Final Report of the SIM.QM-S8 Supplementary Comparison

Trace Metals in Drinking Water

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Authors:

Lu Yang (NRC)[1], Kenny Nadeau (NRC)[1], Indu Gedara Pihillagawa (NRC)[1], Juris Meija (NRC)[1], Zoltan Mester (NRC)[1], Romina Napoli (LATU)[2], Ramiro Pérez Zambra (LATU)[2], Elizabeth Ferreira (LATU)[2], Diego Alejandro Ahumada Forigua (NMIC)[3], Johanna Paola Abella Gamba (NMIC)[3]

[1] National Research Council Canada, Canada
[2] Laboratorio Tecnológico del Uruguay, Uruguay
[3] Instituto Nacional de Metrología de Colombia, Colombia

Coordinated by:

Lu Yang (NRC): Lu.yang@nrc-cnrc.gc.ca
Zoltan Mester (NRC)

Abstract

After completing a supplementary comparison SIM.QM-S7, the National Metrology Institute of Colombia (INMC) requested to National Research Council of Canada (NRC) a subsequent bilateral comparison, because INMC considered that its results in SIM.QM-S7 unrepresentative of its standards. In this context, NRC agreed to coordinate this bilateral comparison with the aim of demonstrating the measurement capabilities of trace elements in fresh water. Participants included INMC and LATU. No measurement method was prescribed by the coordinating laboratory. Therefore, NMIs used measurement methods of their choice. However, the majority of NMIs/DIs used ICP-MS.

This SIM.QM-S8 Supplementary Comparison provides NMIs 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. After completing a key comparison SIM.QM-S7 (2016), the National Metrology Institute of Colombia (NMIC) requested to National Research Council of Canada (NRC) a subsequent bilateral comparison, because NMIC considered that its results in SIM.QM-S7 unrepresentative of its standards. In this context, NRC agreed to coordinate this supplementary comparison with the aim of demonstrating the measurement capabilities of trace elements in fresh water of the NMI participants, which provides NMIs with the needed evidence for CMC claims for trace elements in fresh waters and similar matrices.

Table 1. Timetable of SIM.QM-S8

Dec. 2016	Proposal agreed by IAWG chair
Jan.20, 2017	Call for participating
Jan. 23, 2017	Registration deadline
Jan. 24, 2017	Shipment of the samples
Mar. 03, 2017	Deadline for receipt of data
Mar. 31, 2017	Circulation of preliminary results
April 2017	Results presentation at CCQM IAWG
May 15, 2017	Draft A
Sept., 2017	Second results presentation at CCQM IAWG
Nov., 2017	Draft B

The participation is limited to the two additional laboratories which have approached NRC for this comparison (LATU and NMIC). 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-S8 Supplementary Comparison.

Table 2. Measurands

Measurand	Target Concentration
Ni	0.05 - 5.0 µg/kg
Zn	0.1 – 10 µg/kg
Mg	0.1 – 10 mg/kg
Ca	0.1 – 50 mg/kg

2. Participants

Three NMIs have registered for the SIM.QM-S8 Supplementary Comparison and reported their results, as shown in Table 3.

Table 3. SIM.QM-S8: List of participating institutes

Lab Number	Institute	Country	Results reported	Reporting date
01	NMIC	Colombia	Ni, Zn, Mg, Ca	Mar. 03, 2017
02	LATU	Uruguay	Ni, Zn, Mg	Feb. 24, 2017

3. Results and Discussion

Tables 4-8 summarize results reported by participants for Ni, Zn, Mg and Ca, respectively.

Table 4. SIM.QM-S8: Reported results for mass fraction of Ni

Institute	Country	Reported value µg/kg	$u(w_{\mathrm{Ni}})$ µg/kg	$U(w_{\mathrm{Ni}})$ µg/kg	Method
NMIC	Colombia	0.440	0.028	0.055	EC and SA ICPMS
LATU	Uruguay	0.471	0.007	0.014	ID ICP-SFMS

Table 5. SIM.QM-S8: Reported results for mass fraction of Zn

Institute	Country	Reported value µg/kg	$u(w_{\mathrm{Zn}})$ µg/kg	$U(w_{\mathrm{Zn}})$ µg/kg	Method
NMIC	Colombia	1.06	0.050	0.10	EC and SA ICPMS
LATU	Uruguay	1.016	0.021	0.042	ID ICP-SFMS

Table 6. SIM.QM-S8: Reported results for mass fraction of Mg

Institute	Country	Reported value mg/kg	$u(w_{\mathrm{Mg}})$ mg/kg	$U(w_{\mathrm{Mg}})$ mg/kg	Method
NMIC	Colombia	1.910	0.030	0.060	EC-IC and EC-FAAS
LATU	Uruguay	1.926	0.018	0.036	SA ICPOES

Table 7. SIM.QM-S8: Reported results for mass fraction of Ca

Institute	Country	Reported value mg/kg	$u(w_{\mathrm{Ca}})$ mg/kg	$U(w_{\mathrm{Ca}})$ mg/kg	Method
NMIC	Colombia	8.16	0.12	0.24	EC-IC EC-FAAS

3.1. Supplementary Comparison Reference Values (SCRVs)

As documented in the Technical protocol for the SIM.QM-S8, this is a bilateral comparison, thus results from NMIC and LATU are compared to NRC values. The Supplementary Comparison Reference Values (SCRVs) are based on only NRC results which were obtained by ID HR-ICPMS for Ni, Mg and Zn, and standard addition calibration ICPOES for Ca, shown in Table 8.

Table 8. SIM.QM-S8 SCRV, *u*(SCRV) and *U*(SCRV) and U_r(SCRV)

Measurand	SCRV	*u*(SCRV)	*U*(SCRV)	U_r(SCRV),%
Ni, µg/kg	0.458	0.007	0.014	3.1
Zn, µg/kg	0.992	0.023	0.046	4.6
Mg, mg/kg	1.908	0.030	0.060	3.1
Ca, mg/kg	8.25	0.095	0.19	2.3

As suggested by members at the CCQM IAWG meeting in Paris on April 24-25, 2017, more supporting data to the SCRVs should be provided. It is evident that results obtained from the second method are in agreement with the assigned SCRVs which are based on the NRC's data of ID ICP-SFMS for Ni, Zn, Mg and standard addition ICPOES for the Ca, as shown in Table 9, confirming the accuracy of the results. In addition, results obtained from all participants are in agreement with the SCRVS within the reported uncertainties.

Table 9. Results obtained in SIM.QM-S8 using the second method

Measurand	Mass fraction	*u*	Method
Ni, µg/kg	0.469	0.051	Standard addition QQQ-ICPMS
Zn, µg/kg	1.040	0.087	Standard addition QQQ-ICPMS
Mg, mg/kg	1.988	0.041	Standard addition QQQ-ICPOES
Ca, mg/kg	8.27	0.14	Standard addition ICP-SFMS

3.2. Measurand mass fraction results

The reported results for Ni, Zn, Mg and Ca are presented in Figures 1-4. SCRVs and uncertainties are based on NRC's results using ID ICP-SFMS for Ni, Zn and Mg, and standard additions ICPOES for Ca.

Figure 1. Results for SIM.QM-S8 mass fraction of Ni µg/kg (*u*, *k* = 1)

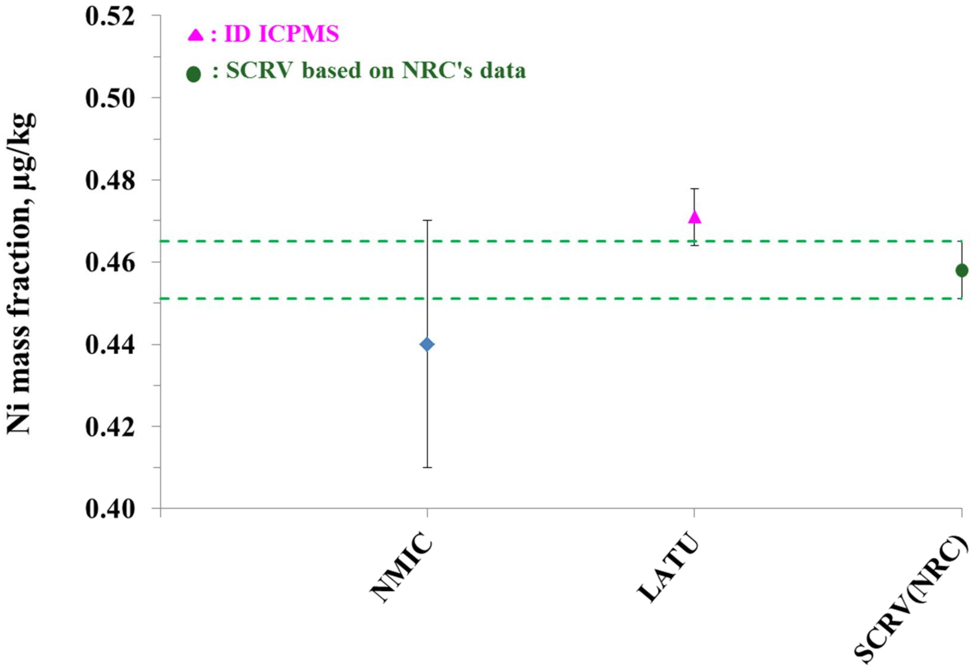


Figure 2. Results for SIM.QM-S8 mass fraction of Zn µg/kg (*u*, *k* = 1)

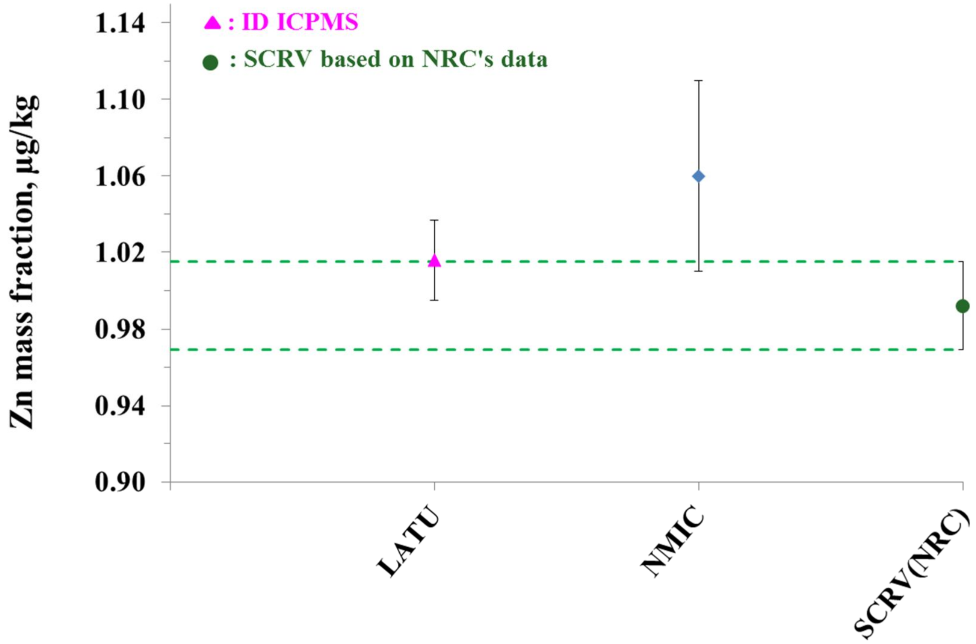


Figure 3. Results for SIM.QM-S8 mass fraction of Mg, mg/kg (*u*, *k* = 1)

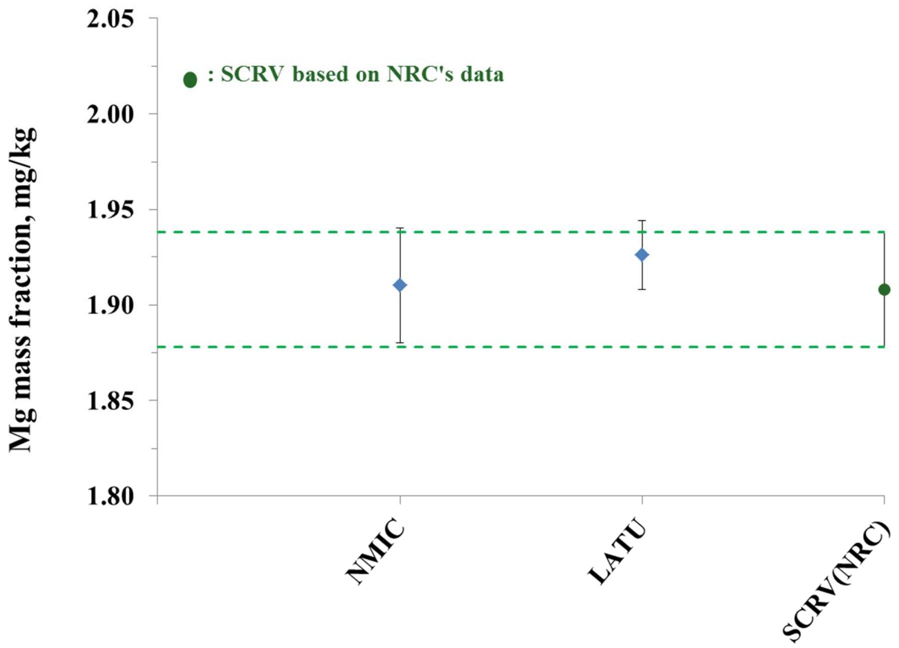
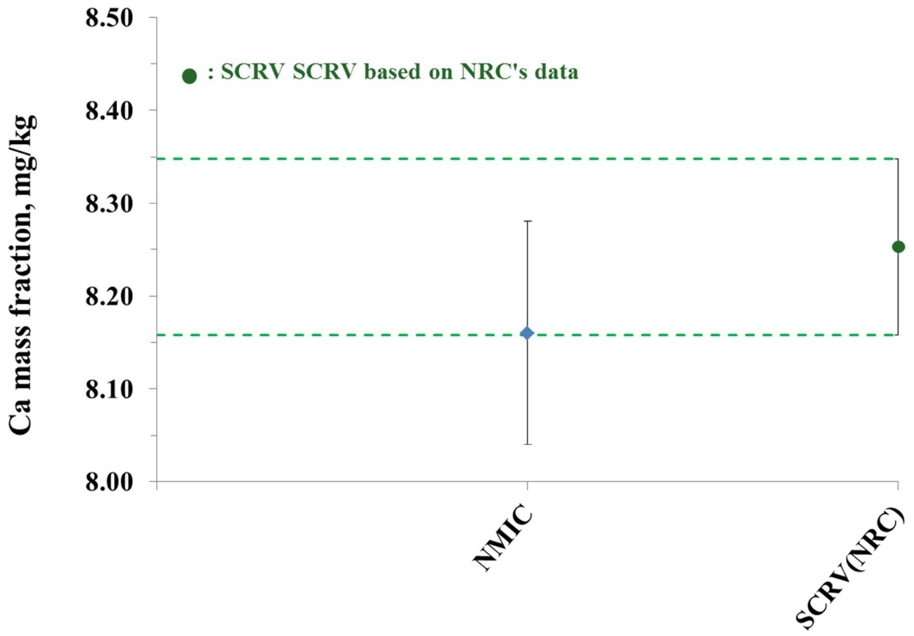


Figure 4. Results for SIM.QM-S8 mass fraction of Ca, mg/kg (*u*, *k* = 1)



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 are calculated using the following Eq. 3-4. Results are presented in Table 10.

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

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

Table 10. SIM.QM-S8: Equivalence statements

Measurand	Institute	Country	d_i	U(d_i	|d_i/U(d$_\mathrm{i}$)|
Ni, µg/kg	NMIC	Colombia	-0.018	0.062	0.40
	LATU	Uruguay	0.013	0.020	0.63
Zn, µg/kg	LATU	Uruguay	0.024	0.062	0.20
	NMIC	Colombia	0.068	0.11	0.52
Mg, mg/kg	LATU	Uruguay	0.002	0.085	0.17
	NMIC	Colombia	0.018	0.070	0.31
Ca, mg/kg	NMIC	Colombia	-0.093	0.31	0.30

Figure 5. Equivalence statement for SIM.QM-S8 Ni

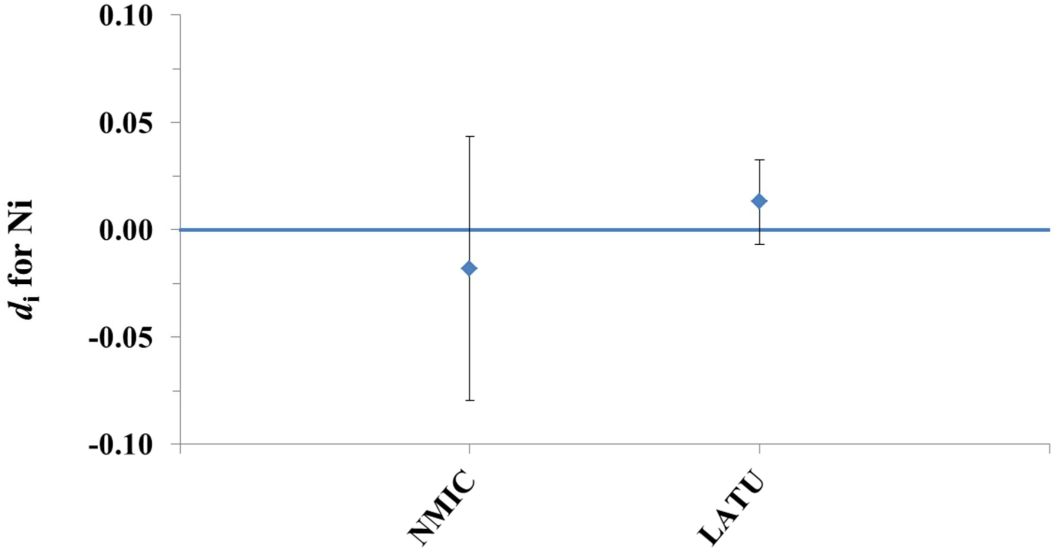


Figure 6. Equivalence statement for SIM.QM-S8 Zn

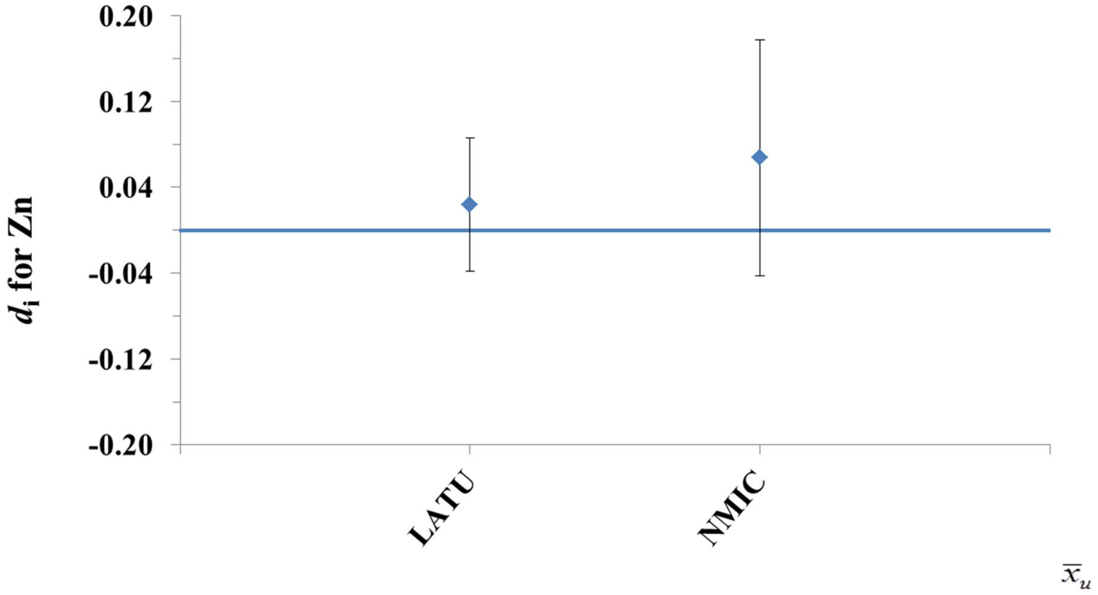


Figure 7. Equivalence statement for SIM.QM-S8 Mg

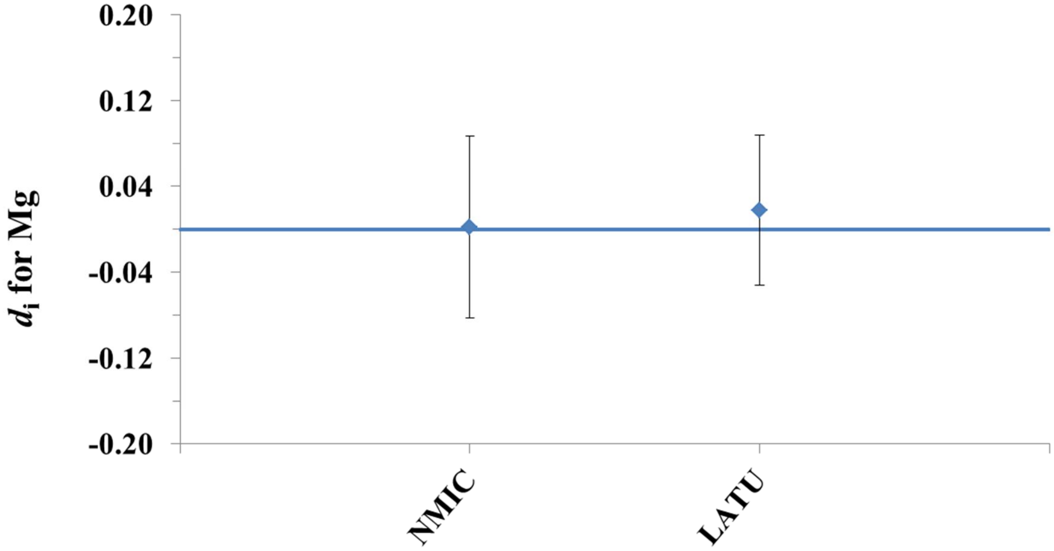
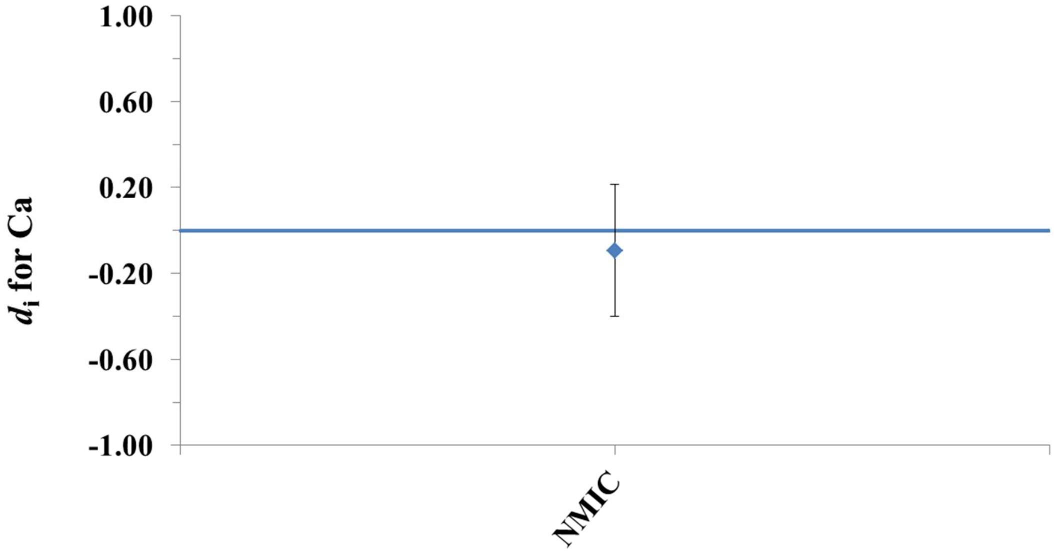


Figure 8. Equivalence statement for SIM.QM-S8 Ca



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-S8 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-S8 is a successful supplementary comparison, as indicated by results from all NMIs/DIs are in agreement with the SCRVs with their expanded uncertainties.

6. Acknowledgements

Dr. Mike Sargent is thanked for his support and advice during the SIM.QM-S8. Dr. Patricia Grinberg is thanked for ensuring the shipping of the materials to the participants.

Appendix A

Inorganic Core Capabilities
Summary Table

CCQM Study: SIM.QM-S8, Trace Metals in Drinking Water

Institute(s): NRC and LATU

Method: ID-ICP-MS

Analyte(s): Ni, Zn and Mg

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.*		NRC (Ni, Zn, Mg) LATU (Ni, Zn)	High purity acids used and bank subtracted (NRC) Samples and calibrants were prepared using high purity nitric acid (in-house sub-boiling distilled) in an ISO 14644-1 Class 6 cleanroom to avoid contamination (LUTA)
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		
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		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	NRC LATU		
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		
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		
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*	NRC LATU		

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
procedures, but not vapor generation procedures.			
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample.*		NRC LATU	
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.*		NRC (Ni, Zn, Mg) LATU (Ni, Zn)	Signal is adequate (NRC) Both, Ni and Zn were present in the sample at low levels. (LATU)
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		NRC (Ni, Zn, Mg) LATU (Ni, Zn)	
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.*		NRC (Ni, Zn, Mg) LATU (Ni, Zn)	MR was used for Ni and Zn, HR was used for Mg. (NRC) For Ni and Zn medium resolution (R>4000) was used to resolve interferences.
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*		NRC (Ni, Zn, Mg) LATU (Ni, Zn)	
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*		NRC (Ni, Zn, Mg) LATU (Ni, Zn)	
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution.*		NRC (Ni, Zn, Mg) LATU (Ni, Zn)	Exact matching IDMS

Inorganic Core Capabilities
Summary Table

CCQM Study: SIM.QM-S8, Trace Metals in Drinking Water

Institute(s): NMIC

Method: ICPMS (without ID)

Analyte(s): Ni and Zn

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.*		Ni, Zn	Efforts to control and check
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.*	blank level.		
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.*	Ni, Zn		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	Ni, Zn		
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.*	Ni, Zn		
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.*	Ni, Zn		
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.*	Ni, Zn		
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		Ni, Zn	Standard addition and external matrix matched calibration
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.*		Ni, Zn	Measurements of ^{58}Ni, ^{60}Ni and ^{64}Zn, ^{66}Zn. Rh was internal standard
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		Ni, Zn	Clean of introduction sample system between samples with nitric acid.
Correction or removal of isobaric/polyatomic interferences *Any techniques used to remove, reduce, or mathematically correct for interferences caused by mass*		Ni, Zn	Use of KED with helium

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
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.			
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.*	Ni, Zn		
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	Ni, Zn		
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	Ni, Zn		

CCQM Study: SIM.QM-S8, Trace Metals in Drinking Water

Institute(s): NRC and LATU

Method: ICP-OES

Analyte(s): Mg and 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.*		LATU (Mg)	
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.*	LATU (Mg)		
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.*	LATU (Mg)		
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	NRC (Ca) LATU (Mg)		
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.*	LATU (Mg)		
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.*	LATU (Mg)		
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.*	LATU (Mg)		
Calibration of analyte concentration *The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.*		LATU (Mg)	Standard additions calibration

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
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..*		LATU (Mg)	
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		LATU (Mg)	
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.*		LATU (Mg)	
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.*		NRC (Ca) LATU (Mg)	Standard additions calibration was used

Inorganic Core Capabilities
Summary Table

CCQM Study: SIM.QM-S8, Trace Metals in Drinking Water

Institute(s): NIMC

Method: ETA-AAS (or GF-AAS)

Analyte(s): Ca and Mg

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Contamination control and correction *All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.*		Ca, Mg	Blank evaluation in each batch and correction for AA. Degree of Difficulty: low
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.*	Ca, Mg		
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.*	Ca, Mg		The sample was diluted in the pure deionized water by gravimetric method for IC and nitric acid for AA.
Volatile element containment *All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.*	Ca, Mg		
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.*	Ca, Mg		
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.*	Ca, Mg		
Hydride preconcentration/matrix separation of volatile species. *Coupling of a hydride system to the ETA-AAS and optimization of conditions.*	Ca, Mg		
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.*		Ca, Mg	AAS – IC: bracketing external calibration. Calibration solutions corresponds to 0.5 % nitric acid for AA and for IC the final concentration was 0.01 %
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*		Ca, Mg	AAS: light source to 589.00 nm IC: Signal processed by area.

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
signal processing conditions (peak area or height).			
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.*		Ca, Mg	Clean of introduction sample system between samples with nitric acid for AA
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.*	Ca, Mg		
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.*		Ca, Mg	AAS: deuterium lamp correction