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SIM-QM-S2 Supplemental

Trace Elements in Drinking Water

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Table of Contents

Introduction	3
Sample preparation.....	4
Homogeneity Study.....	5
Reference Value	6
Participants and Sample Distribution	7
Methods	8
Results	11
Equivalence Statements	16
Conclusions	22
Appendix 1. Protocol	
Appendix 2. Core Capabilities	

Introduction

This exercise was intended to address laboratory capability for the determination of trace elements in drinking water. SIM.QM.S2 and the corresponding pilot SIM.QM.P22 are follow-up studies to two SIM intercomparison exercises SIM 8.10P, Part I and Part II, organized in 2003 and 2004 and coordinated by NRC Canada. Seventeen laboratories participated in both Part I and Part II. Following each of these two exercises the results were discussed by the participants at SIM workshops in Costa Rica (February 2004) and Margarita Is. Venezuela (November 2004).

In order to support CMC submissions for several SIM members, SIM.QM.S2 was planned in 2008 and authorized as a Supplemental Exercise at the April 2010 meeting of the Inorganic Analysis Working Group (IAWG) of the Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM).

Table 1. Timeline for SIM.QM.S2 and SIM.QM.P22

October, 2008	Project discussed and authorized at SIM CMWG, Honduras
April 2010	Protocol submitted to IAWG, CCQM
July 9, 2010	Deadline for registration
July 2010	Shipment of the samples
January 7, 2011	Deadline for receipt of results

The target analytes were chosen to be Ni, Cd, Pb and Ca. Target concentrations were selected to be at or near the World Health Organization Guidelines for Drinking-water Quality¹. Calcium was included in this study to permit laboratories to participate that may not have suitable instrumentation to determine the other analytes at the low target concentrations. Although there is no WHO health-based guideline value for Ca, it may affect drinking water acceptability in terms of taste, hardness and scale deposition.

Table 2. WHO Guidelines for Drinking Water

Element	WHO Guideline value ¹
Ni	0.07 mg/litre
Cd	0.003 mg/litre
Pb	0.01 mg/litre
Ca	none

Sample Preparation

The initial plan entailed use of an untreated river water sample as a source of drinking water. However, it was subsequently decided to use high purity laboratory water as the matrix permitting accurately determined gravimetric spikes to be used as the reference values.

A precleaned 20 L polyethylene carboy was partially filled with high purity water. This water was treated by reverse osmosis followed by a final ion exchange treatment using a Milli-Q® Element Water Purification System. Based on NRC's previous experience preparing natural water CRM's, the water was acidified to pH 1.6 to stabilize the analytes. High purity sub-boiled distilled nitric acid prepared in-house using a Milestone DuoPur Acid Still was used to adjust the pH. No stability issues are expected with these samples. Several 250 ml aliquots were removed for baseline analysis of the sample prior to addition of the analyte spikes.

Table 3 summarizes the sources and purity of the spikes added to the sample. High purity Cd and Pb metal are NRC primary standards of established purity and provide traceability to the SI through a comprehensive analysis at NRC using Glow-Discharge Mass Spectrometry (GD-MS). This technique enables the detection of impurities from almost all elemental constituents at the ng/g mass fraction. Calibration of the GD-MS is achieved against international CRMs. For Ni, a sample distributed by BAM for CCQM P62 was used for spiking; the purity reported in Table 3 was determined by NRC GD-MS. NIST SRM 3109a (Lot 050825) was used as the spiking solution for Ca.

Table 3. Source and Purity of Spiking Solutions

Mesureand	Source	Purity ± U (k=2)
Ni metal	CCQM P62	99.9972 ± 0.0068 %
Cd metal	NRC Primary Standard	99.99993 ± 0.00018 %
Pb metal	NRC Primary Standard	99.9993 ± 0.0018 %
Ca solution	NIST SRM 3109a	10.025 ± 0.017 mg/g

Individual primary standard solutions (approximately 1000 ug/g) of Ni, Cd and Pb were prepared by dissolving the surface cleaned metal in high purity nitric acid. The mass fractions of the resulting solutions were determined according to Equation 1.

$$w = p \cdot \frac{\text{Bu(A)}}{\text{Bu(S)}} \cdot \frac{m_2 - m_1}{m_4 - m_3} \quad (1)$$

Where:

w is the mass fraction of the analyte in solution

p is the purity of the metal

m₁ is the mass of the weighing boat

m₂ is the mass of the weighing boat + metal

m₃ is the mass of the empty bottle

m₄ is the mass of the empty bottle + solution

Bu (A) – is the buoyancy correction factor for the mass of metal
Bu(S) – is the buoyancy correction factor for the mass of solution

Weighed aliquots of the individual primary standard solutions were added to the carboy to achieve concentrations within the proposed target levels listed in Table 4. A Mettler Toledo AG245 analytical balance was used to weigh the stock solutions. A Sartorius Signum 2 balance (capacity 65 kg) was used to weigh the carboy. The balances were calibrated through weights calibrated by the NRC INMS Mass Standards Group.

The associated uncertainty accounts for purity of the spikes, uncertainty in weighing (repeatability, linearity) and buoyancy corrections including air density estimations.

Table 4. Target Concentrations

Element	Target Concentration
Cd	1 - 5 µg/kg
Ni	50 - 80 µg/kg
Pb	5 - 30 µg/kg
Ca	5 - 25 µg/g

The contents of the carboy were well mixed and 130 precleaned 125 ml polyethylene bottles were filled. The sequence of bottle filling was recorded.

Homogeneity study

The between bottle homogeneity was evaluated according to the recommendation of ISO Guide 35.² The prepared sample was tested for homogeneity at NRCC using ID-ICP-MS for Cd, Pb and Ni, and ICPAES for Ca. Results from ten bottles were evaluated using ANOVA.

No between bottle differences were detected for any of the analytes. Equation 2 can be used as the best estimate of maximum between bottle variability (u_{bb}) when the repeatability standard deviation does not indicate potential between unit variations.

$$u_{bb} = \sqrt{\frac{MSW}{n}} \sqrt[4]{\frac{2}{v_{MSW}}} \quad (2)$$

Where:

MSW – mean squares within units

n – measurements per unit

v_{MSW} – degrees of freedom for MSW

The values of u_{bb} using equation 2 were <0.35% RSD for all measurands. NRC has many years of experience preparing natural water CRMs with analyte concentrations several orders of magnitude lower than the target concentrations of this SIM study.

Based on this experience and the above results, a contribution to the uncertainty budget due to homogeneity can reasonably be assumed to be insignificant compared to the final uncertainty and was not considered further.

Reference Value

The reference value for this study was equated to the gravimetric amount content and calculated from the gravimetric spike addition to the acidified water. Equation 1 was used for this calculation, again taking into account buoyancy correction factors. The results from the gravimetric calculations are summarized in Table 6. The associated uncertainty (u_{spike}) accounts for purity of the spikes, uncertainty in weighing (repeatability, linearity) and buoyancy corrections, including air density estimations.

In addition to the added spike, the “blank” contribution from the unspiked matrix was also included in the final reference value, i.e.,

$$x_R = x_{\text{spike}} + x_0 \quad (3)$$

Where:

x_R – is the reference value

x_{spike} – is the mass fraction due to the gravimetric spike

x_0 – is the endogenous mass fraction due to the unspiked matrix (carboy blank)

In order to determine x_0 several samples of acidified water were removed from the carboy prior to spiking for determination of Cd, Pb and Ni by ICP-MS and Ca by ICPAES. The carboy blank for Ca was found to be 0.0010 ± 0.0002 ug/g and considered negligible for this study. For Ni, Cd and Pb, the signal intensities from the x_0 sample were similar to background levels. Repeat measurements of the x_0 sample were compared to a freshly prepared pH 1.6 blank; no significant difference was found based on a t-test. The concentration of Ni, Cd and Pb in the unspiked solution was assigned as equal the LOD, based on 3 times the SD of repeat measurements of x_0 . No contribution to the gravimetric mean value was considered necessary. However, an uncertainty associated with the LOD (u_0) was included in the calculation of the reference value. A rectangular distribution of half the calculated LOD was used as an estimate for u_0 .

$$u_0 = \frac{\text{LOD}/2}{\sqrt{3}} \quad (4)$$

Thus for Ni, Cd and Pb, the combined uncertainty of the reference value (U_{RV}) incorporates both the uncertainty from the gravimetric addition of the spike and the uncertainty in the determination of the carboy blank. Results are presented in Table 5.

$$U_{RV} = 2 \cdot \sqrt{(u_{\text{spike}})^2 + (u_0)^2} \quad (5)$$

Table 5. Calculation of the Reference Value

Element	Gravimetric		Carboy Blank	$U_{RV, (k=2)}$
	Result	U_{spike}	u_o	
Ni, ng/g	68.61	0.12	0.013	0.25
Cd, ng/g	4.04	0.014	0.003	0.03
Pb, ng/g	24.22	0.08	0.007	0.16
Ca, ug/g	8.84	0.015	0.0002	0.03

Participants and Sample Distribution

Two samples were shipped to participants listed in Table 6 on July 29 and 30, 2010. An email notification stating the courier waybill number was sent to the laboratory contact. In a few cases, the samples were delayed in customs, but generally delivery was made within a few days. The protocol distributed with the samples is presented in Appendix 1. All SIM.QM.S2 participants were also requested to complete a core capabilities matrix. Appendix 2 contains this data.

Table 6. Participants for SIM.QM.S2

Institute	Country	Contact
INTI – Instituto Nacional de Tecnologia Industrial	Argentina, SIM	Liliana Valiente Margarita Piccinna Lorena Iribarren
INMETRO – Instituto Nacional de Metrologia, Normalização e Qualidade Industrial	Brazil, SIM	Rodrigo Caciano de Sena Lindomar A. dos Reis Lílian da Silva Marcelo Dominguez de Almeida Maria Cristina B. Quaresma Monique G. de Mello Renata Souza e Silva
NRC – National Research Council	Canada, SIM	Zoltan Mester Lu Yang Christine Brophy Scott Willie
GL – Government Laboratory	Hong Kong, China APMP	Dr. Alvin Wai hong Fung
CENAM – Centro Nacional de Metrologia	Mexico, SIM	Dr. Yoshito Mitani M. Sc. Edith Valle Moya M. Sc. María del Rocío Arvizu Torres M. Sc. Griselda Rivera Sanchez B. Sc. J. Velina Lara Manzano

Institute	Country	Contact
INDECOPI – Instituto Nacional de Defensa de la Competencia y de la Proteccion de la Propiedad Intelectual	Peru, SIM	Christian Uribe Galia Ticona Steve Acco
INM(RO) – National Institute of Metrology	Romania, EURAMET	Mirella Buzoianu
VNIIM – D. I. Mendeleev Institute for Metrology	Russian Federation, COOMET	Leonid A. Konopelko M. Bezruchko
HSA – Health Sciences Authority	Singapore, APMP	Dr Richard Shin Dr Tong Kooi Lee
NIMT – National Institute of Metrology of Thailand	Thailand, APMP	Pranee Phukphatthanachai Charun Yafa
UME – Tubitak Ulusal Metrologi Enstitüsü	Turkey	Prof. Dr. Oktay Cankur Dr. F. Gonca Coşkun Emrah Uysal Murat Tunç

Methods

Results from eleven laboratories were received for SIM.QM.S2 prior to the deadline of January 7, 2010. The methods used by the participants are listed in Table 7. INMETRO submitted Ca results from pooled data from different instrumental methods and was given the opportunity to identify one set for inclusion in the SIM.QM.S2 exercise with the other results included into the pilot P22 exercise.

Table 7. Participant Methods for SIM.QM.S2

Element	Method	Traceability
INTI		
Ni	ETAAS, external calibration	NIST SRM 3136, NIST 1643e
Cd	ETAAS, external calibration	NIST SRM 3108 NIST 1643e
Pb	ETAAS, external calibration	NIST SRM 3128 NIST 1643e
Ca	FAAS, external calibration	NIST SRM 3109a NIST 1643e

Element	Method	Traceability
INMETRO		
Ni	ICPMS, ⁶⁰ Ni measured, sample 10 x dilute, external calibration	NIST SRM 3136, INMETRO CRM 05.1/08.0001
Cd	ICPMS, ¹¹⁴ Cd measured, external calibration	NIST SRM 3108, INMETRO CRM 05.1/08.0001
Pb	ICPMS, isotope dilution	NIST SRM 991 (²⁰⁶ Pb), INMETRO CRM 05.1/08.0001
Ca	FAAS, 422.7 nm, air-acetylene flame, external calibration	NIST SRM 3109a, 1643e
NRC		
Ni	ICP-SFMS, ⁶⁰ Ni/ ⁶¹ Ni measured, sample 10 x dilute, isotope dilution medium resolution	NRC Ni primary standard
Cd	ICP-SFMS, ¹¹⁴ Cd/ ¹¹¹ Cd measured, isotope dilution	NRC Cd primary standard
Pb	ICP-SFMS, ²⁰⁸ Pb/ ²⁰⁷ Pb measured, sample 10 x dilute, isotope dilution	NRC Pb primary standard, NIST SRM 981
Ca	ICPAES, external calibration	NRC CaCO ₃ primary standard
HKGL		
Ni	ICP-HRMS, medium R, ⁶⁰ Ni, ⁶² Ni measured, Sc, Rh internal standard, gravimetric standard addition calibration	NIST SRM 3108, NIST SRM 1643e
Cd	ICP-HRMS, Low R, ¹¹¹ Cd, ¹¹⁴ Cd measured, Rh, Tb, Ho internal standard, gravimetric standard addition calibration	NIST SRM 3108, NIST SRM 1643e
Pb	ICP-HRMS, Low R, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb measured, Tb, Ho internal standard, gravimetric standard addition calibration	NIST SRM 3128, NIST SRM 1643e
Ca	ICP-OES, 317.933 nm measured, Lu, Sc internal standard, gravimetric standard addition calibration	NIST SRM 3109a, NIST SRM 1643e
CENAM		
Ni	Exact matching double Isotope dilution with SFICPMS, ⁶⁰ Ni/ ⁵⁸ Ni, ⁶⁰ Ni/ ⁶¹ Ni, ⁶⁰ Ni/ ⁶² Ni, ⁶⁰ Ni/ ⁶⁴ Ni measured	CENAM DMR – 465a
Cd	Exact matching double Isotope dilution with SFICPMS, ¹¹¹ Cd/ ¹¹⁰ Cd, ¹¹¹ Cd/ ¹¹² Cd, ¹¹¹ Cd/ ¹¹³ Cd, ¹¹¹ Cd/ ¹¹⁴ Cd measured	CENAM DMR 461a
Pb	Exact matching double Isotope dilution with SFICPMS, ²⁰⁴ Pb/ ²⁰⁶ Pb, ²⁰⁶ Pb/ ²⁰⁷ Pb and ²⁰⁶ Pb/ ²⁰⁸ Pb measured	NIST SRM 981
Ca	Exact matching double Isotope dilution with SFICPMS, ⁴² Ca/ ⁴³ Ca, ⁴² Ca/ ⁴⁴ Ca measured	B07 Slovak Institute of Metrology
INDECOPI		
Ni	ETAAS, bracketing external calibration	NIST SRM 3136
Cd	ETAAS, bracketing external calibration	NIST SRM 3108
Pb	ETAAS, bracketing external calibration	NIST SRM 3128

Element	Method	Traceability
Ca	FAAS, bracketing external calibration	NIST SRM 3109a
INM		
Ni	ICPMS, ⁶⁰ Ni measured, external calibration	NIST SRM 3136
Cd	ICPMS, ¹¹⁴ Cd measured, external calibration	BCR and NIST SRM
Pb	ICPMS, ²⁰⁸ Pb measured, external calibration	NIST SRM 3128
Ca	ICPMS, ⁴³ Ca measured, external calibration	NIST SRM 3109a
VIINM		
Ni	ICP-QMS, external calibration	GSO 7442-98
Cd	ICP-QMS, external calibration	GSO 7451-98
Pb	ICP-QMS, external calibration	GSO 7447-98
Ca	ICP-QMS, external calibration	GSO 8065-94
HSA		
Ni	Exact matching isotope dilution with ICP-HR-MS and ICP-MS, ⁶¹ Ni/ ⁶⁰ Ni, ⁶¹ Ni/ ⁶² Ni measured	NIST SRM 3136, NIST SRM 1643e
Cd	Exact matching isotope dilution with ICP-HR-MS and ICP-MS, ¹¹¹ Cd/ ¹¹⁴ Cd, ¹¹¹ Cd/ ¹¹² Cd measured	NIST SRM 3108, NIST SRM 1643e
Pb	Exact matching isotope dilution with ICP-HR-MS and ICP-MS, ²⁰⁸ Pb/ ²⁰⁶ Pb, ²⁰⁷ Pb/ ²⁰⁶ Pb measured	NIST SRM 981, SRM 3128 NIST SRM 1643e
Ca	ICP-OES, 396.85nm measured, standard addition calibration ICP-MS, ⁴⁴ Ca measured, standard addition calibration	NIST SRM 3109a, NIST SRM 1643e
NIMT		
Ni	ICP-QMS, isotope dilution, ⁶⁰ Ni/ ⁶¹ Ni measured, 2x sample dilute	NIST SRM 3136
Cd	ICP-QMS, isotope dilution, ¹¹² Cd/ ¹¹¹ Cd measured, 2x sample dilute	NIST SRM 3108
Pb	ICP-QMS, isotope dilution, ²⁰⁸ Pb/ ²⁰⁶ Pb measured, 2x sample dilute	NIST SRM 3128
Ca	ICP-QMS, isotope dilution, ⁴⁴ Ca/ ⁴² Ca measured, 2x sample dilute	NIST SRM 3109a
UME		
Ni	ICP-HRMS, ⁶⁰ Ni, ⁶¹ Ni, ⁶² Ni measured, standard addition calibration with different dilution factors, In internal standard	NIST SRM 3136
Cd	ICP-HRMS, ¹¹⁰ Cd, ¹¹¹ Cd, ¹¹² Cd, ¹¹⁴ Cd measured, standard addition calibration with different dilution factors, In internal standard	NIST SRM 3108
Pb	ICP-HR MS, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb measured, standard addition calibration with different dilution factors, In internal standard	NIST SRM 3128
Ca	ICP-HR MS, ⁴³ Ca, ⁴⁴ Ca, ⁴⁸ Ca measured, standard addition calibration with different dilution factors, In internal standard	NIST SRM 3109a

Results

The following summarizes data submitted by laboratories for the SIM.QM S2 intercomparison. Triplicate results are listed along with the mean and reported standard uncertainty. Only the mean and associated uncertainty is listed for those laboratories that did not report individual replicates or reported more than three replicates.

The reference value is shown by the dotted line on the graphs and the standard uncertainty of this value indicated by the solid lines. Since the range of the reference value is small the delineation of the graphs is not always sufficient to properly distinguish these lines.

A summary of basic statistics from the submitted data are listed in Table 8.

Table 8. Statistical Analysis of Reported Results.

	Ni, ng/g	Cd, ng/g	Pb, ng/g	Ca, ug/g
Mean	68.59	4.10	24.33	8.58
Standard Dev	1.23	0.27	0.82	0.99
Median	68.68	4.079	24.1	8.873
Reference value ±U(k=2) based on gravimetric data	68.61 ± 0.25	4.04 ± 0.03	24.22 ± 0.16	8.84 ± 0.03

The results from this report were discussed at the April 2011 meeting of the CCQM IAWG in Paris and the SIM CMWG meeting in San Jose Costa Rica in May 2011.

Table 9. Submitted SIM.QM.S2 Results for Nickel

	Mean ng/g	u_c ng/g	k	U ng/g	Replicates, ng/g		
<i>Supplementary S2</i>							
INTI	65.7	1.75	2	3.5			
NIMT	67.7	1.05	2	2.1	67.7	68.3	67.2
UME	68.1	1.0	2	2.0	67.2	68.2	69.0
CENAM	68.5	0.55	2	1.1			
HSA	68.55	0.39	2	0.78			
VNIIM	68.68	1.99	2	3.98			
NRC	68.76	0.75	2	1.50	68.73	68.93	68.63
GLHK	69.2	0.8	2	1.6	69.0	69.2	69.5
INMETRO	69.21	0.405	2	0.81	69.07	69.35	69.21
INDECOPI	69.4	0.65	2	1.3	69.0	69.5	69.7
INM	70.67	2.81	2	5.62	70.47	70.53	71.01

Figure 1: Nickel mass fraction as reported by the SIM.QM.S2 participants. Error bars denote the standard uncertainty as reported. The dotted red line shows the reference value. The solid red lines indicate the range of the standard uncertainty in the reference value.

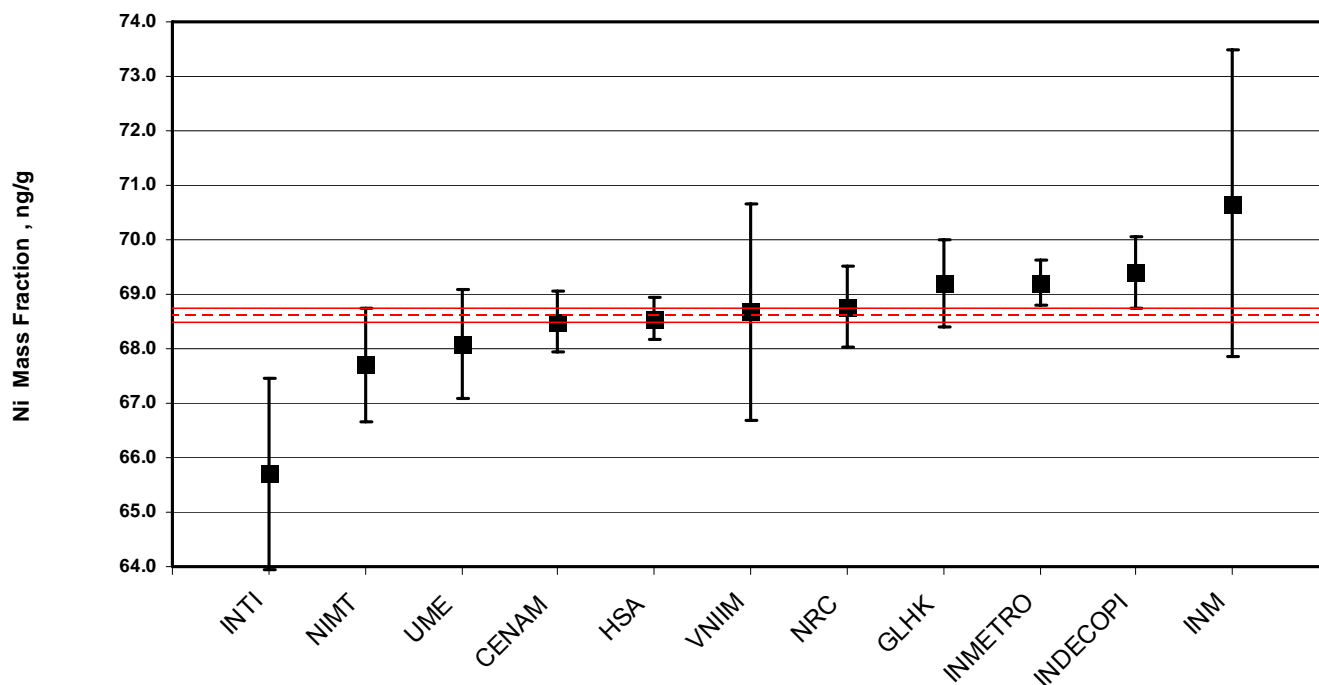


Table 10. Submitted SIM.QM.S2 Results for Cadmium

	Mean ng/g	u_c ng/g	k	U ng/g	Replicates, ng/g		
<i>Supplementary S2</i>							
INTI	3.50	0.15	2	0.29			
INDECOPI	3.976	0.039	2	0.077	3.976	3.995	3.958
GLHK	4.03	0.06	2	0.12	4.00	4.01	4.06
HSA	4.03	0.025	2	0.05			
NRC	4.06	0.04	2	0.08	4.07	4.07	4.05
CENAM	4.079	0.018	2	0.036			
UME	4.09	0.07	2	0.13	4.04	4.07	4.16
NIMT	4.1	0.1	2	0.2	4.1	4.2	4.0
VNIIM	4.189	0.059	2	0.117			
INM	4.503	0.207	2	0.414	4.598	4.515	4.396
INMETRO	4.509	0.032	2	0.063	4.511	4.513	4.505

Figure 2: Cadmium mass fraction as reported by the SIM.QM.S2 participants. Error bars denote the standard uncertainty as reported. The dotted red line shows the reference value. The solid red lines indicate the range of the standard uncertainty in the reference value.

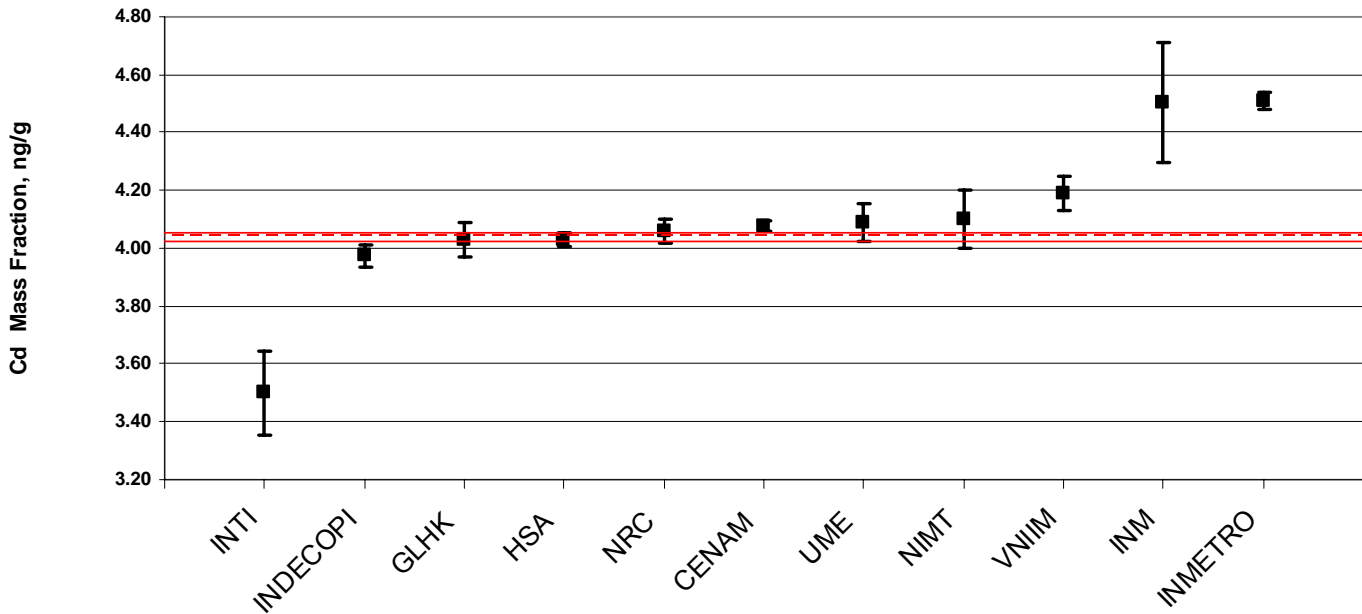


Table 11. Submitted SIM.QM.S2 Results for Lead

	Mean ng/g	u_c ng/g	k	U ng/g	Replicates, ng/g		
<i>Supplementary S2</i>							
VNIIM	23.60	0.36	2	0.71			
NIMT	23.9	0.3	2	0.6	23.9	23.6	24.2
HSA	24.03	0.17	2	0.33			
CENAM	24.07	0.08	2	0.16			
INM	24.10	0.97	2	1.94	23.89	24.80	23.61
UME	24.1	1.05	2	2.1	23.1	24.8	24.2
INDECOPI	24.13	0.23	2	0.46	24.01	24.15	24.24
NRC	24.16	0.29	2	0.57	24.29	24.11	24.08
INMETRO	24.22	0.10	2	0.2	24.23	24.22	24.22
GLHK	24.66	0.31	2	0.62	24.52	24.63	24.81
INTI	26.7	1.50	2	3.0			

Figure 3: Lead mass fraction as reported by the SIM.QM.S2 participants. Error bars denote the standard uncertainty as reported. The dotted red line shows the reference value. The solid red lines indicate the range of the standard uncertainty in the reference value.

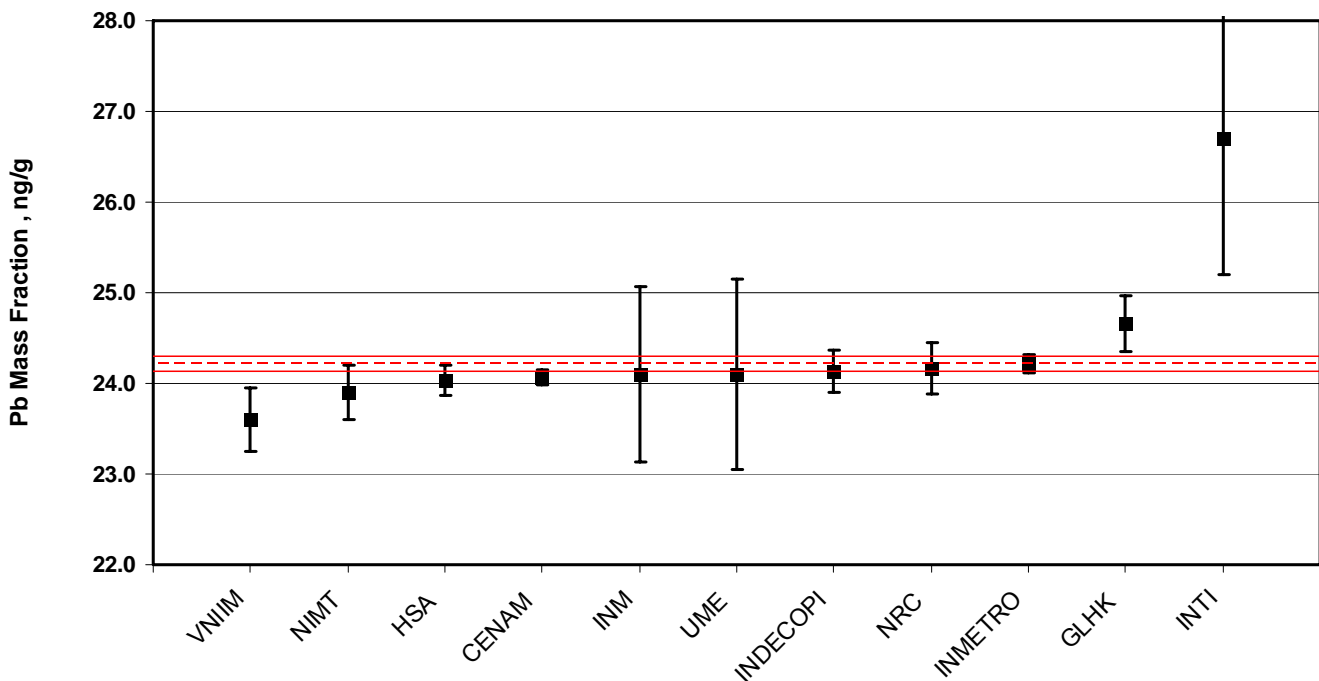
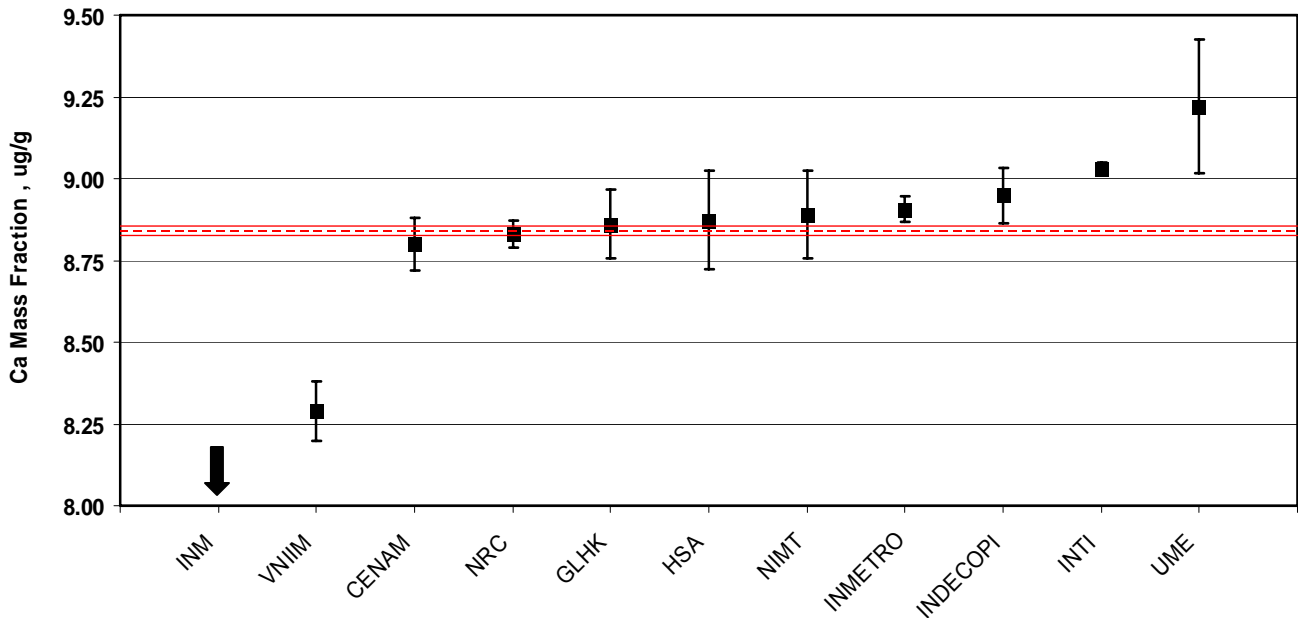


Table 12. Submitted SIM.QM.S2 P22 Results for Calcium

	Mean ug/g	u_c ug/g	k	U ug/g	Replicates, ug/g		
<i>Supplementary S2</i>							
INM	5.684	0.130	2	0.260	5.693	5.626	5.733
VNIIM	8.288	0.091	2	0.182			
CENAM	8.80	0.08	2	0.16			
NRC	8.83	0.04	2	0.08	8.83	8.82	8.84
GLHK	8.86	0.105	2	0.21	8.79	8.84	8.96
HSA	8.873	0.1515	2	0.303			
NIMT	8.89	0.135	2	0.27	8.89	8.91	8.88
INMETRO	8.907	0.04	2	0.08	8.909	8.985	8.828
INDECOPI	8.95	0.085	2	0.17	8.94	8.91	8.99
INTI	9.030	0.0195	2	0.039			
UME	9.22	0.205	2	0.41	9.03	9.30	9.32

Figure 4: Calcium mass fraction as reported by the SIM.QM.S2 participants. Error bars denote the standard uncertainty as reported. The dotted red line shows the reference value. The solid red lines indicate the range of the standard uncertainty in the reference value.



Equivalence Statements

Degree of equivalence (D_i) calculations were performed using equations 5 and 6.

ISO Guide 35:2006 Reference materials -- General and statistical principles for certification

$$D_i = (x_i - x_R) \quad (5)$$

and

$$U_i = 2 \cdot \sqrt{u_i^2 + u_R^2} \quad (6)$$

where:

D_i – is the difference between the reported value and the reference value

x_i – is the reported value

x_R - is the reference value

U_i – is the expanded uncertainty ($k=2$) of the difference

u_i – is the reported measurement standard uncertainty

u_R – is the standard uncertainty associated with x_R

As the reference value was calculated from gravimetric data and not the participants values, no covariance term was included in the subsequent calculations.

Tables summarizing the degree of equivalence calculations and the graphical representations are presented in Tables 13 to 16 and Figures 5 to 8. Results that include zero within their uncertainty interval are considered to be consistent with the reference value.

Table 13. Degree of Equivalence Table for Ni

Lab i	Reported Value, x_i ng/g	Reported U_i ng/g	k	D_i	U_i
INTI	65.7	3.5	2	-2.91	3.5
NIMT	67.7	2.1	2	-0.91	2.1
UME	68.1	2.0	2	-0.51	2.0
CENAM	68.5	1.1	2	-0.11	1.1
HSA	68.55	0.78	2	-0.06	0.8
VNIIM	68.68	3.98	2	0.07	4.0
NRC	68.76	1.50	2	0.15	1.5
GLHK	69.2	1.6	2	0.59	1.6
INMETRO	69.21	0.81	2	0.60	0.8
INDECOPI	69.4	1.3	2	0.79	1.3
INM	70.67	5.62	2	2.06	5.6
$x_R = 68.61$ ng/g $U_R (k=2) = 0.25$ ng/g					

Figure 5. Graph of equivalence for Ni for data reported by SIM.QM.S2 participants. Black dots represent the degree of equivalence D_i , while the error bars signify the expanded uncertainty associated with the degree of equivalence U_i ($k=2$) according to eq. 6.

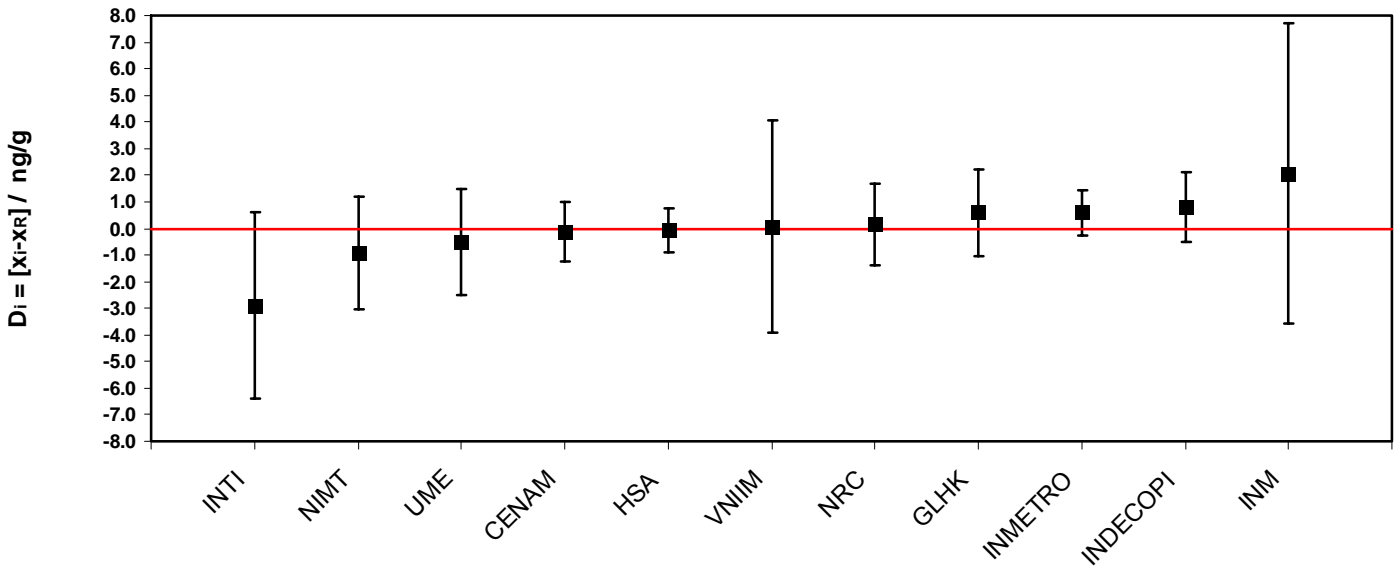


Table 14. Degree of Equivalence Table for Cd

Lab i	Reported Value, x_i ng/g	Reported U, ng/g	k	D_i	U_i
INTI	3.50	0.29	2	-0.54	0.29
INDECOPI	3.976	0.077	2	-0.06	0.08
GLHK	4.03	0.12	2	-0.01	0.12
HSA	4.03	0.05	2	-0.01	0.06
NRC	4.06	0.08	2	0.02	0.09
CENAM	4.079	0.036	2	0.04	0.05
UME	4.09	0.13	2	0.05	0.13
NIMT	4.1	0.2	2	0.06	0.20
VNIIM	4.189	0.117	2	0.15	0.12
INM	4.503	0.414	2	0.46	0.42
INMETRO	4.509	0.063	2	0.47	0.07
$x_R = 4.04 \text{ ng/g}$ $U_R (k=2) = 0.03 \text{ ng/g}$					

Figure 6. Graph of equivalence for Cd for data reported by the SIM.QM.S2 participants. Black dots represent the degree of equivalence D_i , while the error bars signify the expanded uncertainty associated with the degree of equivalence U_i ($k=2$) according to eq. 6.

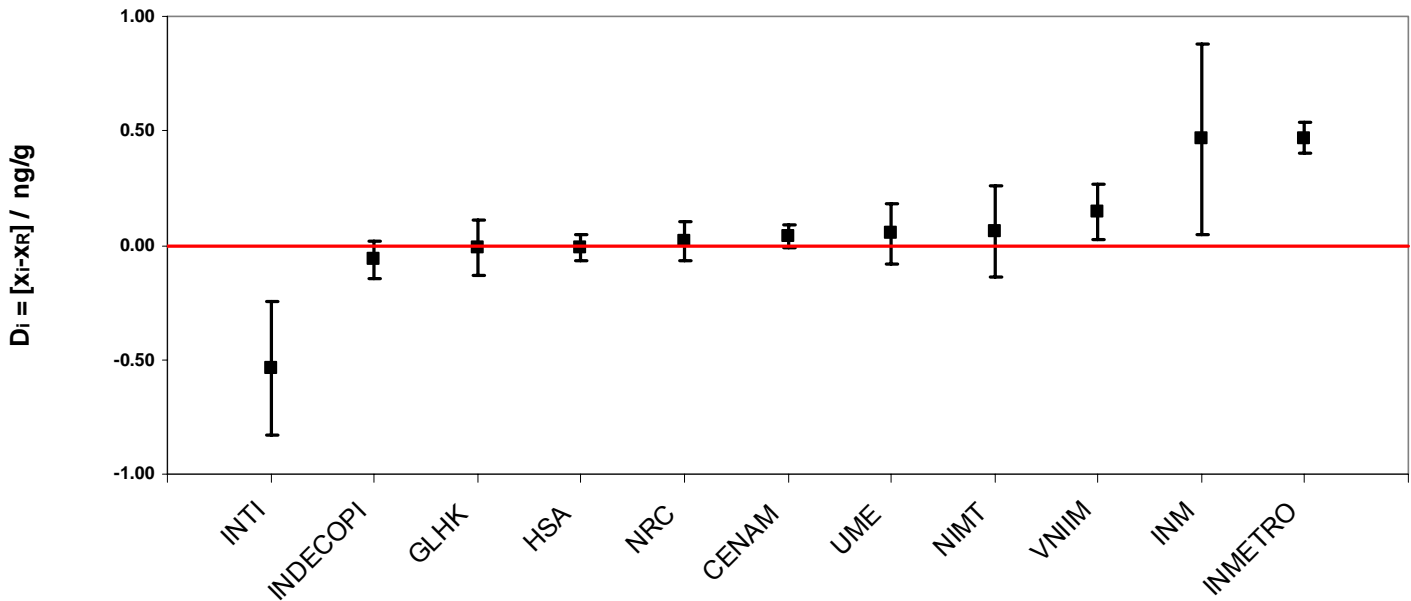


Table 15. Degree of Equivalence Table for Pb

Lab i	Reported Value, x_i ng/g	Reported U_i ng/g	k	D_i	U_i
VNIIM	23.60	0.71	2	-0.62	0.73
NIMT	23.9	0.6	2	-0.32	0.62
HSA	24.03	0.33	2	-0.19	0.37
CENAM	24.07	0.16	2	-0.15	0.23
INM	24.10	1.94	2	-0.12	1.95
UME	24.1	2.1	2	-0.12	2.11
INDECOPI	24.13	0.46	2	-0.09	0.49
NRC	24.16	0.57	2	-0.06	0.59
INMETRO	24.22	0.2	2	0.00	0.26
GLHK	24.66	0.62	2	0.44	0.64
INTI	26.7	3.0	2	2.48	3.00
$x_R = 24.22$ ng/g $U_R (k=2) = 0.16$ ng/g					

Figure 7. Graph of equivalence for Pb for data reported by the SIM.QM.S2 participants. Black dots represent the degree of equivalence D_i , while the error bars signify the expanded uncertainty associated with the degree of equivalence U_i according to eq. 6, calculated applying a coverage factor of $k = 2$.

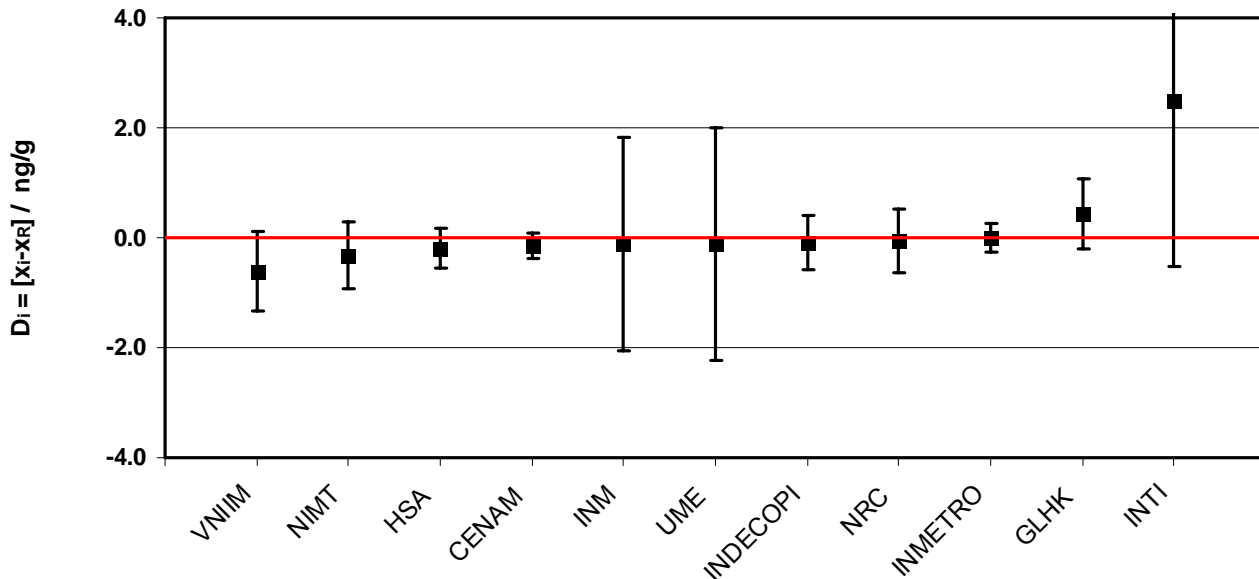
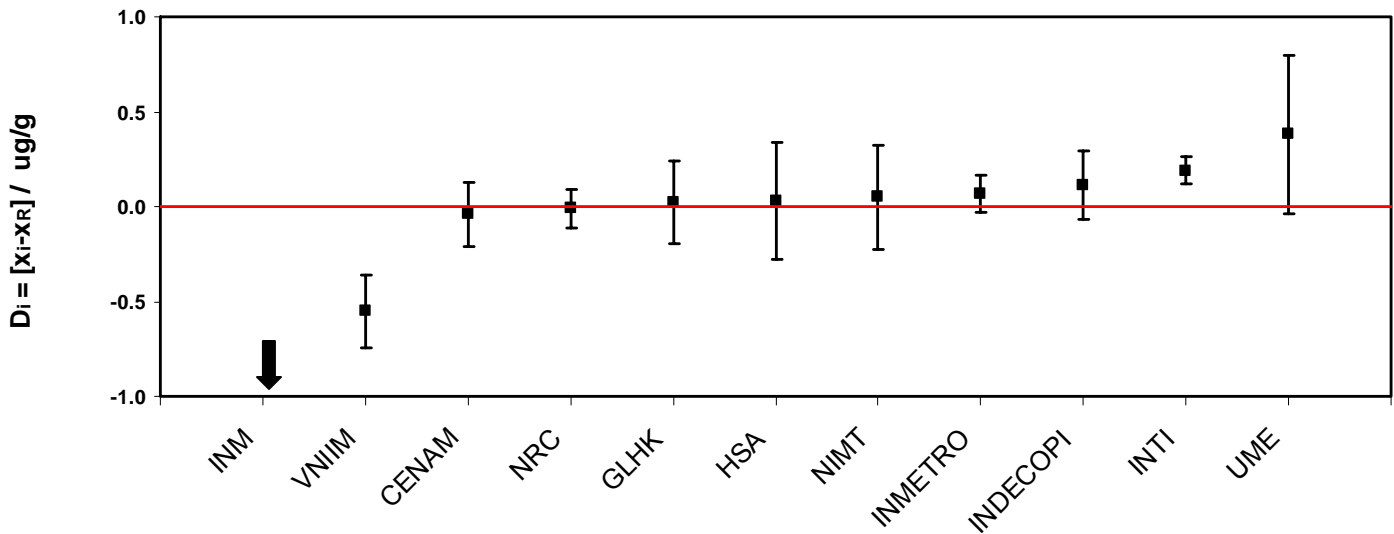


Table 16. Degree of Equivalence Table for Ca

Lab i	Reported Value, x_i ug/g	Reported U_i ug/g	k	D_i	U_i
INM	5.684	0.26	2	-3.16	0.27
VNIIM	8.288	0.182	2	-0.55	0.19
CENAM	8.8	0.16	2	-0.04	0.17
NRC	8.83	0.08	2	-0.01	0.10
GLHK	8.86	0.21	2	0.02	0.22
HSA	8.873	0.303	2	0.03	0.31
NIMT	8.89	0.27	2	0.05	0.28
INMETRO	8.907	0.08	2	0.07	0.10
INDECOPI	8.95	0.17	2	0.11	0.18
INTI	9.030	0.039	2	0.19	0.07
UME	9.22	0.41	2	0.38	0.41
$x_R = 8.84$ ug/g $U_R (k=2) = 0.03$ ug/g					

Figure 8. Graph of equivalence for Ca for data reported by the SIM.QM.S2 participants. Black dots represent the degree of equivalence D_i , while the error bars signify the expanded uncertainty associated with the degree of equivalence U_i , according to eq. 6, calculated applying a coverage factor of $k = 2$.



Uncertainty

Participants were asked to report the major sources of uncertainty for their measurements. Table 17 summarizes responses.

Table 17. Major Sources of Uncertainty

Major sources of uncertainty	
INTI	
Ni, Cd, Pb,Ca	Calibration, SRM concentration
INMETRO	
Ni, Ca	Repeatability, std dilution
Cd	Calibration, repeatability
Pb	Measurement of ratio, abundance reference isotope
NRC	
Ni, Cd, Pb	Measurement of the reference- to-spike ratio, measurement of the reverse spike ratio, spike mass
Ca	Measurement precision, calibration
HKGL	
Ni, Cd, Pb,Ca	Precision, trueness
CENAM	
Ca, Cd, Ni	Method (sample preparation), mass fraction of the primary assay standard, and measured isotope amount ratio of blend (R_{bx})
Pb	Method(sample preparation), sum of all the corrected (by mass bias correction factor) isotope amount ratios in the sample ($K_{ix}R_{ix}$), and corrected (by mass bias correction factor) isotope amount ratios in the blend ($K_{bx}R_{bx}$)
INDECOPI	
Ni, Cd, Pb,Ca	Calibration, SRM concentration
INM	
Ni, Cd, Pb,Ca	Measurement reproducibility, calibration, standard
VIINM	
Ni, Cd, Pb,Ca	Calibration, CRM concentration

Major sources of uncertainty

HSA

Ni	Method recovery, calibration std, method precision
Cd	Method recovery, bias due to ion pair, calibration std
Pb	Method recovery, bias due to ion pair, method precision
Ca	Method precision, concentration of analyte, bias due to choice of instrument

NIMT

Ni	Blank correction factor, isotope ratio in spike, isotope ratio in calibration blend
Cd	Blank correction factor, isotope ratio in spike, concentration of std
Pb	Blank correction factor, amount ratio, concentration of std
Ca	Blank correction factor, isotope ratio in spike, isotope ratio in calibration blend

UME

Ni, Cd, Pb,Ca	Repeatability, accuracy, calibration standard
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Conclusions

Laboratories participating in SIM.QM. S2 generally agree within stated uncertainties with the reference value. This analysis is relatively easy as the matrix is simple and the mass fractions are above ICP-MS detection limits for Cd, Pb and Ni and with that for Ca also well above the detection limit for ICP-OES and FAAS. The Ca results for all but two laboratories are traceable to the same NIST SRM used to spike the solution, resulting in a comparison of calibration solution preparation rather than a matrix sample.

Core capability forms submitted by the SIM.QM.S2 participants generally agreed this exercise demonstrated a low level of difficulty. It would be expected potential CMC claims as a result of this study could not be extended beyond similar water samples with a simple matrix.

References

1. World Health Organization 2006. Guidelines for Drinking-water Quality: First Addendum to 3rd Edition. Vol. 1, Recommendations.
2. ISO Guide 35:2006 Reference materials -- General and statistical principles for certification, Geneva, Switzerland

Acknowledgements

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SIM-QM-S2 Supplemental and SIM-QM-P22 Pilot Comparison

Trace Elements in Drinking Water - Protocol

1. Background

The determination of trace metals in drinking water is an important and commonly performed measurement responsibility. There is no single approach that is universally applicable, as the nature and regulations for drinking water standards may vary among countries and regions.

The World Health Organization's Guidelines for Drinking-water Quality¹ were used to determine the target values for this study. Target concentrations were chosen to approach the maximum acceptable WHO limits. The relatively high mass fraction of calcium simulates the matrix of a natural fresh water.

An earlier Key Comparison in this area was conducted under the auspices of the CIPM as CCQM-K2, but this is now more than 10 years old with the result that it will come into question when used in support of CMC claims if other more recent equivalent comparisons are available. SIM-QM-S2 will provide NMIs and DIs with the needed evidence for CMC claims for trace elements in fresh waters or calibration standards and is being operated as a Supplemental because there will be no link to the earlier CCQM-K2. Note that those laboratories wishing to utilize this exercise for support of CMC claims must register for the Supplemental and *not* the Pilot Comparison. Although this is organized as a SIM regional comparison, it is open to other participants of the MRA throughout all RMOs. Results for the Supplemental will be registered on the BIPM Key and Supplemental database, the KCDB.

The same sample will be used for both the Supplemental and Pilot comparisons.

2. Material

Laboratory grade pure water (ASTM Type 1) was acidified with high-purity nitric acid for preservation of gravimetrically spiked measurands. A relatively high amount content of Ca is intended to simulate a natural water matrix. Reference values were determined gravimetrically and supported with primary measurement methods (ID-MS) from the coordinating laboratory. Bottle-to-bottle homogeneity was evaluated and determined to be fit for purpose. Samples will be made available in pre-cleaned polyethylene bottles (100 mL).

Canada

3. Measurands

Element	Target Concentration
Cd	1 - 5 µg/kg
Ni	50 - 80 µg/kg
Pb	5 - 30 µg/kg
Ca	5 - 25 µg/g

4. Choice of Method / Procedure

Participants may use any method of their choice.

5. Test Sample Receipt / Handling

Samples will be distributed by courier to the participants. Each laboratory will receive two bottles of the sample.

- Please inform the coordinator immediately if the test sample has been compromised in any way and arrives in questionable condition.
- Results for each measurand should be reported in triplicate as the element content mass fraction (mass/mass) on test aliquots drawn from either of the two bottles.
- Each laboratory shall provide a complete description of the method(s) used, including calibration technique(s) along with their metrological traceability and a GUM compliant uncertainty assessment.
- The three major sources of uncertainty should be identified.

6. Time Schedule

Registration deadline:- July 9, 2010

Ship date for test samples:- July, 2010

Deadline for receipt of results: January 7, 2011

Preparation/distribution of draft A report: February, 2011

Discussion of the results and draft A report at CCQM IAWG, April 2011

Draft B report following discussion at SIM CMWG meeting: (tentatively) May, 2011

7. References

World Health Organization 2006. Guidelines for Drinking-water Quality: First Addendum to 3rd Edition. Vol. 1, Recommendations.

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Appendix 2 Inorganic Core Capabilities

Study: SIM.QM.S2

Institute(s): CENAM, HSA, INMETRO, NIMT, NRCC

Method: ID-ICP-MS

Analyte(s): CENAM – Ca, Ni, Cd, Pb
 HSA – Ni, Cd, Pb
 INMETRO – Pb
 NIMT – Ca, Ni, Cd, Pb
 NRCC – Ni, Cd, Pb

Capabilities/Challenges	ID-ICP-MS Degree of Difficulty			Explanation
	Low	Moderate	High	
Contamination control and correction <i>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.</i>	All			
Digestion/dissolution of organic matrices <i>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.</i>	NA			
Digestion/dissolution of inorganic matrices <i>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.</i>	NA			
Volatile element containment <i>All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.</i>	NA			
Pre-concentration <i>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.</i>	NA			
Vapor generation <i>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.</i>	NA			
Matrix separation <i>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.</i>	NA			
Spike equilibration with sample <i>The mixing and equilibration of the enriched isotopic spike with the sample.</i>	All			

Capabilities/Challenges	ID-ICP-MS Degree of Difficulty			Explanation
	<i>Low</i>	<i>Moderate</i>	<i>High</i>	
Signal detection <i>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.</i>	All			
Memory effect <i>Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.</i>	All			
Correction or removal of isobaric/polyatomic interferences <i>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.</i>	All			
Detector deadtime correction <i>Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.</i>	All			
Mass bias/fractionation control and correction <i>Techniques used to determine, monitor, and correct for mass bias/fractionation.</i>	All			
Spike calibration <i>Techniques used to determine the analyte concentration in the enriched isotopic spike solution.</i>	All			

**Inorganic Core Capabilities
Summary Table**

Study: SIM.QM.S2

Institute(s): GLHK, INMETRO, INM, UME, VNIIM

Method: ICP-MS (without Isotope Dilution)

Analyte(s): GLHK – Ni, Cd, Pb
 INMETRO – Ni, Cd
 INM – Ca, Cd, Pb
 UME- Ca, Ni, Cd, Pb
 VNIIM – Ca, Ni, Cd, Pb

Capabilities/Challenges	ICP-MS (without Isotope Dilution) Degree of Difficulty			Explanation
	Low	Moderate	High	
Contamination control and correction <i>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.</i>	All			
Digestion/dissolution of organic matrices <i>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.</i>	NA			
Digestion/dissolution of inorganic matrices <i>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.</i>	NA			
Volatile element containment <i>All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.</i>	NA			
Pre-concentration <i>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.</i>	NA			
Vapor generation <i>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.</i>	NA			
Matrix separation <i>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.</i>	NA			
Calibration of analyte concentration <i>The preparation of calibration standards and the</i>	All			

Capabilities/Challenges	ICP-MS (without Isotope Dilution) Degree of Difficulty			Explanation
	<i>Low</i>	<i>Moderate</i>	<i>High</i>	
<i>strategy for instrument calibration. Includes external calibration and standard additions procedures.</i>				
Signal detection <i>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.</i>	All			
Memory effect <i>Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.</i>	NA			
Correction or removal of isobaric/polyatomic interferences <i>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.</i>	All			
Correction or removal of matrix-induced signal suppression or enhancement <i>Chemical or instrumental procedures used to avoid or correct for matrix-induced signal suppression or enhancement.</i>	All			
Detector deadtime correction <i>Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.</i>	All			
Mass bias/fractionation control and correction <i>Techniques used to determine, monitor, and correct for mass bias/fractionation.</i>	All			

**Inorganic Core Capabilities
Summary Table**

Study: SIM.QM.S2

Institute: GLHK, HSA, NRCC

Method: ICP-OES

Analyte(s): GLHK – Ca
HSA - Ca
NRCC - Ca

Capabilities/Challenges	ICP-OES Degree of Difficulty			Explanation
	<i>Low</i>	<i>Moderate</i>	<i>High</i>	
Contamination control and correction <i>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.</i>	All			
Digestion/dissolution of organic matrices <i>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.</i>	NA			
Digestion/dissolution of inorganic matrices <i>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.</i>	NA			
Volatile element containment <i>All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.</i>	NA			
Pre-concentration <i>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.</i>	NA			
Vapor generation <i>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.</i>	NA			
Matrix separation <i>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.</i>	NA			
Calibration of analyte concentration <i>The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.</i>	All			
Signal detection	All			

Capabilities/Challenges	ICP-OES Degree of Difficulty			Explanation
	<i>Low</i>	<i>Moderate</i>	<i>High</i>	
<i>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..</i>				
Memory effect <i>Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.</i>	All			
Complex spectral backgrounds <i>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.</i>	All			
Correction or removal of matrix-induced signal suppression or enhancement <i>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.</i>	All			

**Inorganic Core Capabilities
Summary Table**

Study: SIM.QM.S2

Institute(s): INDECOPI, INTI

Method: ETA-AAS (or GF-AAS)

Analyte(s): INDECOPI - Ni, Cd, Pb
INTI - Ni, Cd, Pb

Capabilities/Challenges	ETA-AAS Degree of Difficulty			Explanation
	<i>Low</i>	<i>Moderate</i>	<i>High</i>	
Contamination control and correction <i>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.</i>	All			
Digestion/dissolution of organic matrices <i>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.</i>	NA			
Digestion/dissolution of inorganic matrices <i>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.</i>	NA			
Volatile element containment <i>All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.</i>	NA			
Pre-concentration <i>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.</i>	NA			
Matrix separation <i>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.</i>	NA			
Hydride preconcentration/matrix separation of volatile species. <i>Coupling of a hydride system to the ETA-AAS and optimization of conditions.</i>	NA			
Calibration of analyte concentration <i>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.</i>	All			
Signal detection <i>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</i>	All			

Capabilities/Challenges	ETA-AAS Degree of Difficulty			Explanation
	<i>Low</i>	<i>Moderate</i>	<i>High</i>	
<i>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).</i>				
Memory effect <i>Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.</i>	NA			
Optimization of the furnace temperature program <i>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.</i>	<i>All</i>			
Correction or removal of matrix effects or interferences <i>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.</i>	<i>All</i>			

**Inorganic Core Capabilities
Summary Table**

Study: SIM.QM.S2

Institute(s): INDECOPI, INTI

Method: Flame-AAS

Analyte(s): INDECOPI - Ca
INMETRO - Ca
INTI - Ca

Capabilities/Challenges	Flame -AAS Degree of Difficulty			Explanation
	Low	Moderate	High	
<p>Contamination control and correction <i>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.</i></p>	All			
<p>Digestion/dissolution of organic matrices <i>All techniques and procedures used to bring a sample that is primarily organic in nature into solution suitable for liquid sample introduction to the flame.</i></p>	NA			
<p>Digestion/dissolution of inorganic matrices <i>All techniques and procedures used to bring a sample that is primarily inorganic in nature into solution suitable for liquid sample introduction to the flame.</i></p>	NA			
<p>Volatile element containment <i>All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.</i></p>	NA			
<p>Pre-concentration <i>Techniques and procedures used to increase the concentration of the analyte introduced to the flame.. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.</i></p>	NA			
<p>Matrix separation <i>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.</i></p>	NA			
<p>Hydride preconcentration/matrix separation of volatile species. <i>Coupling of a hydride system to the flame and optimization of conditions.</i></p>	NA			
<p>Calibration of analyte concentration <i>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. Non-linear absorption response to concentration is avoided by setup conditions or corrected for.</i></p>	All			

Capabilities/Challenges	Flame -AAS Degree of Difficulty			Explanation
	<i>Low</i>	<i>Moderate</i>	<i>High</i>	
Signal detection <i>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.</i>	All			
Memory effect <i>Any techniques used to avoid, remove or reduce the carry-over of analyte between consecutively measured standards and/or samples.</i>	All			
Background correction <i>Any of various techniques used to correct for interference due to absorption and scattering from coexisting molecules/atoms in the sample. Certain matrices will present a greater challenge, particularly with low atomic absorption signals.</i>	All			
Optimization of the flame conditions <i>Optimization of flame stoichiometry and composition. Certain elements present a greater challenge.</i>	All			
Correction or removal of non-spectral matrix effects or interferences <i>Chemical or instrumental procedures used to avoid or correct for non-spectral interferences. Includes effects of differences in viscosity, chemical equilibrium states of analyte between the standard and sample, and ionization.</i>	All			