Final Report of the SIM.QM-S7 Supplementary Comparison

Trace Metals in Drinking Water

Oct. 03, 2017

Authors:

Lu Yang (NRC)[1], Kenny Nadeau (NRC)[1], Indu Gedara Pihillagawa (NRC)[1], Juris Meija (NRC)[1], Patricia Grinberg (NRC)[1], Zoltan Mester (NRC)[1], Edith Valle Moya (CENAM)[2], Faviola Alejandra Solís González (CENAM)[2], María del Rocio Arvizu Torres (CENAM)[2], Oscar Yañez Muñoz (CENAM)[2], Judith Velina Lara-Manzano (CENAM)[2], Gisela Mazzitello (INTI)[3], Pedro Prina (INTI)[3], Osvaldo Acosta (INTI)[3], Romina Napoli (LATU)[4], Ramiro Pérez Zambra (LATU)[4], Elizabeth Ferreira (LATU)[4], Vladimir Dobrovolskiy (VNIIFTRI)[5], Aleksei Aprelev (VNIIFTRI)[5], Aleksei Stakheev (VNIIFTRI)[5], Dmitriy Frolov (VNIIFTRI)[5], Leonid Gusev (VNIIFTRI)[5], Veronika Ivanova (BIM)[6], Teemu Näykki (SYKE)[7], Timo Sara-Aho (SYKE)[7], Jimmy Venegas Padilla (LACOMET)[8], Carlos Acuña Cubillo (LACOMET)[8], Dwyte Bremmer (BSJ)[9], Ruel Freemantle (BSJ)[9], Sutthinun Taebunpakul (NIMT)[10], Nongluck Tangpaisarnkul (NIMT)[10], Patumporn Rodruangthum (NIMT)[10], Nattikarn Kaewkhomdee (NIMT)[10], Usana Thiengmanee (NIMT)[10], Tararat Tangjit (NIMT)[10], Mirella Buzoianu (NIMR)[11], Diego Alejandro Ahumada Forigua (NMIC)[12], Johanna Paola Abella Gamba (NMIC)[12], Luis Alfredo Chavarro Medina (NMIC)[12], Egor Sobina (UNIIM)[14], Tatyana Tabatchikova (UNIIM)[14], Charalambos Alexopoulos (GCSL)[15], Elias Kakoulides (GCSL)[15], Mabel Delgado (IBMETRO)[16], Liliana Flores (IBMETRO)[16], Saira Knox (TTBS)[17], Kester Siewlal (TTBS)[17] and Avinash Maharaj (TTBS)[17]

[1] National Research Council Canada, Canada
[2] Centro Nacional de Metrologia, Mexico
[3] Instituto Nacional de Tecnologia Industrial, Argentina
[4] Laboratorio Tecnológico del Uruguay, Uruguay
[5] Russian Metrological Institute of Technical Physics and Radio, Russia
[6] Bulgarian Metrology Institute, Bulgaria
[7] Finnish Environment Institute, Finland
[8] Laboratorio Costarricense de Metrología, Costa Rica
[9] The Bureau of Standards Jamaica, Jamaica
[10] National Institute of Metrology Thailand, Thailand
[11] National Institute of Metrology, Romania
[12] National Metrology Institute of Colombia, Colombia
[14] Ural Scientific Research Institute for Metrology, Russia
[15] General State Chemical Laboratory, Greece
[16] Instituto Boliviano de Metrología, Bolivia
[17] Trinidad and Tobago Bureau of Standards, Trinidad

Coordinated by:

Lu Yang (NRC): Lu.yang@nrc-cnrc.gc.ca
Patricia Grinberg (NRC)
Zoltan Mester (NRC)
Maria del Rocio Arvizu Torres (CENAM)
J. Velina Lara Manzano (CENAM)

Abstract

SIM.QM-S7 was performed to assess the analytical capabilities of National Metrology Institutes (NMIs) and Designated Institutes (DIs) of SIM members (or other regions) for the accurate determination of trace metals in drinking water. The study was proposed by the coordinating laboratories National Research Council Canada (NRC) and Centro Nacional de Metrologia (CENAM) as an activity of Inorganic Analysis Working Group (IAWG) of *Consultative Committee for Amount of Substance – Metrology in Chemistry and Biology* (CCQM). Participants included 16 NMIs/DIs from 15 countries. No measurement method was prescribed by the coordinating laboratories. Therefore, NMIs used measurement methods of their choice. However, the majority of NMIs/DIs used ICP-MS.

This SIM.QM-S7 Supplementary Comparison provides NMIs/DIs with the needed evidence for CMC claims for trace elements in fresh waters and similar matrices.

1. Introduction and background

The determination of trace metals in drinking water is an important and commonly performed analysis. There is no single approach that is universally applicable, as the nature and regulations for drinking water standards may vary among countries and regions. An earlier Key comparison of CCQM-K124 in this area was conducted under the auspices of the CIPM in 2014 and quite a few SIM members did not participate in this comparison. In October 2015, the IAWG approved the SIM.QM-S7 Supplementary Comparison (no link to CCQM-K124), which provides NMIs/DIs with the needed evidence for CMC claims for trace elements in fresh waters and similar matrices.

Table 1. Timetable of SIM.QM-S7

Oct. 2015	Proposal agreed by IAWG
April 2016	Further discussion and update
Nov. 2015 to Feb. 2016	Homogeneity study
April 2016	Call for participating
April 19, 2016	Registration deadline
May 02, 2016	Shipment of the samples
Aug. 31, 2016	Deadline for receipt of data
Sept. 25, 2016	Circulation of preliminary results
Oct. 04 2016	Preliminary results presentation at CCQM IAWG
Dec. 31, 2016	Draft A
Mar. 31, 2017	Draft B circulation
April, 2017	CCQM IAWG meeting approval of report
May 15, 2017	Draft B Final report

Although this is organized as a SIM regional comparison, it is open to other participants of the MRA throughout all RMOs. The drinking water used in this exercise was collected in Ottawa, filtered and acidified to pH 1.6 to provide stability. Thus analyte mass fractions are representing their natural levels, and four analytes were selected for this comparison. Participants may use any method of their choice. Table 1 summarizes the timetable of the SIM.QM-S7 Supplementary Comparison.

Table 2. Measurands

Analyte	Target Concentration
Cu	1 - 30 µg/kg
Sr	1 - 100 µg/kg
Pb	0.1 – 30 µg/kg
Na	0.5 – 25 mg/kg

2. Participants

Seventeen NMIs/DIs have registered for the SIM.QM-S7 Supplementary Comparison and sixteen NMIs/DIs from fifteen countries reported their results, as shown in Table 3.

Table 3. SIM.QM-S7: List of participating institutes

Lab Number	Institute	Country	Results reposted	Reposting date
01	INTI	Argentina	Cu, Pb, Na	Aug. 30, 2016
02	LATU	Uruguay	Cu, Pb, Na	Aug. 30, 2016
03	VNIIFTRI	Russia	Cu, Sr, Pb, Na	Aug. 30, 2016
04	BIM	Bulgaria	Cu, Pb	Aug. 25, 2016
05	SYKE	Finland	Pb	Aug. 25, 2016
06	LACOMET	Costa Rica	Pb, Na	Aug. 31, 2016
08	BSJ	Jamaica	Cu, Sr, Pb, Na	Aug. 31, 2016
10	NIMT	Thailand	Cu, Sr, Pb, Na	Aug. 31, 2016
11	INM	Romania	Cu, Sr, Pb, Na	Aug. 30, 2016
12	NMIC	Colombia	Cu, Pb, Na	Aug. 31, 2016
13	OIAT-INTN	Paraguay	No data	Not reporting
14	UNIIM	Russia	Cu, Sr, Pb, Na	Aug. 04, 2016
15	EXHM/GCSL	Greece	Cu, Sr, Pb, Na	Aug. 31, 2016
16	IBMETRO	Bolivia	Cu, Pb, Na	Aug. 31, 2016
17	TTBS	Trinidad	Cu, Na	Aug. 31, 2016
07 (Pilot lab)	CENAM	Mexico	Cu, Sr, Pb, Na	Aug. 31, 2016
09 (Pilot lab)	NRC	Canada	Cu, Sr, Pb, Na	Aug. 24, 2016

3. Results and Discussion

As documented in the technical protocol of SIM.QM-S7, the Supplementary Comparison Reference Value (SCRV) was originally proposed to be derived from NRC and CENAM results only. However, at the IAWG Oct. 4-6, 2016 meeting in Korea, it was suggested to use more data from participating NMIs to calculate the SCRVs. Based on this suggestion, the pilot labs (NRC and CENAM) have decided to consider all results from participants for the calculation of SCRVs, in alignment with previous CCQM-KCs. Tables 4-8 summarize results reported by participants for Cu, Sr, Pb and Na, respectively.

Table 4. SIM.QM-S7: Reported results for mass fraction of Cu

Institute	Country	Reported value µg/kg	$u(w_{\mathrm{cu}})$ µg/kg	$U(w_{\mathrm{Cu}})$ µg/kg	Method
TTBS	Trinidad	1.48*	0.05	0.10	FAAS
NMIC	Colombia	6.90*	0.08	0.16	EC ICPMS
BSJ	Jamaica	7.28	0.26	0.52	EC ICPMS
INTI	Argentina	7.34	0.14	0.28	EC ICPMS
CENAM	Mexico	7.38	0.10	0.19	ID ICP-SFMS
NRC	Canada	7.46	0.06	0.12	ID ICP-SFMS+ICPOES
LATU	Uruguay	7.539	0.038	0.077	ID ICP-SFMS
UNIIM	Russia	7.583	0.25	0.49	ID ICPMS
NIMT	Thailand	7.64	0.06	0.12	ID ICPMS
VNIIFTRI	Russia	7.77	0.38	0.76	SA ICPMS
EXHM/GCSL	Greece	7.80	0.10	0.21	ID HR-ICPMS
INM	Romania	8.06	0.30	0.60	SA+IS ICPMS
IBMETRO	Bolivia	10.07*	0.50	1.00	GFAAS
BIM	Bulgaria	11.30*	0.20	0.40	SA ICPMS

* Results are not included in the final calculation of SCRV

Table 5. SIM.QM-S7: Reported results for mass fraction of Sr

Institute	Country	Reported value µg/kg	$u(w_{\mathrm{Sr}})$ µg/kg	$U(w_{\mathrm{Sr}})$ µg/kg	Method
VNIIFTRI	Russia	34.50	0.7	1.4	ID ICPMS
INM	Romania	34.80	1.5	3.0	SA+IS ICPMS
NIMT	Thailand	34.90	0.3	0.6	SA ICPMS
CENAM	Mexico	35.10	0.34	0.68	ID ICP-SFMS+ID QQQ-ICP-MS
EXHM/GCSL	Greece	35.32	0.6	1.2	SA HR-ICPMS
UNIIM	Russia	35.60	0.8	1.6	ID ICPMS
BSJ	Jamaica	35.99	0.6	1.18	EC ICPMS
NRC	Canada	36.05	0.24	0.48	ID ICP-SFMS+ICPOES

Table 6. SIM.QM-S7: Reported results for mass fraction of Pb

Institute	Country	Reported value µg/kg	$u(w_{\mathrm{Pb}})$ µg/kg	$U(w_{\mathrm{Pb}})$ µg/kg	Method
LACOMET	Costa Rica	1.03*	0.07	0.14	SA ETAAS
NMIC	Colombia	1.13*	0.02	0.04	EC ICPMS
BSJ	Jamaica	1.14*	0.060	0.12	EC ICPMS
VNIIFTRI	Russia	1.27*	0.02	0.04	ID ICPMS
INTI	Argentina	1.27*	0.02	0.04	EC ICPMS
NRC	Canada	1.365	0.017	0.034	ID ICP-SFMS
IBMETRO	Bolivia	1.38	0.1	0.2	GFAAS
NIMT	Thailand	1.39	0.02	0.04	ID ICPMS
UNIIM	Russia	1.40	0.05	0.10	ID ICPMS
INM	Romania	1.410	0.07	0.14	SA+IS ICPMS
LATU	Uruguay	1.412	0.015	0.030	ID ICP-SFMS
SYKE	Finland	1.416	0.012	0.024	ID ICPMS
CENAM	Mexico	1.453	0.019	0.038	ID ICP-SFMS
EXHM/GCSL	Greece	1.454	0.023	0.046	ID HR-ICPMS
BIM	Bulgaria	1.52	0.05	0.1	SA ICPMS

* Results are not included in the final calculation of SCRV.

Table 7. SIM.QM-S7: Reported results for mass fraction of Na

Institute	Country	Reported value mg/kg	$u(w_{\mathrm{Na}})$ mg/kg	$U(w_{\mathrm{Na}})$ mg/kg	Method
EXHM/GCSL	Greece	11.79*	0.19	0.38	SA ICPOES
UNIIM	Russia	11.87	0.73	1.5	EC ICPMS
BSJ	Jamaica	13.33	0.31	0.62	AAS
CENAM	Mexico	13.33	0.19	0.38	IS+SA ICPOES
NIMT	Thailand	13.66	0.08	0.16	IC
LATU	Uruguay	13.68	0.10	0.20	SA ICPOES
NRC	Canada	13.73	0.17	0.34	IS+SA ICPMS/ICPOES
NMIC	Colombia	13.82	0.16	0.32	EC FAAS
INTI	Argentina	13.90	0.24	0.48	EC ICPOES
VNIIFTRI	Russia	13.95	0.38	0.76	SA ICPMS
IBMETRO	Bolivia	14.1	0.12	0.24	FAAS
LACOMET	Costa Rica	14.17	0.06	0.12	EC FAAS
INM	Romania	14.33	0.35	0.69	SA ICPMS
TTBS	Trinidad	15.018*	0.05	0.10	FAAS

* Results are not included in the final calculation of SCRV.

3.1. Supplementary Comparison Reference Values (SCRVs)

3.1.1. Screening the data for consistency and outlier rejection

From our preliminary inspection of all data submitted, it was evident that a few individual values were inconsistent with the majority. According to the CCQM Guidance note[1] in section 5.2.2 and Appendix 1 (page 18), a consistency check was applied for the four sets of data (Cu, Sr, Na and Pb), and it was found that all data sets were mutually inconsistent based on chi-squared test.

Subsequently, outliers are identified based on median calculation and 99% confidence level; values are considered as outliers when outside $x_{\mathrm{median}} \pm 3 \cdot u_{\mathrm{median}}$ (approximately 99% confidence level), as suggested in 6.3.4 section on page 13 of the CCQM Guidance note[1]. Calculation for Median and its standard uncertainty followed equations on page 25 in the CCQM Guidance note[1]. A simple t-test is thus applied conveniently to compare the $d_i/U(d_i)$ (ratio of absolute difference between the individual value and the median, and its expanded uncertainty) and the critical t value at 99% of $t_{\mathrm{critical\text{-}99\%}}$ for the purpose of identifying outliers. An individual value is considered as an outlier when $d_i/U(d_i)$ is greater than the $t_{\mathrm{critical\text{-}99\%}}$ at given degree of freedom. All data are included and degree of freedom is calculated using n-1 (n: number of data).

Outliers are not included in the calculation of final SCRVs and associated uncertainties. As a result of this evaluation, two low values (1.48±0.05 and 6.90±0.08, µg/kg, k=1) and two high values (10.07±0.50 and 11.30±0.20, µg/kg, k=1) were identified as outliers for Cu; five low values (1.03±0.07, 1.13±0.02, 1.14±0.06, 1.27±0.02, and 1.27±0.02, µg/kg, k=1) were identified as outliers for Pb; and one low value (11.79±0.19, mg/kg, k=1) and one high value (15.018±0.05, µg/kg, k=1) were identified as outliers for Na.

To support the above statistic rejection of outlier results, and following the CCQM Guidance Note[1] in section 5.2.2.3's first requirement, performances of NMIs/DIs (identified as outliers) in previous CCQM comparisons were evaluated. It was found that NMIs/DIs (TTBS, NMIC, IBMETRO and BIM) identified as outliers for Cu, have not participated in previous key comparisons for Cu. For Pb, INTI has CMCs in category 8 and 9 for high level Pb, but has not shown any evidence of participation in previous key comparisons at low level of Pb, which is more challenge at the low level. Other NMIs identified as outlier (LACOMET, NMIC, BSJ and VNIIFTRI) for Pb, also do not have evidence of participation in previous key comparisons. For Na, EXHM/GCSL has evidence of participation in key comparisons for other elements and matrixes at high levels, but does not have evidence in Na measurements. TTBS does not have evidence of participation in previous key comparisons for Na. Clearly, this evaluation confirms that NMIs/DIs identified as outliers lack technical supports to be considered in the calculation of the KCRV, supporting the exclusion of results identified as outliers in the above statistical analysis.

Note that after the rejection of outliers, consistency check results still show mutual inconsistency for Cu, Pb and Na, and borderline consistency for Sr.

3.1.2. Selection of calculation methods for SCRVs

As suggested on page 12 section 6.3.3 in the CCQM Guidance note[1], when a data set is lacking mutual consistency with no individual anomalous values, which is the case for Sr (with the calculated Birge ratio of 1.9 >1.5), at the intermediate levels of over-dispersion, the Mandel-Paule, the DerSimonian-Laird (DSL)[1-2] or the Vangel-Ruhkin estimators are recommended to calculate the KCRV and uncertainty.

Similarly, on page 14 section 6.3.4 (6.3.4.1 ii) in the CCQM Guidance note[1], when data sets are lacking mutual consistency with one or more anomalous values (which is the case for Cu, Pb and Na) and over-dispersion is attributable to a random additive effect, then Mandel-Paule, the DerSimonian-Laird (DSL)[1-2] or the Vangel-Ruhkin estimators are recommended for data sets of size 7 or larger after excluding extreme values at 99% level.

Mandel-Paule is an iterative method whereas DSL method is not, but a simple direct calculation. In addition, the latter provides very similar results to Mandel-Paule, and it has been suggested as a preferred calculation where calculation simplicity is desired (page 28 in the CCQM Guidance note[1]). Following these suggestions, DSL is thus chosen for the final calculation of SCRVs and associated uncertainties.

The DSL-mean (x_{DSL}) and its uncertainty are calculated using Eq. 1 and 2 from individual result (x_{i}) and its uncertainty (u_{i}).

$$x_{\mathrm{DSL}} = \frac{\sum_{\mathrm{i}} w_{\mathrm{i}}^{*} x_{\mathrm{i}}}{\sum_{\mathrm{i}} w_{\mathrm{i}}^{*}} \qquad (1)$$

where

$$w_\mathrm{i}^* = \frac{1}{u_\mathrm{i}^2 + \lambda}$$

$$\lambda = \max\left[0, \frac{\sum_{\mathrm{i}=1}^{\mathrm{p}} w_\mathrm{i}(x_\mathrm{i} - \bar{x})^2 - p + 1}{w_1 - w_2 / w_1}\right]$$

$$\bar{x} = \frac{1}{w_1}\sum_{\mathrm{i}=1}^{\mathrm{p}} w_\mathrm{i} x_\mathrm{i} \ \text{ and}$$

$$w_\mathrm{i} = \frac{1}{u_\mathrm{i}^2}\ \ i\text{=1,}\ldots p,\ \ w_1 = \sum_{\mathrm{i}=1}^{\mathrm{p}} w_\mathrm{i}\ ;\ w_2 = \sum_{\mathrm{i}=1}^{\mathrm{p}} w_\mathrm{i}^2$$

$$u_\mathrm{DSL}^2 = \frac{1}{\sum_\mathrm{i} w_\mathrm{i}^*} \qquad (2)$$

3.1.3. SCRVs and associated uncertainty for SIM.QM-S7

Table 8 summarizes SCRVs and uncertainties obtained using DSL, Mean, Median, W-Mean (with correction of dispersion) calculations (calculation equations given on pages 23-26 and 28 in the CCQM Guidance note[1]). It is evident that the DSL method provides very similar results to other approaches, furthermore, unlike the mean and median, which ignore the individual uncertainty of each value, DSL uses individual uncertainties for the calculation. Proper uncertainty estimation of each individual data is essential in order to maintain measurement traceability for that NMI, and it should be considered in the final calculation of SCRVs and uncertainties.

Table 8. SIM.QM-S7 SCRV, *u*(SCRV) and *U*(SCRV) and U_r(SCRV)

		SCRV	*u*(SCRV)	*U*(SCRV)	U_r(SCRV),%
Cu, µg/kg	Mean	7.58	0.076	0.15	2.0
	Median	7.56	0.115	0.23	3.0
	W-Mean	7.54	0.038	0.08	1.0
	DSL-Mean	7.55	0.049	0.10	1.3
Sr, µg/kg	Mean	35.28	0.20	0.40	1.1
	Median	35.21	0.26	0.52	1.5
	W-Mean	35.46	0.20	0.41	1.1
	DSL-Mean	35.37	0.24	0.47	1.3
Pb, µg/kg	Mean	1.420	0.014	0.029	2.0
	Median	1.411	0.015	0.031	2.2
	W-Mean	1.414	0.010	0.020	1.4
	DSL-Mean	1.417	0.012	0.024	1.7
Na, mg/kg	Mean	13.59	0.18	0.37	2.7
	Median	13.78	0.13	0.27	1.9
	W-Mean	13.90	0.09	0.17	1.2
	DSL-Mean	13.78	0.10	0.21	1.5

3.2. Measurand mass fraction results

The reported results for Cu, Sr, Pb and Na are presented in Figures 1-4. SCRVs and uncertainties are based on DSL method after rejection of outliers as described earlier in sections 3.1.1-3.1.3.

Figure 1. Results for SIM.QM-S7 mass fraction of Cu µg/kg (*u*, *k* = 1)

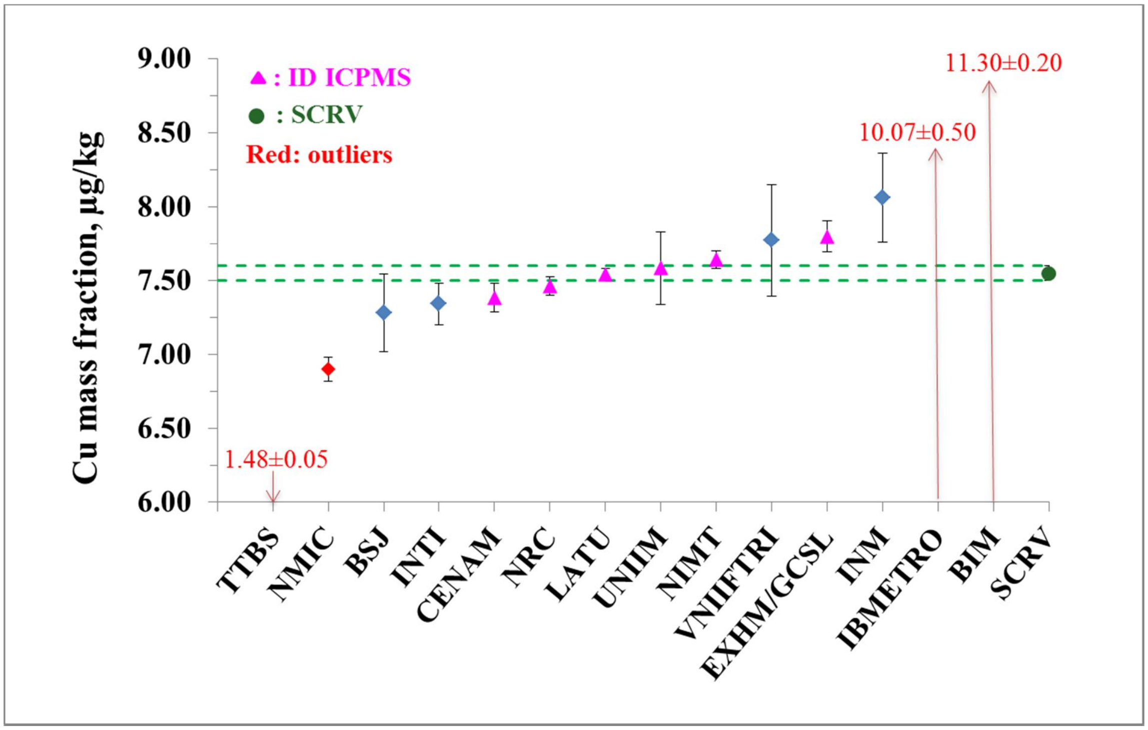


Figure 2. Results for SIM.QM-S7 mass fraction of Sr µg/kg (*u*, *k* = 1)

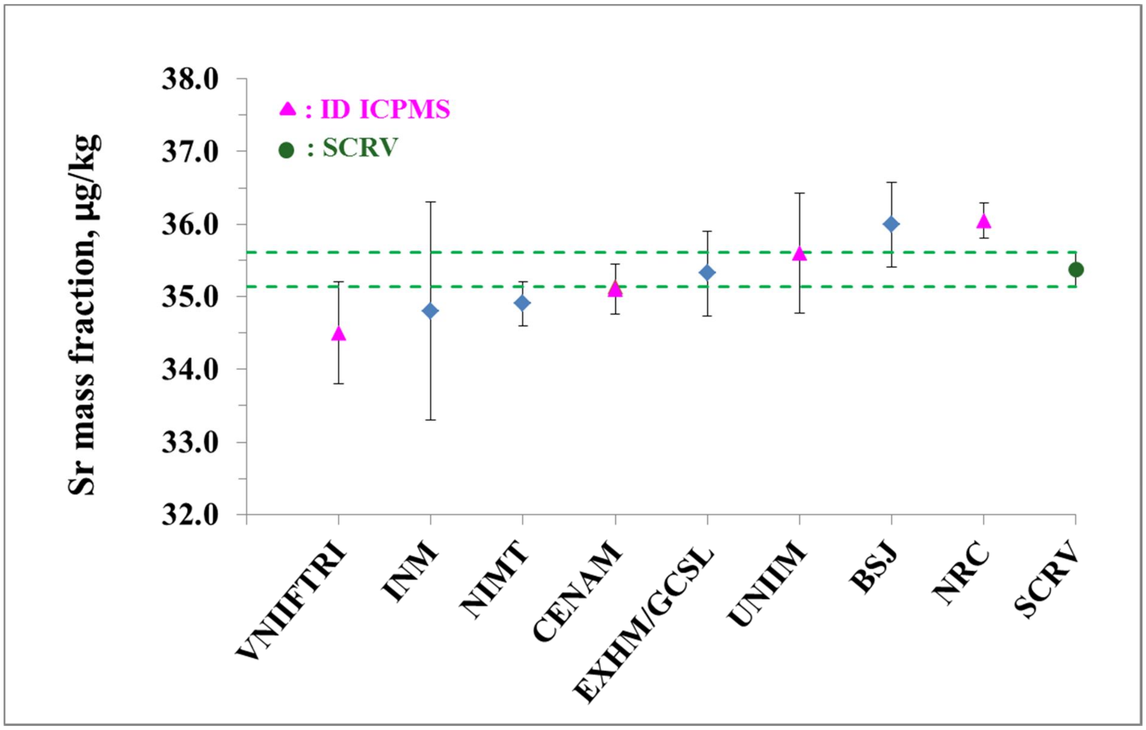


Figure 3. Results for SIM.QM-S7 mass fraction of Pb, µg/kg (*u*, *k* = 1)

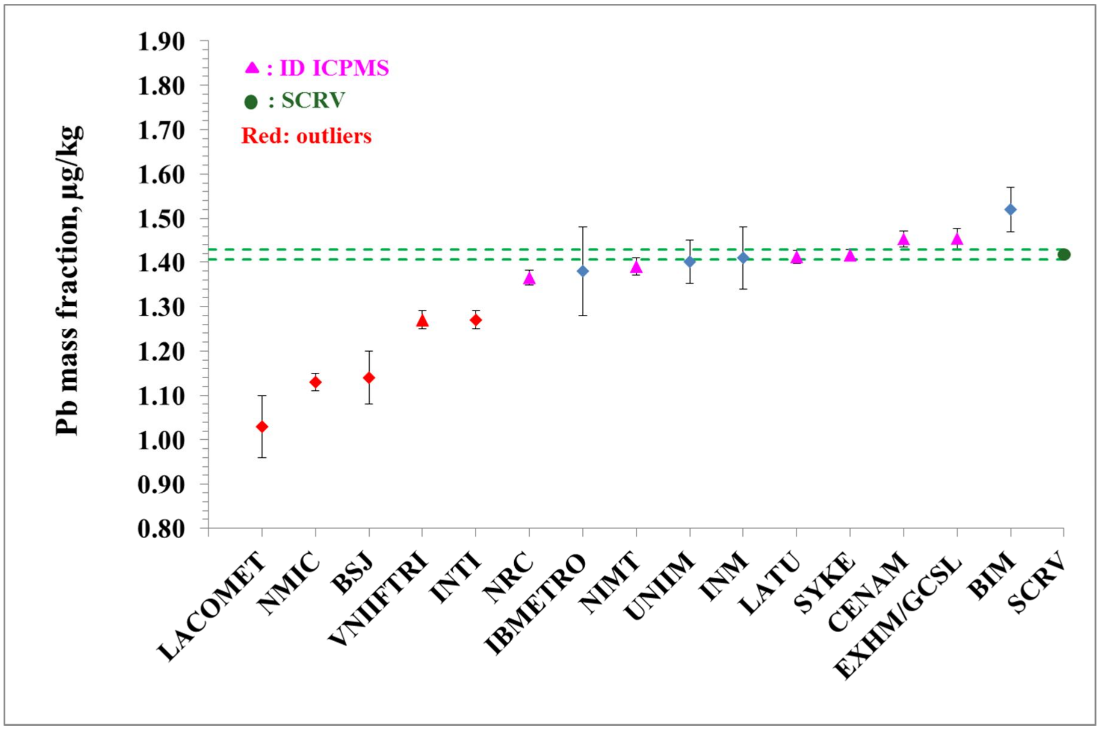
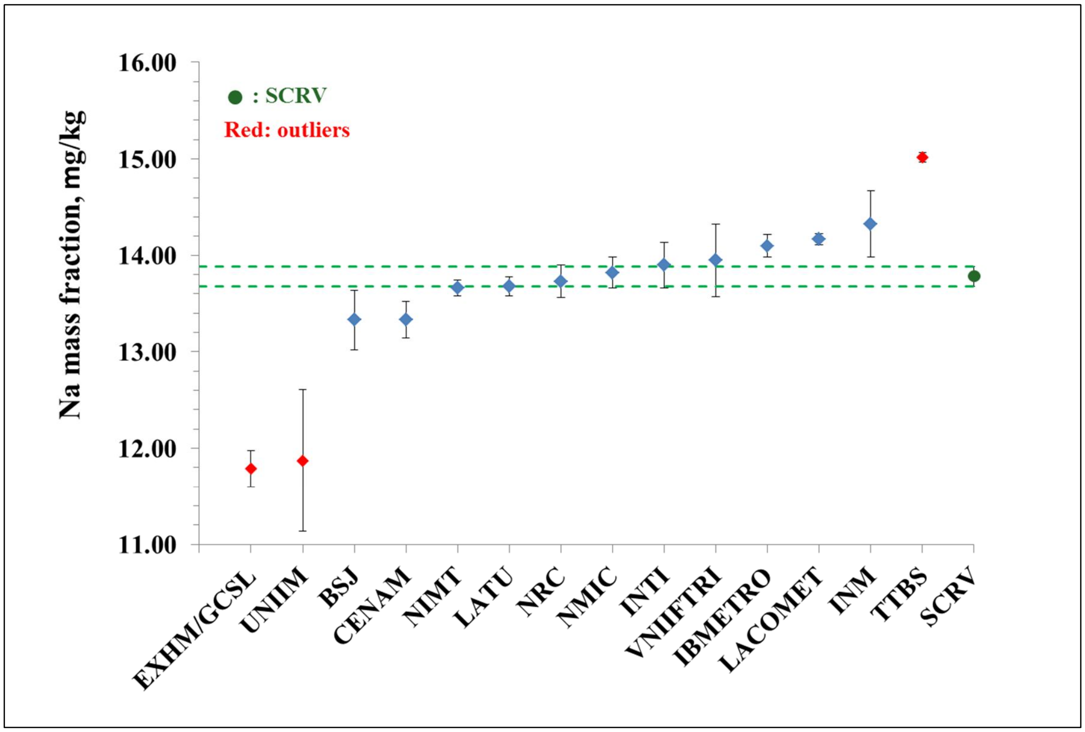


Figure 4. Results for SIM.QM-S7 mass fraction of Na, mg/kg (*u*, *k* = 1)



3.3. Equivalence statements

The degree of equivalence (DoE) and its uncertainty of a measurement result reported by a participating NMIs/DIs relative to the SCRV based on DSL calculation are calculated using the following Eq. 3-5, as outlined on page 28 of the CCQM Guidance note[1].

$$d_{\mathrm{i}} = x_{\mathrm{i}} - x_{\mathrm{DSL}} \tag{3}$$

$$u^2(\mathrm{d_i}) = u_{\mathrm{i}}^2 + \lambda - u_{\mathrm{DSL}}^2 \tag{4}$$

where the value x_{i} is included in the calculation.

$$u^2(\mathrm{d_i}) = u_{\mathrm{i}}^2 + \lambda + u_{\mathrm{DSL}}^2 \tag{5}$$

where the value x_{i} is not included in the calculation.

Note that λ is the variance due to differences between the submitted results from participating labs and its contribution was included in the uncertainty of DoE. As a result, DSL is the most conservative estimation (compared to Mean, Median and Weighted-Mean) which provides the least number of labs with $|d_{\mathrm{i}}/U(\mathrm{d_i})| > 1$, fewer labs were excluded. Results of DoE are shown in Tables 9-12.

Table 9. SIM.QM-S7: Equivalence statement for Cu

Institute	Country	Based on DSL		
		d_i µg/kg	**$U(d_i)$ µg/kg**	**$\|d_i/U(d_i)\|$**
TTBS	Trinidad	-6.1	0.24	25
NMIC	Colombia	-0.65	0.27	2.4
BSJ	Jamaica	-0.27	0.55	0.49
INTI	Argentina	-0.21	0.33	0.63
CENAM	Mexico	-0.17	0.26	0.64
NRC	Canada	-0.09	0.21	0.41
LATU	Uruguay	-0.01	0.19	0.040
UNIIM	Russia	0.04	0.52	0.071
NIMT	Thailand	0.09	0.21	0.45
VNIIFTRI	Russia	0.22	0.78	0.29
EXHM/GCS	Greece	0.25	0.27	0.93
INM	Romania	0.51	0.62	0.82
IBMETRO	Bolivia	2.5	1.0	2.5
BIM	Bulgaria	3.8	0.46	8.2

Table 10. SIM.QM-S7: Equivalence statement for Sr

Institute	Country	Based on DSL		
		d_i µg/kg	**$U(d_i)$ µg/kg**	**$\|d_i/U(d_i)\|$**
VNIIFTRI	Russia	-0.87	1.6	0.55
INM	Romania	-0.57	3.1	0.18
NIMT	Thailand	-0.47	0.94	0.50
CENAM	Mexico	-0.27	0.99	0.27
EXHM/GCS	Greece	-0.05	1.3	0.036
UNIIM	Russia	0.23	1.8	0.13
BSJ	Jamaica	0.62	1.3	0.45
NRC	Canada	0.68	0.86	0.79

Table 11. SIM.QM-S7: Equivalence statement for Pb

Institute	Country	Based on DSL		
		d_i µg/kg	**$U(d_i)$ µg/kg**	**$\|d_i/U(d_i)\|$**
LACOMET	Costa Rica	-0.39	0.15	2.6
NMIC	Colombia	-0.29	0.070	4.1
BSJ	Jamaica	-0.28	0.13	2.1
VNIIFTRI	Russia	-0.15	0.070	2.1
INTI	Argentina	-0.15	0.070	2.1
NRC	Canada	-0.052	0.057	0.91
IBMETRO	Bolivia	-0.037	0.21	0.18
NIMT	Thailand	-0.027	0.061	0.45
UNIIM	Russia	-0.016	0.11	0.15
INM	Romania	-0.007	0.15	0.050
LATU	Uruguay	-0.005	0.055	0.10
SYKE	Finland	-0.001	0.052	0.026
CENAM	Mexico	0.036	0.060	0.60
EXHM/GCS	Greece	0.037	0.065	0.56
BIM	Bulgaria	0.10	0.11	0.93

Table 12. SIM.QM-S7: Equivalence statement for Na

Institute	Country	Based on DSL		
		d_i mg/kg	**U(d_i) mg/kg**	**|d_i/U(d_i)|**
EXHM/GCS	Greece	-1.99	0.72	2.8
UNIIM	Russia	-1.91	1.59	1.2
BSJ	Jamaica	-0.45	0.82	0.55
CENAM	Mexico	-0.45	0.66	0.69
NIMT	Thailand	-0.12	0.56	0.22
LATU	Uruguay	-0.10	0.57	0.18
NRC	Canada	-0.053	0.64	0.083
NMIC	Colombia	0.037	0.62	0.059
INTI	Argentina	0.12	0.72	0.16
VNIIFTRI	Russia	0.17	0.93	0.18
IBMETRO	Bolivia	0.32	0.59	0.54
LACOMET	Costa Rica	0.39	0.55	0.70
INM	Romania	0.55	0.87	0.63
TTBS	Trinidad	1.24	0.62	2.0

Figure 5. Equivalence statement for SIM.QM-S7 Cu

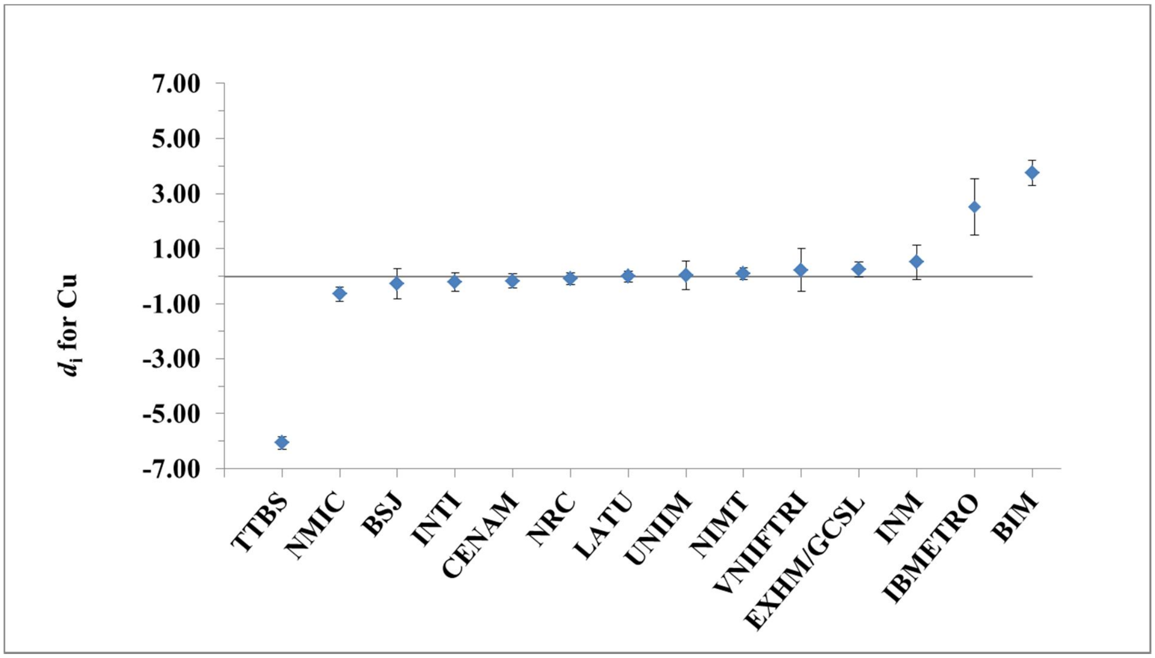


Figure 6. Equivalence statement for SIM.QM-S7 Sr

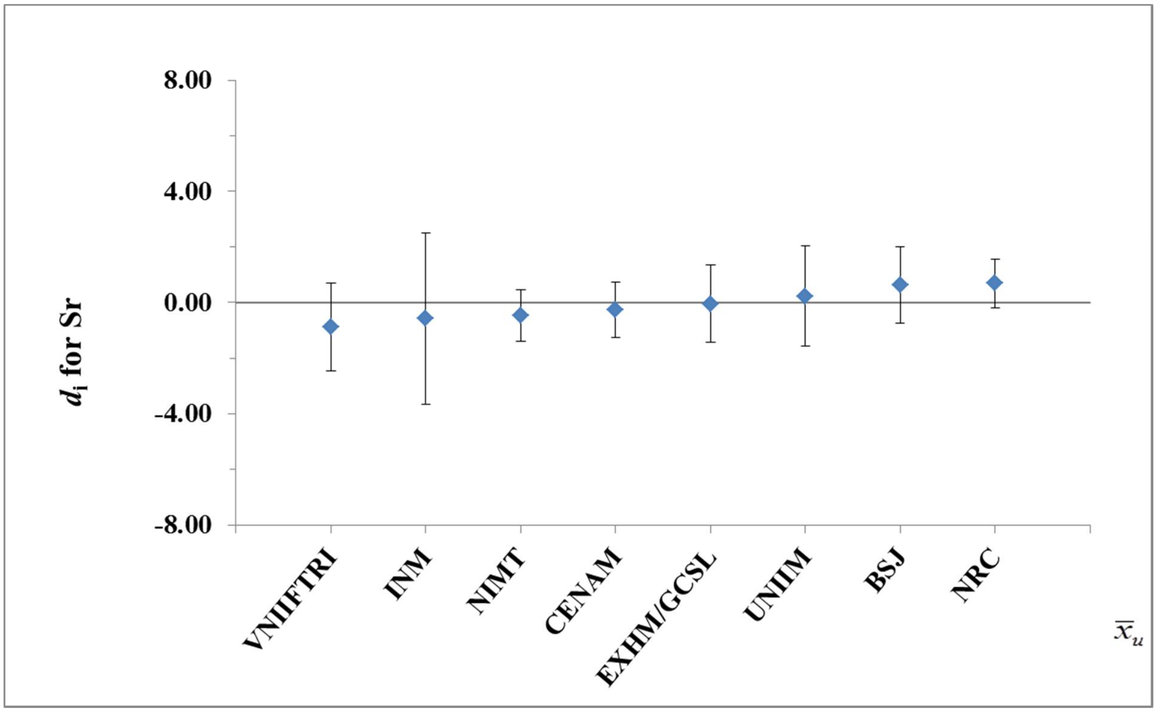


Figure 7. Equivalence statement for SIM.QM-S7 Pb

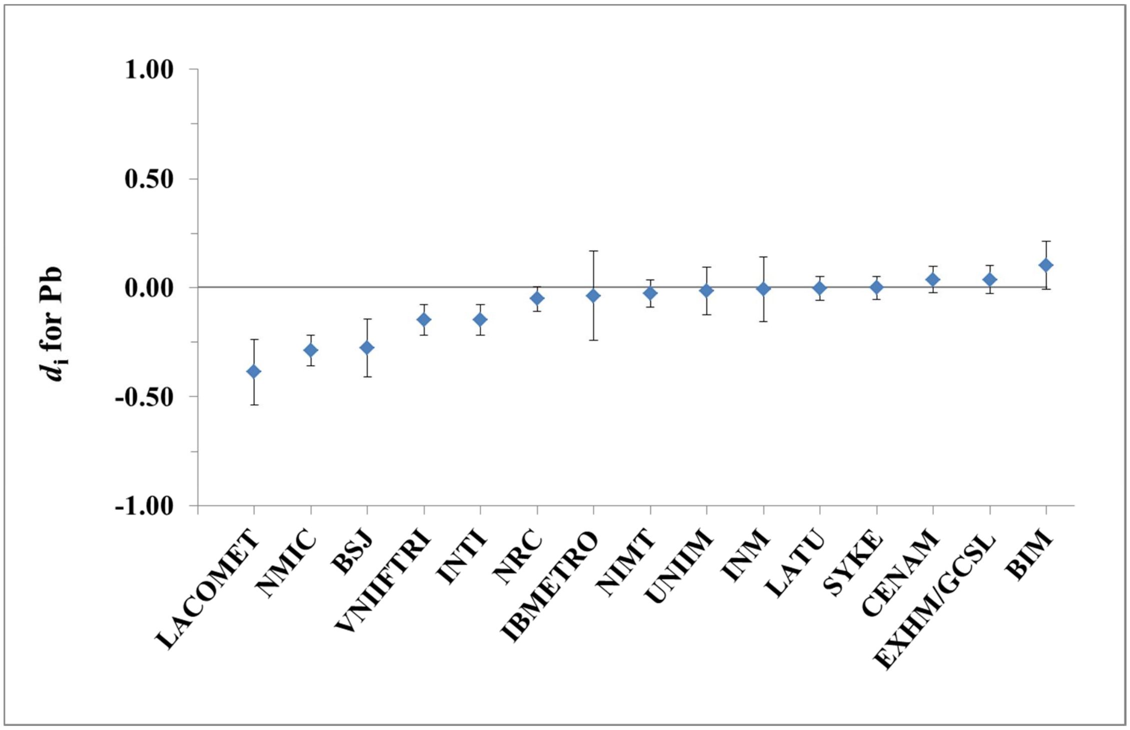
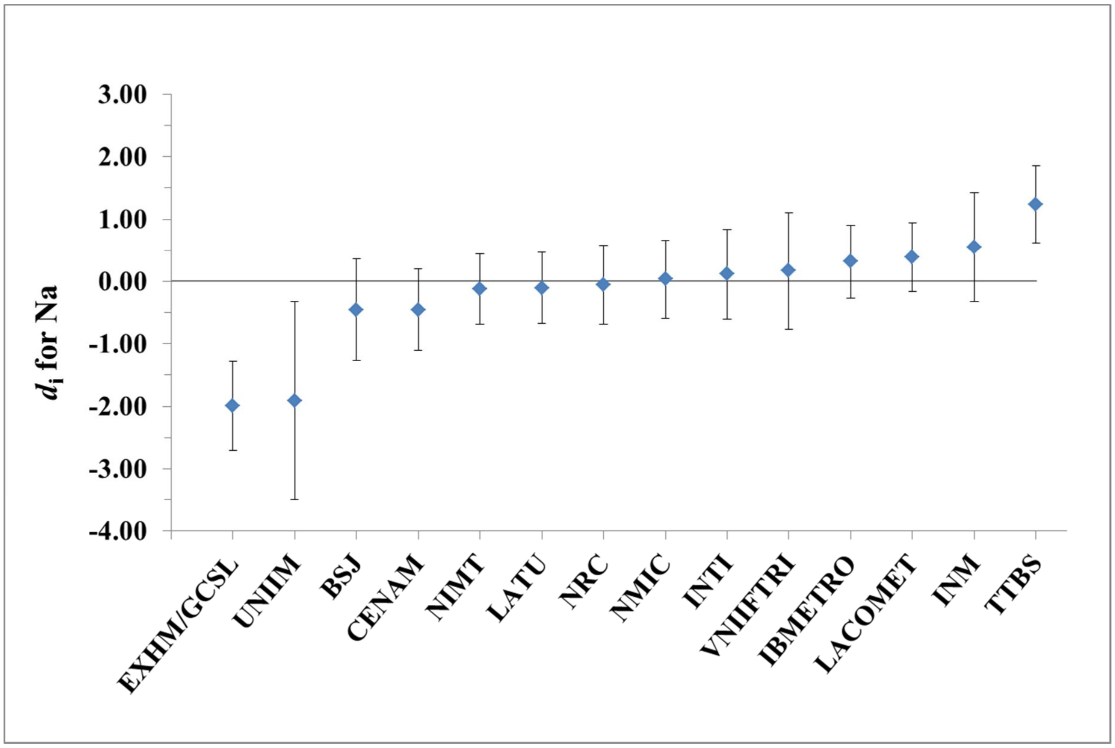


Figure 8. Equivalence statement for SIM.QM-S7 Na



4. Demonstrated Core capabilities

As agreed in CCQM IAWG meetings, the Core Capability Approach can be used to support CMC claims by NMIs/DIs for a similar matrix based on NMIs/DIs successfully demonstrating their measurement capabilities by participating in SIM.QM-S7 or other related CCQM-K comparisons. All participants were required to submit Inorganic Core Capability tables, which are summarized in Appendix A.

5. Conclusion

In general, the SIM.QM-S7 is a successful supplementary comparison, as indicated by results from majority NMIs/DIs are in agreement with the SCRV with their expanded uncertainties.

6. Acknowledgements

Dr. Mike Sargent is thanked for his support and advice during the SIM.QM-S7. We thank all participating NMIs/DIs. Drs. Maurice Cox, David Duewer, Steve Ellison, Michal Mariassy and Mike Winchester are thanked for their helpful comments which have improved the quality of this report.

Reference:

1. CCQM Guidance note: Estimation of a consensus KCRV and Associated Degrees of Equivalence, Version 10, 2013-04-12.

2. Rebecca DerSimonian, Nan Laird, Meta-analysis in clinical trials, *Controlled Clinical Trials* 1986, **7**: 177-188.

Appendix A

Inorganic Core Capabilities
Summary Table

CCQM Study: SIM.QM-S7, Trace Metals in Drinking Water

Institute(s): NRC, CENAM, LATU, UNIIM, SYKE, NIMT, EXHM/GCSL, VNIIFTRI

Method: ID-ICP-MS

Analyte(s): Cu, Sr and Pb

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.*	VNIIFTRI (Sr, Pb)	NRC (Cu, Sr, Pb) CENAM (Cu, Sr, Pb) LATU (Cu, Pb) UNIIM (Cu, Sr, Pb) SYKE (Pb) NIMT (Cu, Pb) EXHM/GCSL (Cu, Pb)	High purity acids used and lank subtracted (NRC) Efforts to control and check blank level (NMIC) The contamination was not significant; however it was controlled by preparing samples in class-100 clean room, and also double sub-boiling distillation water, high purity reagents, and enough blank samples were used. (CENAM) Using of software of mass spectrometer NexION 300D (blank) (UNIIM) The instrument is thoroughly rinsed before measurements to ensure a low and contamination free background signal. No background drift due to previous contamination is allowed. Contamination from the laboratory environment is checked using procedural blanks. Six blank samples are prepared at the time of sample preparation using the same diluent. Three of the procedural blanks are measured at the beginning of the run. The test tubes are left open for the duration of the entire run. At the end of the run the same procedural blanks are measured again. The remaining three procedural blanks are opened and measured at the end of the run. The difference between leading and trailing procedural blank results represents the airborne contamination during the run. The difference between the instrument background and the procedural blanks represents the contamination during sample preparation. The purity and cleaning procedure of the test tubes used in sample preparation was investigated during method validation. (SYKE)
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.*	NRC CENAM LATU UNIIM	SYKE	

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
	NIMT VNIIFTRI		
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.*	NRC CENAM LATU UNIIM NIMT VNIIFTRI	SYKE	
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	NRC CENAM LATU UNIIM NIMT VNIIFTRI	SYKE	Standard solutions are stored in bottles of a suitable material at room temperature. The weight of the bottle with contents is recorded before and after opening each time aliquots are taken to check for any evaporative loss. Resealable bags are used to protect the bottle from dust. Sample bottles are stored in resealable bags and refrigerated if necessary. Additional customer instructions are followed if provided. If the samples are stored before measurement, the bottle is weighed without the resealable bag and the mass recorded. After the storage the bottle is weighed again before aliquots are taken to check for any evaporative loss. Working times at the balances are carefully planned and the time is kept to a minimum. Airborne contamination is monitored by preparing procedural blanks during sample preparation. (SYKE)
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.*	NRC CENAM LATU UNIIM NIMT VNIIFTRI	SYKE	Cold vapor generation is only applied mercury measurements. (SYKE)
Matrix separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	NRC CENAM LATU UNIIM NIMT VNIIFTRI	SYKE	Matrix separation is only applied for e.g. salt solution matrices. (SYKE)
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample.*	NIMT	NRC CENAM LATU UNIIM SYKE EXHM/GCSL	Enriched isotopes were spiked to the sample, and then it was mixed and overnight to reach equilibrium (CENAM) Essential for accurate IDMS and needed to mix well (NIMT) Multiple measurements separated by at least

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
		VNIIFTRI	2 hours were carried out to ensure the spike equilibration (VNIIFTRI)
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.*	EXHM/GCSL	NRC CENAM LATU UNIIM SYKE NIMT VNIIFTRI	Element XR is sensitive enough (NRC) Copper was measured in medium resolution some degree of difficulty increased the signal detection (CENAM) Low levels of Cu and Pb present in sample. (NIMT) For Sr: sample was diluted by approximately 20 times with ultrapure water to limit signal count rates between 250 000 and 300 000. For Pb: different dwell times was used for different isotopes (20 ms for Pb204, 10 ms for both Pb206 and Pb207 and 5 ms for Pb208) (VNIIFTRI)
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	NIMT EXHM/GCSL	NRC (Cu, Sr, Pb) CENAM (Pb) LATU (Cu, Pb) UNIIM SYKE VNIIFTRI	No significant memory effect was found for analytes (NRC) Rinse was applied between each measurement of samples with 2 % HNO3 solution. (CENAM) The sample path has a low dead volume. All samples in a run have the same acid matrix, preferably a dilute nitric acid. Between samples repeated rinsing is used until the background has reached acceptable levels, especially when the isotopic composition changes. All samples are screened before sample preparation. Exact matching double IDMS is used which prevents unexpectedly high signals. (SYKE)
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.*	UNIIM NIMT	NRC (Cu) CENAM (Cu, Sr, Pb) LATU (Cu, Pb) UNIIM (Cu, Sr, Pb) SYKE VNIIFTRI	MR was used for Cu Lead in low resolution mode required the correction for Hg interferences of 204Hg in 204Pb. Strontium in high resolution mode required the correction of isobaric interference, 87Rb for 87Sr. For copper, the interference 49Ti16O was solved in medium resolution mode (CENAM) For Cu, medium resolution (R>4000) was used to resolve interferences. (LATU) Isobaric interferences are corrected mathematically using the instrument software. The correction factor is verified experimentally during method validation. Matrix separation is used to remove elements causing polyatomic interferences. (SYKE) Cu, Pb HR-ICP-MS was used (EXHM/GCSL) For Sr: additional masses 83, 86 were scanned. For Pb: additional mass 204 was scanned (VNIIFTRI)
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	UNIIM NIMT	NRC CENAM LATU SYKE EXHM/GCSL	It was controlled by using the ion count rates by applied the appropriate dilution factor (CENAM) The detector deadtime of the instrument is checked before every measurement campaign

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
		VNIIFTRI	and optimized if necessary. Samples are screened in advance and prepared so that unexpectedly high count rates are not encountered. (SYKE) Spike concentration and blend ratios were calculated to ensure equal signal levels for sample, spike and blends. (VNIIFTRI)
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	UNIIM	NRC CENAM LATU SYKE NIMT EXHM/GCSL VNIIFTRI	SRM-981 lead natural isotopic standard was used to measure the mass bias correction factor for isotopic composition of Pb in the samples. SRM-982 equal- atom lead isotopic standard, from NIST was used to determine the mass bias correction factors for Pb ratios in the blends (Rbx and Rbz). (CENAM) Use standard solution to monitor mass bias (NIMT) K-factor measurements were performed for each measured isotope ratio. (VNIIFTRI)
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*	VNIIFTRI	NRC CENAM UNIIM LATU SYKE NIMT EXHM/GCSL	Measurements were performed by exact matching double ID-ICPMS, with ratio correction of Pb, and not ratio correction for Cu and Sr, because the method used cancel out the analyte concentration in the enriched isotopic spike solution. The analytical challenge was to match the isotope ratio in the blends (sample and the primary standard). (CENAM) Cu, Pb: Exact matching IDMS (LATU) Using procedure of preparation (UNIIM) Exact matching double(reverse) IDMS is used. Both the sample and a certified pure reference material, in this case a NIST SRM 981 lead solution, are spiked with an enriched isotope solution (Merck Pb-206). The target isotope ratio of the reference isotope 208Pb and the enriched isotope 206Pb is 1 in both blends. There is no need for mass bias correction due to the use of exact matching double IDMS technique. (SYKE) Reverse IDMS to calibrate the isotopic spike (NIMT) REVERSE IDMS (EXHM/GCSL)

Inorganic Core Capabilities
Summary Table

CCQM Study: SIM.QM-S7, Trace Metals in Drinking Water

Institute(s): NMIC, CENAM, BIM, NIMT, INM, EXHM/GCSL, VNIIFTRI, INTI

Method: ICPMS (without ID)

Analyte(s): Cu, Sr, Na and Pb

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 (Sr) VNIIFTRI (Cu, Na)	NMIC(Pb, Cu) CENAM (Na) BIM (Pb, Cu) INM (Pb, Cu, Sr, Na) EXHM/GCSL (Sr) INTI (Cu, Pb)	Efforts to control and check blank level. (NMIC) The level of Na in deionized water was significant. To minimize and control it, the sample preparation was done in class-100 clean room, and also double sub-boiling distillation water, high purity reagents, and enough blank samples were used. (CENAM) For every experiment, two or three separated blank samples were measured. The blank samples were undergone through all analytical procedure stages and contain all reagents, without a sample itself. The sample preparation was performed in a clean room with special environment conditions. Ultra pure water and suprapure nitric acid was used. (BIM) Blank values for low mass fraction of Pb under control. Contamination control especially for Pb and Na (INM)
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.*	NMIC CENAM BIM NIMT INM EXHM/GCSL VNIIFTRI	INTI (Cu, Pb)	
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*	All		

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
the ICP.			
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.*		NMIC(Pb, Cu) CENAM (Na) BIM (Pb, Cu) NIMT (Sr) INM (Pb, Cu, Sr, Na) EXHM/GCSL (Sr) VNIIFTRI (Cu, Na) INTI (Cu, Pb)	Bracketing external calibration (NMIC) Internal standard with single point standard addition was used. Measurement was performed in medium and high-resolution mode; the ratios measured were ^{25}Na/^{45}Sc. The analytical challenge was to find the best internal standard. (CENAM) External linear calibration with certified standards was applied. for preliminary semiquantitative analysis. For precise quantitative analysis standard addition calibration method was used. (BIM) Instrument calibration with matrix matched CRMs and SRMs. Both external calibration and standard addition procedures (INM) standard additions (EXHM/GCSL)
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.*	CENAM (Na) NIMT (Sr) EXHM/GCSL VNIIFTRI (Cu)	NMIC (Pb, Cu) BIM (Pb, Cu) INM (Pb, Cu, Sr, Na) VNIIFTRI (Na) INTI (Cu, Pb)	Measurements of ^{63}Cu ^{65}Cu ^{206}Pb ^{207}Pb and ^{209}Pb (NMIC) As a rule, the signals (c/s) of the cooper were high. Therefore the samples were diluted with the aim (2÷8)×10^{5} c/s signals to be achieved. (BIM) Due to very high Na23 concentration medium-high detector attenuation mode for signal recording was used. (VNIIFTRI)
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	CENAM (Na) EXHM/GCSL	NMIC (Pb, Cu) BIM (Pb, Cu) NIMT (Sr) INM (Pb, Cu, Sr, Na) VNIIFTRI (Cu, Na) INTI (Cu, Pb)	Clean of introduction sample system between samples with nitric acid. (NMIC) During Pb measuring by ICP MS longer rinsing with 2% nitric acid was applied. (BIM) Reagent blank needed to be measured prior to follow-up measurement. (NIMT) Sequence of calibration and measurements performed in such a way to minimize memory effects (INM) Sr, HR-ICP/MS was used (EXHM/GCSL) It was found that signal from Cu65 arises during each run. To reduce this effect, 10 min rinsing with ultrapure water (18.2 MOm) was applied after each sample or standard addition

Capabilities/Challenges	**Not tested**	**Tested**	**Specific challenges encountered**
			measurement. (VNIIFTRI)
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.*	BIM NIMT VNIIFTRI (Na) INTI	NMIC (Pb, Cu) CENAM (Na) INM (Pb, Cu, Sr, Na) EXHM/GCSL VNIIFTRI (Cu)	Use of KED with helium (NMIC) Interfering species for Na, due the presence the internal standard ($^{45}Sc^{++}$) used was solved using the Peltier chamber and medium resolution mode, For internal standard the interference $^{29}Si^{16}O$ were solved using medium resolution mode and it was confirmed with high resolution mode. (CENAM) Default correction interferences equations set in the software were applied. (BIM) In accordance with the recommendations given in the instrument manual (INM) Due to isobaric interference Cu63 – Ar40Na23 only signal from Cu65 was used. (VNIIFTRI)
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.*	NMIC BIM NIMT CENAM INM VNIIFTRI INTI	EXHM/GCSL	
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	NMIC BIM NIMT CENAM INTI	INM EXHM/GCSL VNIIFTRI	Default detector deadtime correction was used. (BIM) In accordance with the instrument manual recommendations (INM)
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	NMIC CENAM EXHM/GCSL VNIIFTRI INTI	BIM NIMT INM	Obligatory preliminary every-day mass calibration using tuning solution (BIM) In accordance with the instrument procedure and use of CRMs and SRMs (INM)

CCQM Study: SIM.QM-S7, Trace Metals in Drinking Water

Institute(s): NRC, CENAM, LATU, BSJ, EXHM/GCSL, INTI,

Method: ICP-OES

Analyte(s): Na, Cu, Pb

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.*	CENAM	NRC (Na) LATU (Na) BSJ (Sr, Cu, Pb) EXHM/GCSL (Na) INTI (Na)	Clean acid and DI water used to minimize blank (NRC) Ubiquity of Sr. All process waters were filtered through multiple high performance purification systems prior to preparation of calibration standard. (BSJ)
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.*	NRC LATU CENAM EXHM/GCSL INTI	BSJ (Sr, Cu, Pb)	Challenge not encountered or challenge not applicable (BSJ)
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.*	NRC LATU CENAM EXHM/GCSL	BSJ (Sr, Cu, Pb) INTI (Na)	Challenge not encountered or challenge not applicable (BSJ)
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	NRC LATU CENAM EXHM/GCSL INTI	BSJ (Sr, Cu, Pb)	Challenge not encountered or challenge not applicable (BSJ)
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.*	NRC LATU CENAM EXHM/GCSL INTI	BSJ (Sr, Cu, Pb)	Challenge not encountered or challenge not applicable (BSJ)
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.*	NRC LATU CENAM EXHM/GCSL INTI	BSJ (Sr, Cu, Pb)	Challenge not encountered or challenge not applicable (BSJ)
Matrix separation *Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures. Techniques and procedures used to isolate the analyte(s) from the sample matrix to avoid or reduce interferences caused by the matrix. Includes ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.*	NRC LATU CENAM EXHM/GCSL INTI	BSJ (Sr, Cu, Pb)	Challenge not encountered or challenge not applicable (BSJ)
Calibration of analyte concentration *The preparation of calibration standards*		All	Standard additions calibration (NRC) Internal standard with single point standard addition was used. The

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
and the strategy for instrument calibration. Includes external calibration and standard additions procedures.			analytical challenge was to find the best internal standard. (CENAM) (1) Instrument operated in accordance with Operator's Manual. (2) Good laboratory practices employed in all preparations. (3) All dilutions done by mass (4) Analytical sequence composed which avoids successive samples having large differences in analyte concentration. (BSJ) standard additions used (EXHM/GCSL)
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..*	EXHM/GCSL	NRC (Na) CENAM (Na) LATU (Na) BSJ (Sr, Cu, Pb) INTI (Na)	Measurement was performed in Axial mode, the wavelengths measured were the following: Na (589.592)/Y (324.227). (CENAM) Background reduction / quieting procedures applied. E.g. running multiple trial blanks prior to analysis of samples and low level standards. (BSJ)
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	CENAM EXHM/GCSL	NRC (Na) LATU (Na) LATU (Na) BSJ (Sr, Cu, Pb) INTI (Na)	No significant effect(NRC) (1) Analytical sequence composed which avoids successive samples having large differences in analyte concentration (2) Background reduction / quieting procedures applied. E.g. running multiple trial blanks prior to analysis of samples and low level standards. (BSJ)
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.*	CENAM EXHM/GCSL	NRC (Na) LATU (Na) BSJ (Sr, Cu, Pb) INTI (Na)	Choose wave line without significant interference, inter element correction was applied (NRC) Challenge not encountered or challenge not applicable (BSJ)
Correction or removal of matrix-induced signal suppression or enhancement *Chemical or instrumental procedures used to avoid or correct for matrix-induced signal suppression or enhancement. High concentrations of acids, dissolved solids, or easily ionized elements will increase the degree of difficulty.*	CENAM EXHM/GCSL INTI	NRC (Na) LATU (Na) BSJ (Sr, Cu, Pb)	Standard additions calibration was used (NRC) (CsCl was added to the samples as ionization buffer) (LATU) Challenge not encountered or challenge not applicable (BSJ)

Inorganic Core Capabilities
Summary Table

CCQM Study: SIM.QM-S7, Trace Metals in Drinking Water

Institute(s): IBMETRO, NIMC, LACOMET, BSJ, TTBS, INTI

Method: ETA-AAS (or GF-AAS)

Analyte(s): Cu, Pb, Na

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.*	IBMETRO	NMIC (Na) LACOMET BSJ(Na) TTBS (Cu, Na) INTI (Na)	Blank evaluation in each batch and correction for AA. Degree of Difficulty: low (NMIC) Ubiquity of Na. All process waters were filtered through multiple high performance purification systems prior to preparation of calibration standard. (BSJ) Na presented our greatest challenge since this metal is present in most lab grade detergents used to clean glassware. We used a combination of 10% HNO3 and deionized water to clean the glassware (TTBS)
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.*	IBMETRO NMIC LACOMET TTBS INTI	BSJ(Na)	Direct determination of the sample was used. (LACOMET) Challenge not encountered or challenge not applicable (BSJ)
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.*	IBMETR NMIC LACOMET	BSJ(Na) TTBS (Cu, Na) INTI (Na)	Gravimetric dilution of the sample (LACOMET) Challenge not encountered or challenge not applicable (BSJ) Sample digested with 10% HNO3 on hot plate since Microwave digestor was not in service. (TTBS)
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	IBMETRO NMIC LACOMET TTBS INTI	BSJ(Na)	Challenge not encountered or challenge not applicable (BSJ)
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.*	IBMETRO NMIC LACOMET TTBS INTI	BSJ(Na)	Challenge not encountered or challenge not applicable (BSJ)
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.*	IBMETRO NMIC LACOMET TTBS INTI	BSJ(Na)	Challenge not encountered or challenge not applicable (BSJ)
Hydride preconcentration/matrix separation of volatile species. *Coupling of a hydride system to the ETA-AAS and optimization of conditions.*	IBMETRO NMIC LACOMET TTBS	BSJ(Na)	Challenge not encountered or challenge not applicable (BSJ)

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
	INTI		
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	Preparation of calibration curves is from 100 ppm solutions, so there were several dilutions to achieve a proper concentration for preparation of the standards. The balance is calibrated and under metrological control. Adjustment of instrument with Cupper solution to achieve the correct characteristic concentration, according manufacturer recommendations (only for sodium using FAES (IBMETRO) AAS – IC: bracketing external calibration. Calibration solutions corresponds to 0.5 % nitric acid for AA and for IC the final concentration was 0.1 % (NMIC) Standard addition Calibration. A mix of $Mg(NO_3)_2$ + $NH_4H_2PO_4$ was used as matrix modifiers (LACOMET) (1) Instrument operated in accordance with Operator's Manual. (2) Good laboratory practices employed in all preparations. (3) All dilutions done by mass (4) Analytical sequence composed which avoids successive samples having large differences in analyte concentration. (BSJ) 5 point calibration of AAS using AA Standards for each analyte. Calibration blank and standards made with 10% HNO3 to minimize interferences (TTBS)
Signal detection *The detection and recording of the absorption signals of analytes. The degree of difficulty increases for analytes present at low concentrations, of low atomic absorption coefficient. Requires selection of operating conditions such as light source, absorption line, Zeeman background correction conditions. Includes selection of signal processing conditions (peak area or height).*		All	AAS: light source to 589.00 nm IC: Signal processed by area (NMIC) Background reduction / quieting procedures applied. E.g. running multiple trial blanks prior to analysis of samples and low level standards. (BSJ) The Lab's AAS had been recently serviced to repair skewed mirrors. This presented a challenge for the determination of the metal analytes, in particular, Sr and Pb. The PT could not be completed because of this reason. (TTBS)
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*	LACOMET TTBS	IBMETRO (Cu) NMIC (Na) BSJ(Na)	There was a memory effect during measurements of samples and reference materials. The measurements of blank repeatedly until the signals is approximately "0" (IBMETRO) Clean of introduction sample system between samples with nitric acid. (NMIC) (1) Analytical sequence composed which avoids successive samples having large differences in analyte concentration (2) Background reduction / quieting procedures applied. E.g. running multiple trial blanks prior to analysis of samples

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
			and low level standards. (BSJ)
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.*	NMIC (Na) TTBS INTI	IBMETRO (Cu) LACOMET BSJ(Na)	Recommended conditions of manufacturer (taken from cook book) were used. (IBMETRO) Challenge not encountered or challenge not applicable (BSJ)
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.*	TTBS	IBMETRO NIMC LACOMET BSJ INTI	Recommended conditions of manufacturer (taken from cook book) were used. For lead a matrix modifier was used ($NH_4H_2PO_4$ and $Mg(NO_3)_2$). For copper also a matrix modifier was used ($Mg(NO_3)_2$ and $Pb(NO_3)_2$) (IBMETRO) AAS: deuterium lamp correction (NMIC) Addition of KCl (high purity) as ionic suppression (LACOMET) Challenge not encountered or challenge not applicable (BSJ)