 ˚C	Long-term Room temperature
Hexavalent Chromium	0.2849	0.5052	0.9491

As all p-values are greater than 0.05, it was concluded that the β_1 values for all stability tests were not significantly deviated from zero at 95% confident level. Therefore, instability in the test material was not observed in 1-month time at either room temperature or 40 ˚C, and it was also stable throughout the comparison exercise at room temperature.

To monitor the temperature at which the test material could experience during transportation, a temperature recording strip was attached on each bottle of water sample. According to the sample receipt forms returned by the participants, only one bottle of the test material was exposed 40 ˚C during transport, and other bottles experienced temperature around 29 — 34 ˚C.

3.3 Instructions to Participants

Each participant was distributed one bottle of 50 g water sample and was requested to perform at least three independent measurements on three separate portions of the test material in order to determine the mass fraction of Cr(VI).

The participants could use any analytical methods of their choice. The water samples should be thorough mixed before use, and a sample portion of at least 5 g was suggested for each analysis.

To report the measurement results, the participants were requested to submit the mean value of three or more independent measurement data accompanying with the corresponding measurement uncertainty (combined standard uncertainty at 1 sigma level). The reported mass fraction unit was expected to be in µg/kg. The participants were requested to submit their results along with information on the sample preparation, analytical method, calculation of results, uncertainty estimation with a full measurement uncertainty budget (including all potential uncertainty components and their typical values) and sources and purity of reference materials and standards used for calibration.

4. Methods of Measurement

Majority of the participants used chromatographic techniques for the separation of Cr(VI), and the measurement techniques included UV-visible spectrophotometry, ICP-MS, isotope dilution ICP-MS and isotope dilution ICP-QQQ-MS. Analysis of the test material using UV-visible spectrophotometry without prior separation was also reported. The method summary is shown in Table 4.

Table 4. Summary of Analytical Techniques Applied by the Participants

Institute	Sample preparation	Chromatographic technique	Calibration method	Instrumental technique
NIM	Direct measurement	Ion chromatography with post-column derivatization with DPC	External calibration (bracketing)	Ion chromatography with UV-Vis detector
EXHM/ GCSL-EIM	5 g sample was buffered with 0.05 mL pH 9.5 buffer	Ion chromatography with post-column derivatization with DPC	Exact matching , confirmed by standard addition	UV-visible spectrophotometry
GLHK (1) (principle method)	2 g sample + 2 mL 35 mM EDTA buffer at pH 10.1 + 0.9 g ^{50}Cr spike + 5.1 mL Mili-Q water	Anion exchange chromatography	Isotope dilution using the ^{50}Cr/^{52}Cr pair	ICP-MS
GLHK (2) (secondary method)	1) 5.5 g sample + 25 mM EDTA at pH 7.1 2) buffered solution spiked with Cr(VI) soln	Anion exchange chromatography	Gravimetric standard addition	ICP-MS
CENAM	1,5-Diphenylcarbazide (DPC) addition; acidified with H_2SO_4	--	External calibration method with standard addition	UV-visible spectrophotometry
INRAP	1,5-Diphenylcarbazide (DPC) addition; acidified with H_2SO_4	--	External calibration	UV-visible spectrophotometry
TUBITAK UME	Dilution with mobile phase: 0.6 mM EDTA, 1 mM tetrabutyl ammonium hydroxide (TBAH), 2% methanol	Reversed phase HPLC	Standard addition	ICP-MS
LGC	0.11 g sample + 0.55 g ^{53}Cr spike solution in 2.8 mM TPABr, 4 mM EDTA at pH 8.5	Ion-pairing reversed phase HPLC	Isotope dilution using the ^{52}Cr/^{53}Cr pair	ICP-QQQ-MS

Note:

* It was agreed at the CCQM IAWG Meeting in November 2011 that when more than one value was provided by an NMI/DI, the value with the smallest uncertainty should normally be used for the calculation of KCRV. As such, the results submitted by GLHK(1) was the official result which was obtained using the principle method; and the results submitted by GLHK(2) was information value which was obtained by the secondary method and was not included in the calculation of KCRV.

5. Results and Discussion

5.1 General

A total of 52 measurement results were reported from 7 NMIs/DIs for CCQM K124 Part B, and the results were listed in Table 5 in ascending order.

Table 5. Reported Results on Hexavalent Chromium, Cr(VI)

Institute	Reported mass fraction (µg/kg)	Reported std. uncertainty (µg/kg)	Coverage factor, *k* (95% C.L.)	No. of replicate	Measurement technique
INRAP	60.062	0.781	2	5	UV-visible spectrophotometry
TUBITAK UME	61.5	1.4	2	6	HPLC-ICP-MS
CENAM	62.2	4.0	2	3	UV-visible spectrophotometry
EXHM/GC SL-EIM	62.67	1.36	2.13	15	IC- UV-visible spectrophotometry
GLHK (2)	62.7	1.5	2	3	IC-ICP-MS
LGC	62.88	0.45	2	11	Ion pairing-HPLC-ID-ICP-QQQ-MS
GLHK (1)	63.0	0.96	2	3	IC-ID-ICP-MS
NIM	63.16	0.18	2	6	Ion chromatography with UV-Vis detector

Note:

* It was agreed at the CCQM IAWG Meeting in November 2011 that when more than one value was provided by an NMI/DI, the value with the smallest uncertainty should normally be used for the calculation of KCRV. As such, the results submitted by GLHK(1) was the official result which was obtained using the principle method (IC-ID-ICP-MS); and the results submitted by GLHK(2) was information value which was obtained by the secondary method (IC-ICP-MS) and was not included in the calculation of KCRV.

5.2 Traceability of Calibrants used by Participants

Participants were required to provide the information about the traceability of the reference materials/calibrants they used in the comparison exercise. This information is summarised in Appendix AI.

5.3 Calculation of the Reference Mass Fraction Value and Associated Uncertainties

In this report, the calculated consensus values and their respective dispersions estimate using two different location estimators, arithmetic mean and median, were summarised in Table 6.

Table 6. Results of the Calculated Consensus Values and the Respective Dispersion (all data were included except GLHK(2); unit = µg/kg)

Measurand	Arithmetic mean	Standard deviation	Median	MAD_E*
Hexavalent Chromium	62.21	1.10	62.67	0.70

Note:

*MAD_E = median absolute deviation (MAD) × 1.483

As shown in Table 6, a good agreement between the consensus values of the arithmetic mean and the median was observed. However, it is noticed that with arithmetic mean as the location estimator the calculated consensus value would be more sensitive to suspected extreme values (for a consistency check using chi-squared test, see Appendix AII). It would be more appropriate to choose the median model for the estimation of KCRV, especially when the majority of the results are closely similar.

According to the CCQM Guidance Note [2], the *u*(KCRV) with the median approach can be calculated using equation (3) and the MAD_E; the KCRU can then be calculated by multiplying *u*(KCRV) by two. The KCRV and KCRU using the median approach were shown in Table 7.

$$u(\mathrm{KCRV}) = \mathrm{MAD_E} \times \sqrt{\frac{\pi}{2n}} \qquad (3)$$

where

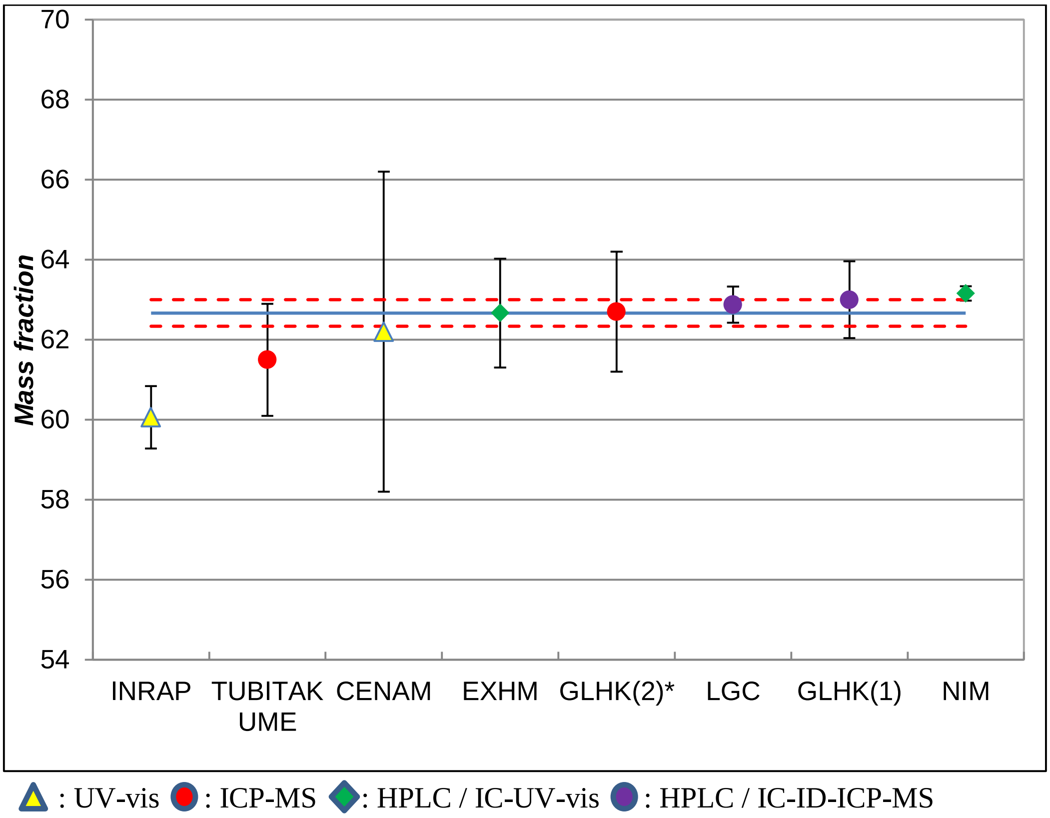
n is number of result submitted (in CCQM K124 Part B, n = 7)

Table 7. The Calculated KCRV and KCRU using the Median Approach

Measurand	KCRV (µg/kg)	*u*(KCRV) (µg/kg)	KCRU (µg/kg)	KCRU (%)
Hexavalent Chromium	62.67	0.329	0.658	1.1%

For a more convenient review, a graphical presentation of the KCRV, *u*(KCRV) and the participants' results for CCQM K124 Part B is given in Figure 1.

Figure 1. CCQM K124 Part B: Participants' Results and Measurement Uncertainties for Hexavalent Chromium (Cr(VI); unit = µg/kg)



Note:

The error bars represent the combined standard uncertainties for the individual participant's results. The horizontal solid blue line represents the KCRV based on the median of all participants' results, and the red dashed lines represent KCRV ± u(KCRV).

(It was agreed at the CCQM IAWG Meeting in November 2011 that when more than one value was provided by an NMI/DI, the value with the smallest uncertainty should normally be used for the calculation of KCRV. As such, the results submitted by GLHK(1) was the official result which was obtained using the principle method; and the results submitted by GLHK(2) was information value which was obtained by the secondary method and was not included in the calculation of KCRV.)

5.4 **Equivalence Statements**

The degree of equivalence and its uncertainty of a reported result by a participant compared to the KCRV were calculated using equations (4) to (6) as follows:

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

$$rel.d_i = \frac{(x_i - \mathrm{KCRV})}{\mathrm{KCRV}} \qquad (5)$$

$$\mathrm{U}(d_i) = \sqrt{(k_i)^2 u(x_i)^2 + (k_U)^2 u(\mathrm{KCRV})^2} \qquad (6)$$

where

x_i is the reported value from a participant (i = 1 to n)

d_i is the difference between the participant's reported value and the KCRV

U(d_i) is the expanded uncertainty of the d_i at a 95% confident level

k_i is the coverage factor given by the participant i

k_U is the coverage factor at a 95% confident level with a degree of freedom of 6 (n-1; n = 7)

$u(x_i)$ is the standard uncertainty given by the participant i

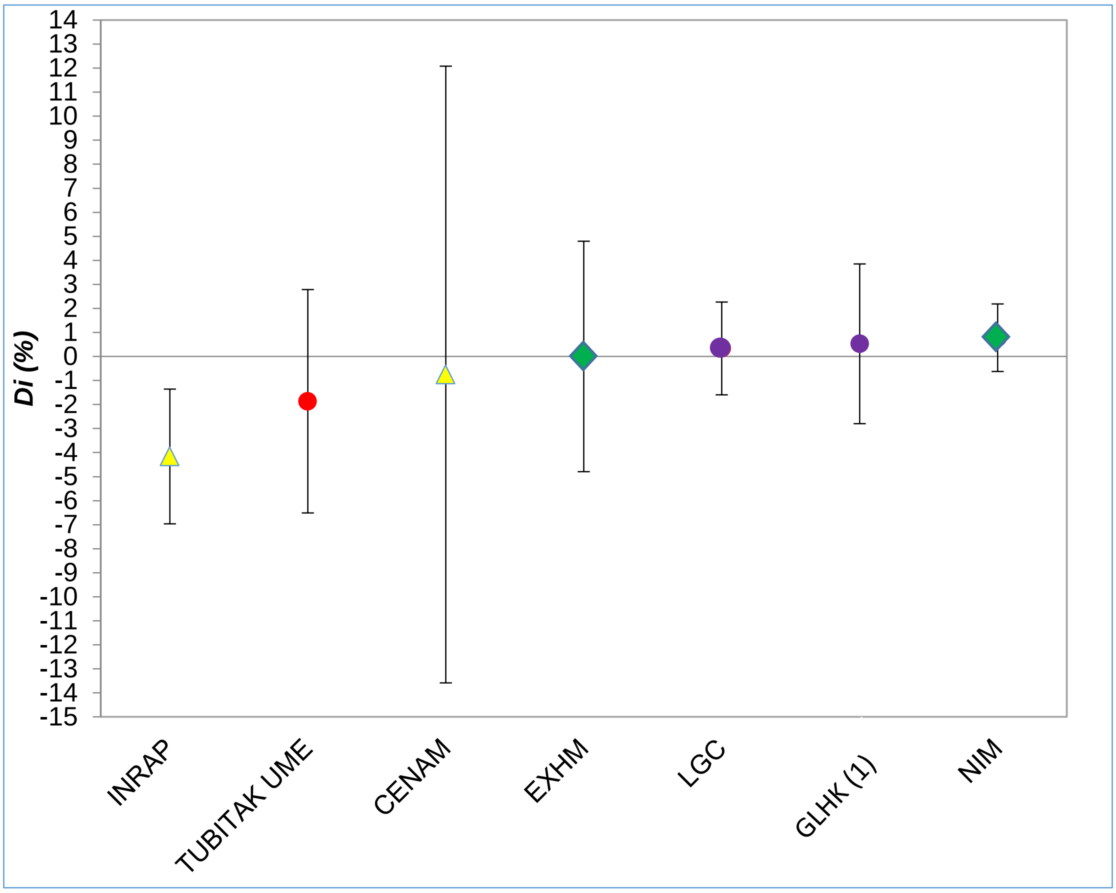
u(KCRV) is the standard uncertainty of the KCRV

The equivalence statements for CCQM K124 Part B based on the calculated KCRV with the median approach are listed in Table 8, and the graphical presentation is given in Figure 2.

Table 8. Equivalence Statements of Hexavalent Chromium for CCQM K124 Part B

Institute	Reported value, x_i, µg/kg	Reported std. uncertainty, $u(x_i)$, µg/kg	Difference from KCRV		U(d_i)	%U(d_i)	d_i/U(d_i)
			d_i	%d_i			
INRAP	60.062	0.781	-2.608	-4.16%	1.758	2.8	-1.48
TUBITAK UME	61.5	1.4	-1.170	-1.87%	2.914	4.6	-0.40
CENAM	62.2	4.0	-0.470	-0.75%	8.040	12.8	-0.06
EXHM/G CSL-EIM	62.27	1.36	0.000	0.00	3.007	4.8	0.00
LGC	62.88	0.45	0.210	0.34%	1.208	1.9	0.17
GLHK (1)	63.0	0.96	0.330	0.53%	2.082	3.3	0.16
NIM	63.16	0.18	0.490	0.78%	0.882	1.4	0.56

Figure 2. Equivalence Statements of Hexavalent Chromium for CCQM K124 Part B



△:UV-vis ●: LC-ICP-MS ◆: HPLC / IC-UV-vis ●: HPLC / IC-ID-ICP-MS

Note:

The error bars represent %U(d_i) for the individual participant's results. The data points represent the relative difference (%d_i) between the participants' reported value and the KCRV.

6. **Demonstration of Core Capabilities**

As agreed in previous CCQM IAWG meetings, a system of Core-Capabilities for inorganic analysis will be employed in key/supplementary comparisons starting from CCQM K75 onwards. 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 submitted their Inorganic Core Capabilities (CCs) Tables to the coordinator for compilation, and they are summarized in the Appendix AIII.

7. **Conclusions**

After the CCQM-IAWG meeting in London, November 2015, it was agreed that the KCRV in CCQM-K124 Part B should be calculated as the median of all reported results. With the median approach, a KCRV value of 62.67 μg/kg with a standard uncertainty u(KCRV) of 0.33 μg/kg for CCQM K124 Part B was calculated. In general, most participants' results on the mass fraction of hexavalent chromium in the test material were found to be consistent according to the equivalence statement.

In terms of methodology, five participants employed chromatographic techniques such as ion chromatography, reverse phase HPLC and ion pairing reverse phase HPLC to separate chromium species prior to the measurement of hexavalent chromium. Chromatography hyphenated ICP-MS, ID-ICP-MS and 1,5-diphenylcarbazide (DPC) derivatisation UV-visible spectrophotometry were employed as more common measurement techniques.

Acknowledgement

We would like to express the most sincere gratitude for the effort and supports from the contact persons and/or analysts of the participating NMIs/DIs.

Institute	Contact person and/or analysts
NIM	Jingbo Chao, Jun Wang
EXHM/GCSL-EIM	Elias Kakoulides
GLHK	Della Wai-Mei Sin, Alvin Wai-Hong Fung
CENAM	Judith Velina Lara Manzano, María del Rocio Arvizu-Torres, Edith Valle-Moya, Griselda Rivera-Sánchez, Francisco Segoviano-Regalado, Francisco Javier Matehuala-Sánchez, Itzel Santiago-Castellanos.
INRAP	Hanen Klich
TUBITAK UME	Süleyman Z. Can, Oktay Cankur, Betül Ari
LGC	Heidi Goenaga Infante

We would like to thank Dr. Mike Sargent for providing guidance throughout the course of this study.

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 6, 2010.

3. CIPM MRA Document: Traceability in CIPM MRA, Document No.: CIPM 2009-24, Latest update: Revised 13 October 2009.

4. D. Duewer: A Robust Approach for the Determination of CCQM Key Comparison Reference Values and Uncertainties.

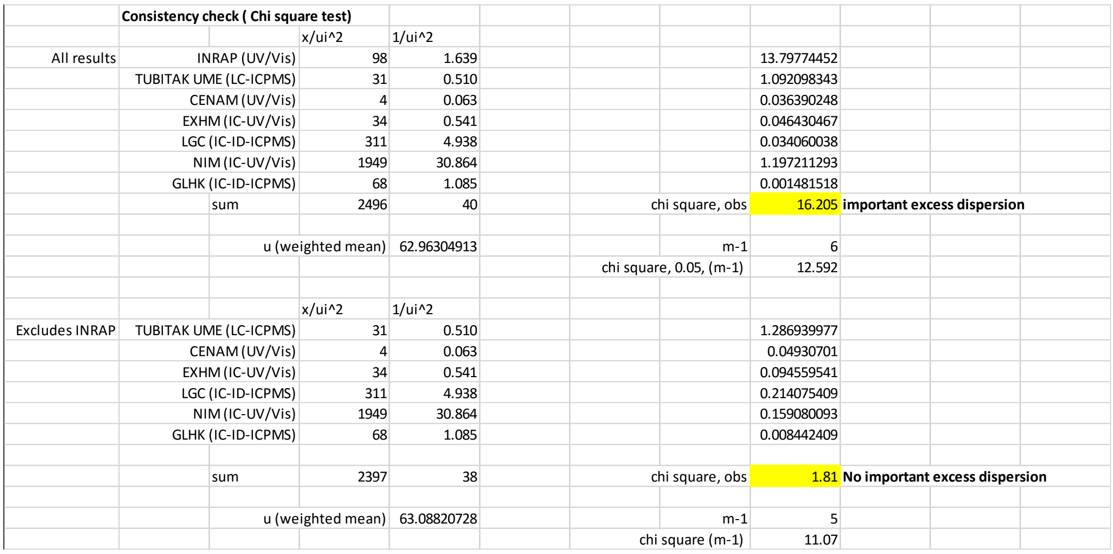
Appendix AI

Traceability of Calibrants/Reference Material used by Participants

Participant	Calibrants/Reference Material used	
	$K_2Cr_2O_7$ (s)	Isotope enriched standard
NIM	GBW 06105e	--
EXHM/GCSL-EIM	NIST SRM 136f	--
LGC	NIST SRM 136f	CK Gas Products (^{53}Cr metal oxide)
CENAM	SMU (batch: A0408209)	--
INRAP	NIST SRM 136f	--
TUBITAK UME	NIST SRM 136f	--
GLHK (1)	NIST SRM 136f	IRMM-624 (^{50}Cr in 1M HCl)
GLHK (2)	NIST SRM 136f	

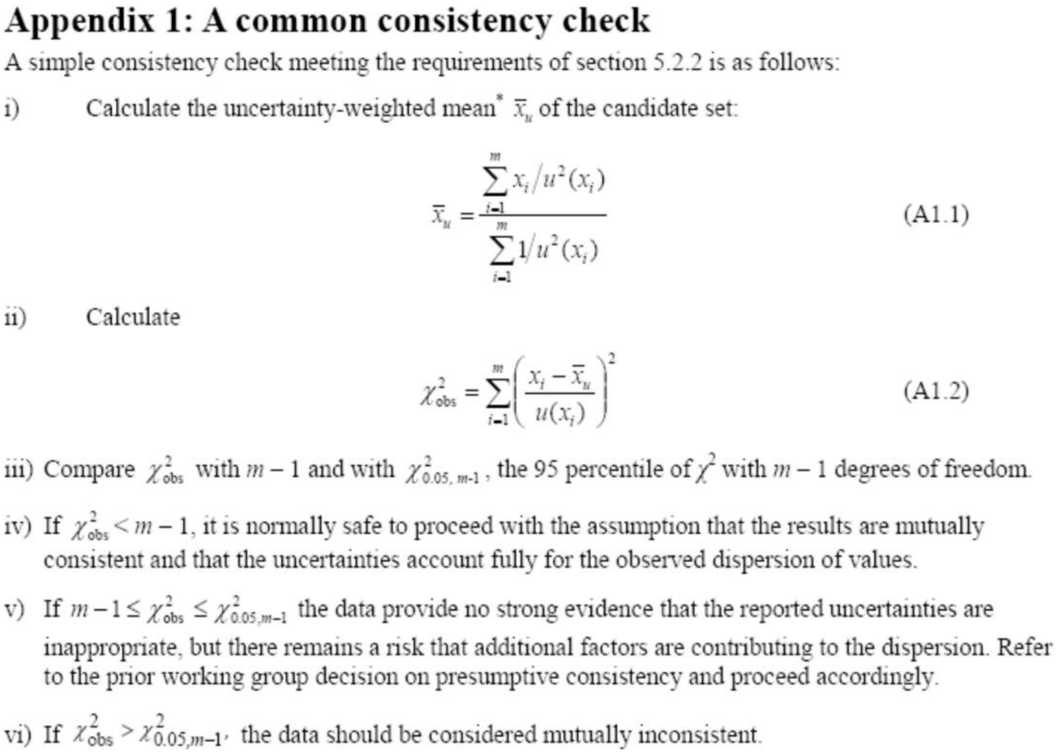
Appendix AII

Consistency Check (chi-squared test)



	Consistency check (Chi square test)					
		x/ui^2	1/ui^2			
All results	INRAP (UV/Vis)	98	1.639		13.79774452	
	TUBITAK UME (LC-ICPMS)	31	0.510		1.092098343	
	CENAM (UV/Vis)	4	0.063		0.036390248	
	EXHM (IC-UV/Vis)	34	0.541		0.046430467	
	LGC (IC-ID-ICPMS)	311	4.938		0.034060038	
	NIM (IC-UV/Vis)	1949	30.864		1.197211293	
	GLHK (IC-ID-ICPMS)	68	1.085		0.001481518	
	sum	2496	40	chi square, obs	16.205	**important excess dispersion**
	u (weighted mean)		62.96304913	m-1	6	
				chi square, 0.05, (m-1)	12.592	
		x/ui^2	1/ui^2			
Excludes INRAP	TUBITAK UME (LC-ICPMS)	31	0.510		1.286939977	
	CENAM (UV/Vis)	4	0.063		0.04930701	
	EXHM (IC-UV/Vis)	34	0.541		0.094559541	
	LGC (IC-ID-ICPMS)	311	4.938		0.214075409	
	NIM (IC-UV/Vis)	1949	30.864		0.159080093	
	GLHK (IC-ID-ICPMS)	68	1.085		0.008442409	
	sum	2397	38	chi square, obs	1.81	**No important excess dispersion**
	u (weighted mean)		63.08820728	m-1	5	
				chi square (m-1)	11.07	

The consistency check scheme was adopted from the CCQM Guidance Note [2]



Appendix 1: A common consistency check

A simple consistency check meeting the requirements of section 5.2.2 is as follows:

i) Calculate the uncertainty-weighted mean* $\overline{x}_u$ of the candidate set:

$$\overline{x}_u = \frac{\sum_{i=1}^{m} x_i / u^2(x_i)}{\sum_{i=1}^{m} 1 / u^2(x_i)} \qquad \text{(A1.1)}$$

ii) Calculate

$$\chi^2_{\text{obs}} = \sum_{i=1}^{m} \left(\frac{x_i - \overline{x}_u}{u(x_i)} \right)^2 \qquad \text{(A1.2)}$$

iii) Compare χ^2_{obs} with $m-1$ and with $\chi^2_{0.05,\,m-1}$, the 95 percentile of χ^2 with $m-1$ degrees of freedom.

iv) If $\chi^2_{\text{obs}} < m-1$, it is normally safe to proceed with the assumption that the results are mutually consistent and that the uncertainties account fully for the observed dispersion of values.

v) If $m-1 \le \chi^2_{\text{obs}} \le \chi^2_{0.05,m-1}$ the data provide no strong evidence that the reported uncertainties are inappropriate, but there remains a risk that additional factors are contributing to the dispersion. Refer to the prior working group decision on presumptive consistency and proceed accordingly.

vi) If $\chi^2_{\text{obs}} > \chi^2_{0.05,m-1}$, the data should be considered mutually inconsistent.

Appendix AIII

Inorganic Core Capabilities

Summary Tables

CCQM Study: K124 Part B Chromium Speciation in Drinking Water

Institute: LGC, GLHK (principle method)

Method: HPLC-ID-ICP-MS

Analyte(s): Hexavalent Chromium

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Extraction of species from the sample matrix *Single- or multi-steps procedures used to efficiently extract the analyte(s) of interest from the sample matrix with preservation of the analyte (s) integrity*		LGC GLHK	Stabilization of Cr (VI) at alkaline pH. was achieved. Alkaline pH was used to stabilise Cr(VI).
Species pre-concentration *Techniques and procedures used to increase the concentration of the species to be analysed by HPLC-ICP-IDMS. Includes solvent evaporation, freeze-drying, etc.*	LGC GLHK		
Achieving compatibility of LC conditions with ICP-MS *Selected chromatographic conditions (e.g mobile phase composition and flow rate) selected to be compatible with conventional nebulisation ICP-MS*		LGC GLHK	Mobile phase selected to contain a relatively low concentration of organic compounds to reduce Ar-C interference. LC system selected for low levels of Cr release into the eluent (background). LC system selected for low levels of Cr release into the eluent (background) and achieved stable background signal.
Selectivity of LC separation *Development of separation systems to separate the target species from other species of the same element and/or to minimise matrix interferences from other compounds that co-elute with the target species and may affect its detection by ICP-MS (e.g high C-compound interference on the detection of Se and As species)*		LGC GLHK	Cr (III) acetylacetonate was irreversibly absorbed in the column and therefore was separated from Cr (VI). Cr (VI) was chromatographically retained on the column and separated from Cr (III) and interferences potentially present in the void volume. Cr (III) and Cr (VI) are well separated by adjusting the LC program and choosing suitable LC column.
Spike equilibration with sample The mixing and equilibration of the enriched isotopic spike with the sample		LGC GLHK	Mixing was achieved by vortex followed by heating at 85°C for one hour to allow isotopic equilibration. Blends were vortexed for one hour to allow isotopic equilibration.

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Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Characterisation of the natural species standard, including purity *All techniques used to know the exact concentration of the natural species standard used as a calibrant*		LGC GLHK	Use of certified reference material with additional checks on the species purity in solution and total Cr by IDMS. Use of certified reference material with additional checks on the species purity in solution.
Transient isotope ratio precision *Any techniques used for improved isotope ratio precision in transient signal analysis (e.g. adequate peak area integration, isotope integration time/number of points per peak, signal intensity, etc).*		LGC GLHK	Dilution performed to reduce signal intensity and peak tailing. Timed end point to peak integration for 52Cr (VI) and 53Cr (VI) peaks. Triplicate injections of each sample blend bracketed by the calibration blend Peak shapes are optimized for ^{52}Cr (VI) and ^{50}Cr (VI) peaks by adjusting the LC program. Sample blend and calibration blend were injected 4 times for obtaining accurate signal ratio.
Control of procedural blank All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for species that are environmentally ubiquitous and also present at very low concentrations in the sample.		LGC GLHK	Plastic-ware was cleaned before use by soaking in acid. The sample diluent was tested for Cr (VI) content prior to use and found to be below LOD; no blank correction was applied. Containers and sample diluent was tested for Cr (VI) content prior to use and found to be below LOD; no blank correction was applied.

Appendix AIII

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.*		LGC GLHK	HPLC needle rinse performed between injections. Needle rinse between injections.
Correction or removal of isobaric/polyatomic interferences *Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species , which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.*		LGC GLHK	The combined use of collision/reaction cell with helium and ammonia gasses effectively removes Ar-C, Cl-O and other potential interferences. Use of collision/reaction cell with helium effectively minimized the polyatomic interferences. Procedural blank indicated no peak observed in the retention time of Cr (VI).
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	LGC GLHK		Not applicable as double isotope dilution applied Double isotope dilution applied.
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	LGC GLHK		Not applicable as double IDMS was used. Sample and calibration blends intensity were closely matched and the detector dead time effect cancels. Double IDMS was used. Sample and calibration blends intensity were close and the dead time effect only causes negligible bias.
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*	GLHK	LGC	Reverse IDMS and ICP-OES measurements evaluated. Not applicable as double isotope dilution was applied.

Appendix AIII

CCQM Study: K124 Part B Chromium Speciation in Drinking Water

Institute: TUBITAK_UME, GLHK(secondary method)

Method: HPLC-ICP-MS

Analyte(s): Hexavalent Chromium

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Extraction of species from the sample matrix *Single- or multi-steps procedures used to efficiently extract the analyte(s) of interest from the sample matrix with preservation of the analyte (s) integrity*	TUBITAK	GLHK	Stabilization of Cr (VI) at neutral pH was achieved.
Species pre-concentration *Techniques and procedures used to increase the concentration of the species to be analysed by HPLC-ICP-MS. Includes solvent evaporation, freeze-drying, etc.*	TUBITAK GLHK		
Achieving compatibility of LC conditions with ICP-MS *Selected chromatographic conditions (e.g mobile phase composition and flow rate) selected to be compatible with conventional nebulisation ICP-MS*	TUBITAK	GLHK	LC system selected for low levels of Cr release into the eluent (background) and achieved stable background signal.
Selectivity of LC separation *Development of separation systems to separate the target species from other species of the same element and/or to minimise matrix interferences from other compounds that co-elute with the target species and may affect its detection by ICP-MS (e.g high C-compound interference on the detection of Se and As species)*		TUBITAK GLHK	The composition and flow rate of the mobile phase was optimized to provide optimum chromatographic separation and reasonable background signal. Cr (III) and Cr (VI) are well separated by adjusting the LC program and choosing suitable LC column.
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		TUBITAK GLHK	Method of matrix matching standard additions was applied. Gravimetric standard addition technique was applied
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.*		TUBITAK GLHK	In order to monitor ^{52}Cr reaction/collision cell was used with H_2 as reaction gas during the ICP MS detection. Use of collision/reaction cell with helium effectively minimized the polyatomic interferences.

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.*		TUBITAK GLHK	The blank solutions were used to check memory effect and no memory effect was observed between runs. HPLC needle rinse performed between injections.
Control of procedural blank *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for species that are environmentally ubiquitous and also present at very low concentrations in the sample.*		TUBITAK GLHK	No significant contribution from reagents and the labware was observed Plastic-ware and sample diluent was tested for Cr (VI) content prior to use and found to be below LOD; no blank correction was applied.
Correction or removal of isobaric/polyatomic interferences *Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species , which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.*		TUBITAK GLHK	Reaction gas H_2 was employed during the measurements. This reduced the background signal on ^{52}Cr to reasonable level. Use of collision/reaction cell with helium effectively minimized the polyatomic interferences. Procedural blank indicated no peak observed in the retention time of Cr (VI).
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	TUBITAK GLHK		
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.*		TUBITAK GLHK	Matrix matching standard addition method was used to minimize the matrix induced suppression or enhancement. Standard addition was used to minimise the matrix effect
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	TUBITAK GLHK		

Appendix AIII

CCQM Study: K124 Part B Chromium Speciation in Drinking Water

Institute: NIM, EXHM/GCSL-EIM

Method: IC-UV-VIS

Analyte(s): Hexavalent chromium

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Extraction of species from the sample matrix *Single- or multi-steps procedures used to efficiently extract the analyte(s) of interest from the sample matrix with preservation of the analyte (s) integrity*	EXHM NIM		The Cr (VI) determined by IC with UV detector after post column derivatization with DPC.
Species pre-concentration *Techniques and procedures used to increase the concentration of the species to be analysed by HPLC-UV-VIS. Includes solvent evaporation, freeze-drying, etc.*	NIM EXHM		
Selectivity of LC separation *Development of separation systems to separate the target species from other species of the same element and/or to minimise matrix interferences from other compounds that co-elute with the target species and may affect its detection by UV-VIS*		NIM EXHM	Cr(III) separated from Cr(VI) withion chromatography on Thermo IonPac AS7
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.*	EXHM	NIM	
Matrix and interfering species separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix and other interfering species to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures.*	NIM	EXHM	the IC separation and the post-column derivatization lead to isolation from any possible interference
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.*		NIM EXHM	Used $K_2Cr_2O_7$ purity CRM as standard. One-point calibration and bracketing method used to calibrate the instrument. matrix-matched calibration exact matching confirmed by standard addition
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 absorptivity. Requires selection of operating conditions such as light source, wavelength, post-column derivatization, background correction conditions.*		NIM EXHM	post-column derivatization with 1,5-diphenylcarbazide signal measured at 530 nm
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	NIM EXHM		

CCQM Study: K124 Part B Chromium Speciation in Drinking Water

Institute: CENAM, INRAP

Method: UV-VIS Spectrophotometry

Analyte(s): Hexavalent chromium

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.*		INRAP CENAM	Blank samples were prepared using double sub-boiling distilled water and all reagents involved in the sample preparation.
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 UV-VIS.*	INRAP		
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 UV-VIS.*	INRAP		
Pre-concentration *Techniques and procedures used to increase the concentration of the analyte introduced to the UV-VIS. Includes evaporation, ion-exchange, extraction, precipitation procedures.*	INRAP		
Matrix and interfering species separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix and other interfering species to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures.*	INRAP		
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.*		INRAP CENAM	External calibration with matrix-matched standards (to minimize the effect of Mo as significant interference founded in the sample). In addition, it was applied Standard addition to check the recovery. Using the technique of UV-Vis for measuring Cr (VI) at low levels in water is an analytical challenge. However, the analytical calibration was made almost at the limit of quantification, with sacrifice of uncertainty.
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 absorptivity. Requires selection of operating conditions such as light source, wavelength, derivatization, background correction conditions.*	INRAP	CENAM	The hexavalent chromium reaction with 1,5-diphenylcarbazide gives stable complex in acid solution.

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	INRAP	CENAM	Before the lecture on each sample, it is necessary to rinse several times the cell using double sub-boiling distilled water and then with the sample. Therefore, it is necessary to have enough sample to properly rinse and avoid the memory effect, which affect at low levels of Cr (VI).
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.*		CENAM	External calibration with matrix-matched standards to minimize any effect from interferences as Mo, which was founded as significant interference in the sample. Also, it was applied Standard addition in order to evaluate the recovery.

CCQM-K124 Protocol

CCQM-K124 & P158

Key comparison & pilot study on “Trace elements and chromium speciation in drinking water”

Call for participants and technical protocol

(July 3, 2014)

1. Introduction

Quality standards for drinking water, like WHO (World Health Organization) Guidelines, have been established in nations and regions around the world. Also, levels of many elements in drinking water are regulated for safety and health concerns.
In the IAWG’s five-year plan, a comparison under the category of water analysis was recommended for the year 2014 and IAWG members were encouraged to attempt as the comparison would involve some basic and important analytical techniques. In this connection, NMIJ and GLHK proposed to coordinate this key comparison and an associated pilot study, CCQM-K124 and CCQM-P158 respectively, for participating NMIs and DIs to demonstrate their analytical capabilities in determination of elements and chromium species in water by various analytical techniques so as to facilitate their claim on the Calibration and Measurement Capabilities (CMC).

This study will investigate the core capabilities of participants to measure the contents of tested elements and chromium species in drinking water. Each participant could use the results of this study as evidence(s) not only for their CMC claims for elements and chromium species in drinking water but also their related CMC claims for them in similar matrices (groundwater and river water etc.) and/or others through a Core Capability Table.

Basically, the analytes to be measured were chosen with reference to existing guidelines or regulatory standards. Also, reference would be made to the analytical techniques to be involved. For the light elements, boron (B) is selected as there was no previous comparison on the determination of this element before. For the alkaline earth metals, calcium (Ca) is selected as the ICP-MS measurement involved would be challenging for participants. Chromium (Cr) is difficult to be measured by ICP-MS since the spectral interference of molecular ions resulting from argon occurs. Arsenic (As) is a mono-isotopic element, so isotope dilution mass spectrometry (IDMS) is not applicable. Molybdenum (Mo) is one of essential trace elements but no study for the measurement of molybdenum in water has been undertaken. Cadmium (Cd) is a representative of elements which can be measured by applying IDMS. Mercury (Hg) is a highly toxic element and its property on volatility would cast problem on the determination due to memory effect.

Chromium exhibits a wide range of possible oxidation states. Elemental metal, trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] are the most commonly observed chromium species in environment. Chromium in water supplies can be either from naturally occurring sources or as the result of industrial activities. Because of the widespread use of Cr in many industrial activities, industrial wastes and effluents become the dominant source of Cr releasing to surface water and groundwater.

WHO has established a guideline value of 0.05 μg/L for total Cr in drinking water. Many governments and safety regulatory agencies have also set maximum allowable limit for total Cr in drinking water to ensure safe consumption. However, toxicity as well as mobility and bioavailability are largely different for different Cr species. Trivalent chromium is an essential micronutrient which plays a vital role in releasing energy from fats and sugars. Hexavalent chromium, in contrast, is highly toxic and has known to be a carcinogen. Therefore, a thorough study on Cr species in drinking water is crucial for evaluating potential hazards and safeguarding the public health.

2. Coordinating laboratory

The CCQM-K124 & P158 are coordinated by NMIJ and GLHK. NMIJ takes responsibility for the part A: Trace elements in drinking water, and GLHK takes responsibility for the part B: Chromium speciation in drinking water.

3. Test material

Part A: Trace elements in drinking water

The test material is a candidate material for a tap water certified reference material (CRM). The tap water was collected by NMIJ (Tsukuba, Ibaraki, Japan) and filtered (pore size: 0.45 µm). Standard solutions (As, Cd, Cr, Hg, Mn and Se) were spiked to the test material at appropriate concentrations, and nitric acid and hydrochloric acid were added so that those final concentrations were adjusted to about 0.1 mol/L and 0.03 mol/L, respectively. The 150 L test material was stirred using a magnetic stirrer for homogenization in a 200-L polypropylene tank. After homogenization, the water sample was filtered (pore size: 0.20 µm) and subdivided in polyethylene bottles (125 mL) by 100 mL each.

The measurands to be determined are the mass fractions of B, Ca, Cr, As, Mo, Cd and Hg. Those nominal values are 20 µg/kg to 100 µg/kg level of B, 1 mg/kg to 10 mg/kg level of Ca, 2 µg/kg to 20 µg/kg level of Cr, 2 µg/kg to 15 µg/kg level of As, 0.5 µg/kg to 5 µg/kg level of Mo, 0.5 µg/kg to 4 µg/kg level of Cd and 0.1 µg/kg to 1 µg/kg level of Hg.

The homogeneity of the material was investigated by analyzing 10 bottles selected from 700 bottles. The data were treated with ANOVA. The relative standard uncertainties due to between-bottle inhomogeneity for B, Ca, Cr, As, Mo, Cd and Hg were found to be 0.45 %, 0.43 %, 0.33 %, 0.28 %, 0.29 %, 0.19 %, and 0.62 %, respectively.

Part B: Chromium speciation in drink water

About 4 L of drinking water was purchased from local market. The drinking water was tested free of incurred chromium species [Cr(III) and Cr(VI)] using an ion-chromatography inductively coupled plasma mass spectrometry (IC-ICP-MS) method with detection limit of 0.1 µg/kg for both Cr(III) and Cr(VI). A standard solution of Cr (III) was gravimetrically prepared from chromium(III) acetylacetonate [$Cr(C_5H_7O_2)_3$] which is a stable complex [1] and can be synthesized according to published procedures [2]. A standard solution of Cr (VI) was gravimetrically prepared from a CRM of potassium dichromate (NIST SRM 136f). A standard solution of potassium peroxodisulfate for preservation was also gravimetrically prepared. Having confirmed that the drinking water was free from incurred Cr species by IC-ICP-MS, Cr(III) and Cr(VI) and potassium peroxodisulfate were gravimetrically taken from the respective standard solutions and added into the drinking water. In order to preserve the test material of chromium-spiked drinking water, potassium peroxodisulfate was deliberately added to the test material. The chromium-spiked drinking water was thoroughly homogenized in a 3-dimensional mixer for 30 minutes. The homogenized water sample was packed into pre-cleaned high-density polyethylene bottles, each of 50 g. Totally 80 sample bottles of water were prepared. All sample bottles of water were vacuum-sealed inside aluminium-coated bags and are stored at room temperature (20 ± 5 °C) inside a Class 1000 clean room prior to distribution or use.

The expected mass fraction of Cr(VI) is in the range of 10 µg/kg to 1000 µg/kg as determined by IC-ICP-MS. The homogeneity study was conducted by analyzing 10 randomly selected bottles from the whole lot of bottles prepared. The data were treated with ANOVA. The relative standard uncertainty due to between-bottle inhomogeneity was found to be 1.28 %. Also, the short-term stability was conducted. No instability was observed for the test material at 20 °C and 40 °C during the 4-week study period. The long-term stability of the test material at room temperature (20 ± 5 °C) will be continued until the deadline for submission of results.

4. Measurands

Part A: Trace elements in drinking water

Each participant will receive **TWO** sample bottles containing approximately **100 mL** of the tap water. Participants are required to acknowledge the receipt of the sample, and send the return receipt to NMIJ by e-mail. If there is any damage on the sample, NMIJ will send a substitute sample on request. A receipt form will be distributed to the participants. The sample after receiving should be kept at the laboratory temperature (15 °C to 25 °C). The seven analytes and their expected mass fractions are listed in Table 1.

Table 1

Analyte	Expected mass fraction
Boron	20 µg/kg to 100 µg/kg
Calcium	1 µg/kg to 10 mg/kg
Chromium	2 µg/kg to 20 µg/kg
Arsenic	2 µg/kg to 15 µg/kg
Molybdenum	0.5 µg/kg to 5 µg/kg
Cadmium	0.5 µg/kg to 4 µg/kg

Mercury	0.1 µg/kg to 1 µg/kg

Part B: Chromium speciation in drinking water

Participating laboratories will be provided with **ONE** sample bottle containing about **50 g** of water. The expected mass fraction of Cr(VI) is in the range of 10 µg/kg to 1000 µg/kg. Participants are requested to acknowledge the receipt of the sample (E-mail: whfung@govtlab.gov.hk). Please report any problems with leaking or damaged bottles immediately so that they can be replaced as fast as possible.

5. Methods/procedures

Part A: Trace elements in drinking water

NMIs or officially designated institutes are welcome to participate in this comparison and participants can use any method(s) of measurement deemed appropriate. Four measurements for each measurand are to be carried out by each participant. Calibrations of analytical instruments should be carried out using standards with metrological traceability.

Each reference value will be probably the median of the submitted data from NMIs and officially designated institutes depending on the decision of the IAWG. If any participant submitted individual results by multiple methods, their best result (*i.e.*, with the smallest uncertainty) will be chosen for the calculation of the reference value.

Part B: Chromium speciation in drinking water

Participants should use any analytical methods of their choice. The sample should be mixed thoroughly before processing and the analysis should be conducted with a recommended sample size of at least 5 g. The participants are requested to perform at least three independent measurements on three separate portions of the sample and to determine the mass fraction of Cr(VI). If any participant submitted individual results by multiple methods, their best result (*i.e.*, with the smallest uncertainty) will be chosen to calculate the reference value.

6. Reporting and submission of results

Part A: Trace elements in drinking water

The result should be reported as the mass fraction of each measurand to NMIJ, accompanied by a full uncertainty budget. Any participant that chooses to use multiple methods can decide only one composite result (*e.g.*, an average value from different methods) or individual results from different methods as the reporting value(s) for each measurand. Reporting the details of the procedure (including details of sample treatment/digestion etc.), the calibration standard and the traceability link, and the instrument(s) used is required. The result should be submitted using the attached Report Form for part A: trace elements in drinking water.

Furthermore, all participants in CCQM-K124 are required to complete a Core Capability Table for the measurement technique which they use. Please choose and download a suitable Core Capability Table from the IAWG website and the filled-out table should be submitted together with the measurement result; if there is no suitable table, please make a suitable one depending on the measurement method.

Please complete and submit the attached Report Form for Part A and the Core Capability Table to NMIJ (E-mail: t-kuroiwa@aist.go.jp) by e-mail before the scheduled deadline.

Part B: Chromium speciation in drinking water

- The mean value of at least 3 independent measurements and its associated measurement uncertainty should be reported;
- Report the mass fraction of Cr(VI) in µg/kg;
- Participants should provide (i) description of analytical methods and (ii) detail of the uncertainty estimation (including complete specification of the measurement equations and description of all uncertainty sources and their typical values); and
- Sources and purity of reference materials used for calibration purposes.

Both the Inorganic Core Capabilities table (please choose and download a suitable Core Capability Table from the IAWG website) and the attached Report Form for Part B should be submitted to GLHK (E-mail: whfung@govtlab.gov.hk) before the scheduled deadline.

7. Program schedule

31 July 2014	Deadline for registration
September 2014	Distribution of samples
28 February 2015	Deadline for submission of results
April 2015	Presentation of results at the CCQM IAWG Meeting

8. Participants

Participation is open to all interested NMIs or officially designated institutes that can perform the determination. An NMI or an officially designated institute is recommended to participate in the key comparison rather than in the pilot study as far as possible. Under the rule of CCQM, an NMI or an officially designated institute may nominate other institutes or laboratories to participate in the pilot study. The qualification for a guest laboratory (neither NMIs nor DIs) to participate in a pilot study was recently decided: the new approval procedure is necessary.

All guest laboratories should follow the new approval procedure. They must complete the new request form in order to obtain approval from the CCQM president. In particular, the guest laboratory must state the value added by the guest participation. (See the request form: http://www.bipm.org/utils/en/pdf/guest_laboratories_request_form.pdf)

We would like to ask NMIs or officially designated institutes to coordinate participation within their economies including inviting participants in the pilot study, shipping samples, and receiving the reports.

9. Registration

Please complete and return the attached registration forms to **NMIJ (E-mail: t-kuroiwa@aist.go.jp) for the participation of Part A: Trace elements in drinking water**, and to **GLHK (E-mail: whfung@govtlab.gov.hk) for the participation of Part B: Chromium speciation in drinking water**. Successful registration will be notified by e-mail. Please register no later than **31 July 2014**.

10. Confidentiality

The participating laboratories will receive the reports giving all results for assessment/comments. They will be identified in the reports. The key comparison and pilot study are conducted in the belief that participants will perform the analysis and report results with scientific rigor. Collusion between participants or falsification of results is clearly against the spirit of this study.

11. Contact

For enquiries, participants may wish to contact the coordinating laboratories as follows:

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12. References

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2. W. C. Fernelius and J. E. Blanch, *Inorganic Syntheses*, 1957, *5*, 130-131.