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SIM.QM-S18

Supplementary Comparison for Cd and Pb in Cacao Powder

Final Report

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Abstract

The SIM Supplementary Comparison SIM.QM-S18, for the determination of Cd and Pb in cacao powder, was jointly organized by the National Research Council Canada (NRC) and the Centro Nacional de Metrología (CENAM). The objective was to assess and demonstrate the analytical capabilities of National Metrology Institutes (NMIs) and Designated Institutes (DIs) of SIM members (or other regions) in the accurate determination of trace elements in cacao powder. This matrix had not previously been tested in CCQM or RMO comparisons and was selected due to its significant relevance to food safety regulations due to the potential presence of elevated levels of toxic metals.

Evidence of successful participation in formal, relevant international comparisons is needed to document calibration and measurement capability claims (CMCs) made by NMIs and DIs.

A total of nineteen NMIs and DIs participated in SIM.QM-S18. Participants were requested to determine the mass fractions, in mg/kg, of cadmium and lead in commercially available cacao powder. A variety of instrumental techniques were employed, including inductively coupled plasma mass spectrometry (ICP-MS), isotope dilution ICP-MS (ID-ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES) and graphite furnace atomic absorption spectrometry (GFAAS). The majority of the participants claimed traceability to NIST primary calibrants or their own certified reference materials (CRMs). Several matrix CRMs were used for quality control.

The NIST decision tree was used to assign the supplementary comparison reference value (SCRV) for each measurand and to calculate the degrees of equivalence of each participating NMI and DI, following the IAWG Guidance on Using NIST Decision Tree for Comparison Reporting from 30 June 2023.

Successful participation in SIM.QM-S18 demonstrates measurement capability for the determination of elements in food matrices. According to the IAWG Core Capability Matrix, cacao powder falls into the matrix challenge called “High organic content”, and the results of this comparison support broad scope CMC claims for transition elements in high organic content materials.

1. Introduction and background

With annual global chocolate consumption of approximately 7.5 million metric tons last year and a global chocolate industry worth approximately US$ 130 billion, the market for cacao-related products is a significant sector of the global food economy.

Cacao beans are the main ingredient for chocolate production. It is well known that some dark chocolates currently available on the market are contaminated with toxic metals (Cd & Pb), and it is mainly due to the presence of these contaminants in the cacao beans used to produce the chocolates. In general, cacao powder has the highest concentration of heavy metals, as it is produced by concentrating the solids of the cacao bean while removing the oils (known as cacao butter).

In recent years, food safety regulations worldwide have tightened the maximum permissible levels of toxic metals in cacao products such as chocolate and cocoa powder. For instance, since 2019, the European Union has prohibited marketing of products that exceed the maximum levels for toxic metals. These regulatory requirements underscore the need for accurate, traceable measurements of toxic metals in cacao matrices to ensure compliance and consumer safety.

This supplementary comparison is thus for the determination of cadmium and lead in cacao powder, a matrix that has not yet been tested previously in CCQM and RMO comparisons. This comparison is organized jointly by the National Research Council Canada (NRC) and Centro Nacional de Metrología (CENAM). Evidence of successful participation in formal, relevant international comparisons is needed to support calibration and measurement capability claims (CMCs) made by NMIs and DIs. Although this is organized as a SIM regional comparison, it is open to other participants of the MRA throughout all RMOs. A pilot study is also conducted in parallel with this comparison.

Results for this supplementary comparison will be registered on the BIPM Key comparison Database (KCDB).

Table 1. Timetable of SIM.QM-S18

Date	**Action**
April/ May, 2023	Sample Preparation
May, 2023	Send Questionnaire
May/ September, 2023	Homogeneity & Stability Studies
June, 2023	Deadline for submission of questionnaire
November, 2023	Presentation of homogeneity and stability studies
December, 2023	Call for participation
January 26, 2024	Deadline for registration
February, 2024	Distribution of samples
October 11, 2024	Deadline for submission of results
December 20, 2024	Extended deadline for submission of results
January 27, 2025	Circulation of compile data among participants
March 26, 2025	First results discussion at SIM WG 8 meeting
April 9, 2025	First results discussion at CCQM IAWG meeting
May 16, 2025	Draft A submitted to participants
July 17, 2025	Breakout meeting with participants
October 28, 2025	Presentation at the SIM WG 8 meeting
November 5, 2025	Presentation at the CCQM IAWG meeting
November 13, 2025	Draft B submitted to participants

2. Study Material

2.1. Preparation of the material

The study material consisted of commercially available cacao powder. The material was sieved through an 850 µm nylon screen, blended and bottled in amber glass containers. After bottling, the material was sterilized using gamma irradiation at a minimum dose of 25 kGy. Following irradiation, each vial was packaged in trilaminate bags. Each unit contained at least 15 g of the material with a fat content of approximately 15 %. All sample preparation was carried out in the Inorganic Chemical Metrology laboratories of the NRC.

The measurands and their expected mass fractions are listed in Table 2 (on a dry mass basis).

Table 2. Measurands and expected mass fraction range.

Element	Expected mass fraction	Natural/Spiked	Description
Cadmium (Cd)	(0.01 - 2) mg/kg	Natural	Toxic element
Lead (Pb)	(0.01 - 2) mg/kg	Natural	Toxic element

The recommended minimum sample mass for analysis is 0.25 g. Participating NMIs/DIs should take at least 5 subsamples for measurement of the measurands. Prior to use, the bottle contents should be well mixed by rotation and shaking.

2.2 Homogeneity

Ten bottles of sample were randomly selected for homogeneity study. Three subsamples were taken from each bottle and were measured for Cd and Pb by ICP-MS.

ANOVA at 95 % level of confidence was applied to assess the between-bottle homogeneity in accordance with ISO Guide 35:2017. The study material was found to be sufficiently homogeneous. The results are summarized in Table 3.

Table 3. Results of the homogeneity assessment for the measurands.

Measurand	ANOVA test		Relative standard uncertainty due to between-bottle (in)homogeneity, u_{bb} (%)
	F-statistics	Critical value	
Cadmium	1.17	2.29	0.4
Lead	1.23	2.29	0.9

2.3 Short-term stability

The short-term stability of the measurands was assessed over a 6 week period at 40 °C using isochronous approach. Two randomly selected sample bottles were transferred from the storage condition (-20 °C) to 40 °C for exposure periods of 2 weeks, 4 weeks, and 6 weeks. Two subsamples were then taken from each bottle for Cd and Pb analysis by ICP-MS. The data were evaluated using Student's *t*-test on the slope of the linear regression of concentration versus time at a 95 % level of confidence, no significant instability of either measurands was observed when the material was exposed to 40 °C for up to 6 weeks. The results are presented in Table 4.

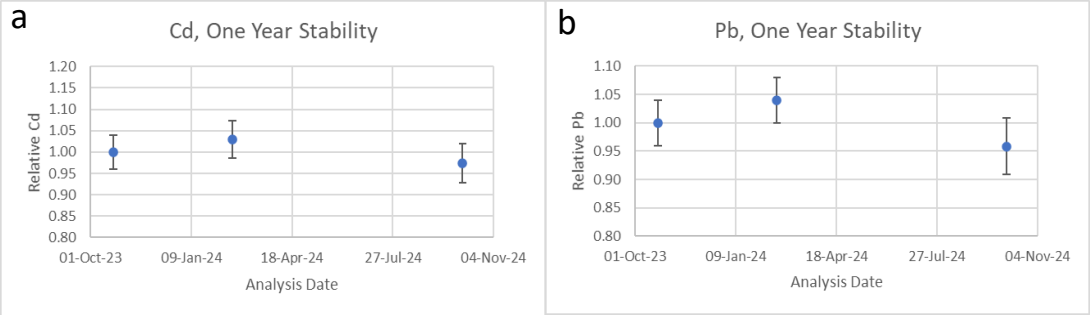
Table 4. Results of the short term stability assessment for the measurands at 40 °C over a period of 6 weeks.

Measurand	Student's *t*-test		*p*-value
	Calculated test statistics	Critical value	
Cadmium	-0.558	4.303	0.588
Lead	-0.644	4.303	0.533

2.4 Long-term stability

The long-term stability of the measurands in the comparison material stored at -20 °C was assessed. The testing was conducted prior to sample dispatch and continuously monitored until completion of the supplementary comparison using the classical approach. For each testing occasion, at least two bottles were randomly selected, and two subsamples were taken from each bottle. Student's t-test on the slope of the linear regression of concentration versus time at a 95 % level of confidence was used for the evaluation of instability of the measurands. The results are graphically presented in Figure 1. The Student's t-test results confirmed that the slope of the linear regression line was statistically insignificant at 95 % level of confidence, confirming its long-term stability.

Figure 1. Long-term stabilities of the measurands at -20 °C for one year: a) cadmium and b) lead.



3. Instructions to Participants

A technical protocol was distributed to all participants of SIM.QM-S18, providing details on approximate analyte contents, sample handling and the data submission format (Microsoft Word format). The technical protocol is presented in Appendix A and the report form in Appendix B.

Each participant received at least one bottle, containing a minimum of 15 g of cacao powder. Each bottle was packaged in a trilaminate foil pouch. Examples of matrix certified references materials as well as primary standards available for use during this comparison were also listed in the technical protocol.

Participants were requested to report results for the measurands for at least 5 subsamples from the bottle as the element content mass fraction (mass/mass, mg/kg) using their preferred method. A reporting template was provided.

To enable a comprehensive evaluation of the comparison results, participants were requested to provide a complete description of the method(s) used, including sample preparation, calibration technique(s) along with their metrological traceability and uncertainty assessment in accordance with JCGM 100:2008 Evaluation of Measurement Data-Guide to the Expression of Uncertainty in Measurement, as well calibration standard, reference materials used, and any specific challenges encountered.

4. Participants Institutes

A total of 16 participants registered for the SIM.QM-S18 supplementary comparison as presented in Table 5 which includes information on the registered analytes, samples distribution, reporting date, and the analyte reported by each registered participant.

Table 5. Registered participants, contacts, analytes registered, shipping and reporting information

Participant	Member/ Associate State	Contact Person	Analytes registered	Sample shipment/deliver date	Reporting date	Analyte reported
EC– JRC	Belgium	James Snell	Cd, Pb	S:Feb 13, 2024 D: Feb 19, 2024	Nov 17, 2024	Cd, Pb
IBMETRO	Bolivia	Jose Luis Gonzales	Cd, Pb	S: Feb 13, 2024 D: 12-Mar-24	Dec 20, 2024	Cd, Pb
NRC	Canada	Patricia Grinberg	Cd, Pb	NA	Dec 17, 2024	Cd, Pb
ISP [b]	Chile	Javier Vera Maldonado	Cd, Pb	S: Feb 13, 2024 D: Feb 29, 2024	Nov 20, 2024	Cd
INM(CO)	Colombia	Cristhian Paredes	Cd, Pb	S: Feb 13, 2024 D: Feb 15, 2024	Dec 6, 2024	Cd, Pb
LACOMET [b]	Costa Rica	Jimmy Venegas Padilla; Eric Ortiz Apuy, Bryan Calderón Jiménez	Cd, Pb	S: March 25, 2024 D: April 18, 2024	Dec 20, 2024	Cd
EXHM/GCSL-EIM	Greece	Ilias Kakoulidis	Cd, Pb	S: Feb 13, 2024 D: Feb 20, 2024	Dec 18, 2024	Cd, Pb
GLHK	Hong Kong, China	Lee Wan-waan	Pb	S: Feb 13, 2024 D: Feb 16, 2024	Oct 2, 2024	Pb
SNSU-BSN	Indonesia	Christine Elishian	Cd	S: Feb 13, 2024 D: Feb 23, 2024	Dec 19, 2024	Cd
CENAM	Mexico	Maria del Rocio Arvizu Torres Edith Valle Moya	Cd, Pb	NA	Dec 20, 2024	Cd, Pb
INACAL	Peru	Elmer Carrasco Solis	Cd, Pb	S: Feb 13, 2024 D: Feb 16, 2024	Dec 20, 2024	Cd, Pb
NMLPhil	Philippines	Alleni T. Junsay	Cd, Pb	S: Feb 13, 2024 D: Feb 22, 2024	Dec 20, 2024	Cd, Pb
NADF[a]	Saint Lucia	Rody Stanislas	Cd, Pb	S: May 13, 2024 D: May 15, 2024	-	-
HSA	Singapore	Richard Shin	Cd, Pb	S: Feb 13, 2024 D: Feb 19, 2024	Sep 27, 2024	Cd, Pb
NIMT	Thailand	Pranee Phukphatthanachai	Cd, Pb	S: Feb 13, 2024 D: Feb 27, 2024	Dec 16, 2024	Cd, Pb
LATU [b]	Uruguay	Cecilia Geisenblosen, Gimena Colombo	Cd, Pb	S: Feb 13, 2024 D: Feb 23, 2024	Dec 20, 2024	Cd

S: shipment date, D: delivery date

[a]NADF did not submit results for either Cd or Pb.

[b]ISP, LACOMET and LATU did not submit results for Pb

Samples were shipped by FedEx to the majority of participants between Feb 15, 2024 to Feb 27, 2024. LACOMET (Costa Rica) and NADF (Saint Lucia) expressed their interest in joining the comparison after the registration deadline had passed. Their requests were forwarded to the SIM.QM WG8 chair, who approved their participation.

The initial deadline for submitting results was set for October 11, 2024. However, several participants requested an extension, which was granted, extending the reporting deadline to December 20, 2024.

ISP Chile and LATU only reported cadmium due to limitations in their measurement capabilities. NADF was unable to submit any results owing to instrumentation issues encountered.

5. Methods of measurement

Participants were free to select their own methods for both sample preparation and measurement method. Table 6 summarises the sample preparation, measurement method (including calibration strategy) and sample mass used.

Table 6. Summary of sample preparation, measurement method and sample mass used.

Participant	Sample preparation	Measurement method (instrument)	Sample mass (g)
EC– JRC	Microwave-assisted acid digestion with HNO_3	ID-MS (Cd reference isotope ^{113}Cd, spiked isotope ^{111}Cd; Pb: reference isotope ^{208}Pb, spiked isotope ^{206}Pb), Pb isotopic standard: NIST SRM 997), Thermo iCap TQ ICP-MS (3Q)	0.5
IBMETRO	Microwave-assisted Acid digestion with HNO_3 and H_2O_2	SA-GFAAS; Perkin Elmer PinAAcle 900T; $NH_4H_2PO_4$ + $Mg(NO_3)_2$ used as modifier; 1-point SA	0.5
NRC	Microwave-assisted acid digestion with HNO_3 and H_2O_2	Reverse IDMS ($^{113}Cd/^{111}Cd$, $^{208}Pb/^{207}Pb$, isotopic std for Pb: NRC CRM HIPB-1), ICP-SF-MS, Thermo Element XR, LR mode,	0.25
ISP	Microwave-assisted acid digestion with HNO_3 and H_2O_2	gravimetric SA-ICP-MS with IS (Rh) Agilent 7700x , He collision cell	0.5
INM(CO)	Microwave-assisted acid digestion with HNO_3	IDMS with a Padé function (Cd reference isotope ^{114}Cd, spiked isotope ^{113}Cd; Pb: reference isotope ^{208}Pb, spiked isotope ^{207}Pb, Pb isotopic standard: NIST SRM 981) ; Perkin Elmer NexION 300D (std mode)	0.5
LACOMET	Microwave-assisted acid digestion with HNO_3 and HF	SA-GFAAS (Pd + $Mg(NO_3)_2$ as modifier) Zeeman	1

Participant	Sample preparation	Measurement method (instrument)	Sample mass (g)
EXHM/GCSL-EIM	Microwave-assisted acid digestion with HNO_3 and H_2O_2	Gravimetric Standard Addition ICP-MS; ICP MS/MS, He & O_2 mode, HR mode, IS: ^{115}In, ^{103}Rh and ^{175}Lu	0.4
GLHK	Microwave-assisted acid digestion with HNO_3, H_2O_2 and HF	Gravimetric SA- ICP-MS with IS (Bi); Thermo iCAP Qc, KED mode	0.5
SNSU-BSN	Microwave-assisted acid digestion with HNO_3, H_2O_2 and HF	Cd, Pb: gravimetric SA- ICP-MS with IS (^{115}In for Cd and ^{209}Bi for Pb); ICP-MS Thermo iCAP RQ (KED mode)	0.5
CENAM	Microwave-assisted acid digestion with HNO_3, H_2O_2 and HF followed by an anion exchange separation method (Dowex 1-X8)	Cd, Pb: Exact matching double ID-MS (Cd: $^{111}Cd/^{112}Cd$, $^{111}Cd/^{113}Cd$ & $^{111}Cd/^{114}Cd$, Pb: $^{206}Pb/^{208}Pb$, $^{206}Pb/^{207}Pb$, Pb isotopic standard: NRC ALED-1); ICP-SF-MS (LR mode)	0.5
INACAL	Microwave-assisted acid digestion with HNO_3 and H_2O_2	SA-ICP-MS with IS (In, Ir)	0.5
NMLPhil	Microwave-assisted acid digestion with HNO_3 & H_2O_2	Pb: Gravimetric EC-ICP-MS with IS (^{89}Y) using KED mode and 0.05 s dwell time Cd: Gravimetric EC-GFAAS with Pyrolysis Temperature of 500 °C and Atomization Temperature of 1450 °C, $Pd/Mg(NO_3)_2$ as modifiers and EDL lamp as light source	Pb:0.5 Cd: 1.0
HSA	Microwave-assisted acid digestion with HNO_3, HF & H_2O_2	Cd: exact-matching ID-MS ($^{111}Cd/^{114}Cd$); Pb:Gravimetric SA-ICP-MS, Agilent 7900 ICP-MS, He mode	Cd: 0.25 Pb: 0.5
NIMT	Microwave-assisted acid digestion with HNO_3	Cd: exact-matching IDMS ($^{112}Cd/^{111}Cd$) Pb: reverse IDMS ($^{208}Pb/^{206}Pb$) and Pb isotopic standard SRM 981 is used to isotope composition of the sample Instrument: Element XR (LR mode)	0.25
LATU	Microwave-assisted acid digestion with HNO_3	Exact matching ID-MS (Reference isotope: ^{114}Cd; Spiked isotope: ^{111}Cd), ICP-SF-MS (Element 2) , LR mode	0.5

EC: external calibration; GFAAS: graphite furnace atomic absorption spectrometry; KED: kinetic energy discrimination; ICP-OES: inductively coupled plasma optical emission spectrometry; ICP-MS: inductively coupled plasma mass spectrometry; ID: isotope dilution; IS: internal standard; LR: low resolution; MS:mass spectrometry; SA: standard addition; SF: sector field

Appendix C presents the Summary of Participants' Analytical Information.

6. Primary standards and CRMs used

The primary standards as well the matrix certified reference materials used are listed in Tables 7 and 8.

Table 7. Calibration Standards used as reported by the participants.

Participant	Cd	Pb
EC– JRC	IRMM-622	NIST SRM 991
IBMETRO	NIST SRM 3108	NIST SRM 3128
NRC	NRC Cd-32862	NRC CRM HIPB-1
ISP	NIST SRM 3108	--
INM(CO)	NIST SRM 3108	NIST SRM 3128 & NIST SRM 981
LACOMET	NIST SRM 3108	--
EXHM/GCSL-EIM	NIST SRM 3108	NIST SRM 3128
GLHK	--	NIST SRM 3128
SNSU-BSN	NIST SRM 3108	NIST SRM 3128
CENAM	CENAM DMR-461a	CENAM DMR-463; NIST SRM-981 NIST SRM 982; NRC ALED-1
INACAL	NIST SRM 3108	NIST SRM 3128
NMLPhil	NIST SRM 3108	NIST SRM 3128
HSA	NIST SRM 3108	NIST SRM 3128
NIMT	NIST SRM 3108	NIST SRM 3128 & NIST SRM 981
LATU	NIST SRM 3108	--

Table 8. Certified reference materials used for quality assurance as reported by the participants.

Participant	CRM used
EC– JRC	NIST SRM 2384 (baking chocolate)
IBMETRO	--
NRC	NRC CRM VORM-1 (mealworm powder) NRC CRM CAME-1 (canola meal) ERM-BD 514 (Cd in cocoa) NIST SRM 2384 (baking chocolate)
ISP	NIST SRM 2384 (baking chocolate)
INM(CO)	NIST SRM 2384 (baking chocolate)
LACOMET	NIST SRM 2384 (baking chocolate)
EXHM/GCSL-EIM	Cd: ERM-BD 513 (Cd in cocoa) Pb: BCR 191 (brown bread)
GLHK	NRC CRM DORM-5 (fish protein)
SNSU-BSN	NRC CRM DORM-5 (fish protein)
CENAM	NIST SRM 2384 (baking chocolate) ERM BD512 (dark chocolate)
INACAL	ERM BD515 (Cd in Cocoa) NIST 1566b (oyster tissue)
NMLPhil	NRC CRM DORM-5 (fish protein)

Participant	CRM used
HSA	Cd: ERM®-BD 515 (cocoa) Pb: NIST SRM 2384 (baking chocolate)
NIMT	NIST SRM 2384 (baking chocolate)
LATU	NIST SRM 2384 (baking chocolate) NRC CRM DORM-5 (fish protein)

7. Results and Discussion

7.1 General

The participants' results reported to the coordinating laboratory are summarized in Tables 9 to 11 and Figures 2 to 4.

7.2 Moisture content

Table 9. Reported results for Moisture content.

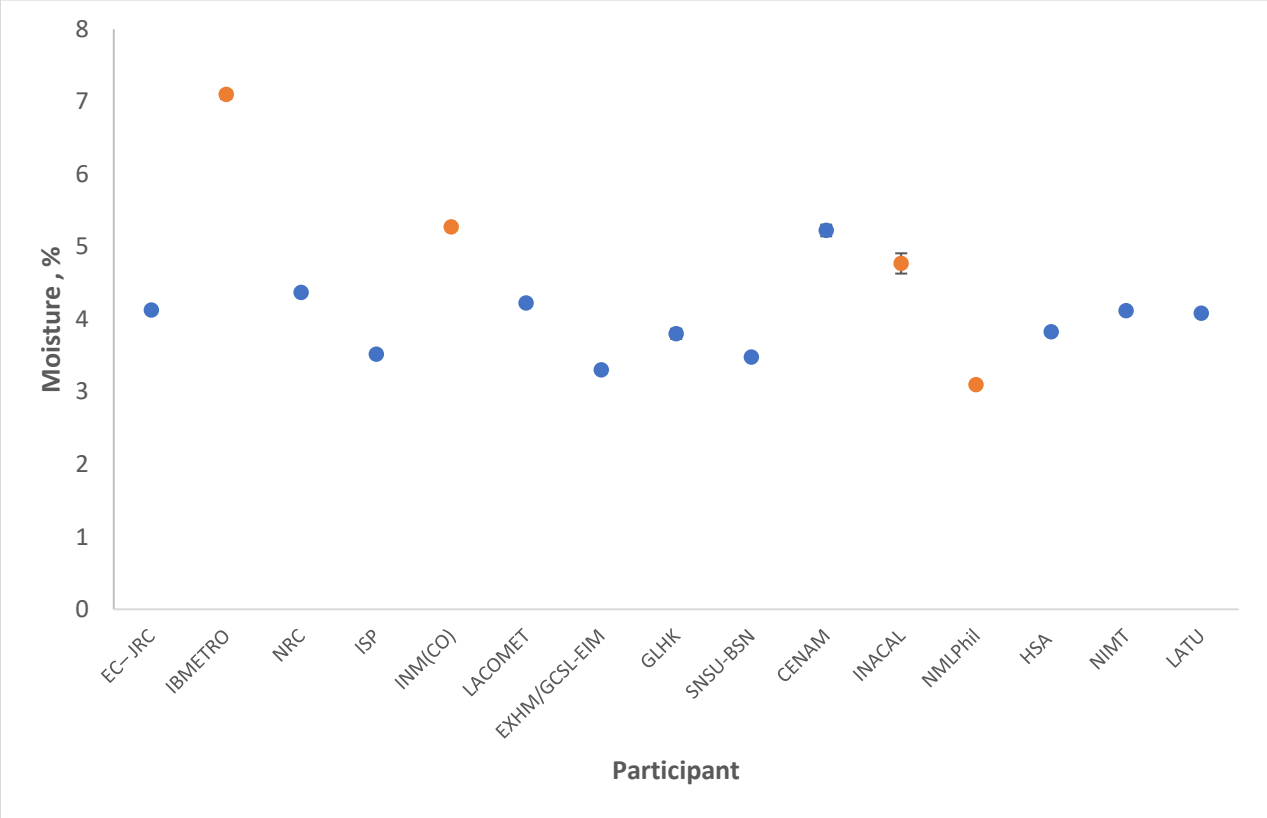
Participant	Sample mass (g)	Reported value (%)	u_c,(%)	*n*	Analytical Method
EC– JRC	1	4.1257012	0.0370715	3	Study protocol
IBMETRO	1	7.1	0.06	3	gravimetric method based in the loss of mass heating the sample at 105 °C
NRC	1	4.37	0.027	14	Study protocol
ISP	1	3.525	0.046	4	Study protocol
INM(CO)	1	5.273	0.029	6	Heated at 105 °C for at least 18 h. Followed by increments of 1h until achieve constant weight
LACOMET	1	4.226	0.042	4	Study protocol
EXHM/GCSL-EIM	0.9	3.3	0.026	5	Study protocol
GLHK	1	3.78	0.07	6	Study protocol
SNSU-BSN	1	3.48	0.02	3	Study protocol
CENAM	1	5.225	0.080	3	Study protocol
INACAL	1	4.77	0.14	5	Dried in a ventilated oven at a temperature of (103 ± 2) °C for at least 16 h.
NMLPhil	1	3.095	0.02	3	Heated at 103 ± 2 °C for a minimum of 16 hours. Followed by increments of 1h until achieve constant weight
HSA	1	3.827	0.019	3	Study protocol
NIMT	1	4.117	0.0004	4	Study protocol
LATU	1	4.085	0.019	3	Study protocol

n: Number of independent replicates

study protocol: The dry mass correction determination must be performed on a minimum of three separate portions of 1 g each. Sub-samples should be dried over anhydrous calcium sulphate (e.g., DRIERITE) or magnesium perchlorate in a desiccator for at

least 10 days until constant mass is attained (as recommendation: successive weights should not differ more than 1 mg). Do not use the sample, which was used for the determination of moisture content, for analysis. The elemental contents determined should be reported based on dry mass.

Figure 2. Moisture content determination as reported by the participants following the moisture determination procedure described in the technical protocol (blue), and participants who employed alternative methods (orange)



Most participants followed the moisture determination procedure described in the technical protocol, which involved drying the material over anhydrous calcium sulphate or magnesium perchlorate in a desiccator for at least 10 days until constant mass was reached. Four participants, IBMETRO, INM(CO), INACAL and NMLPhil, employed alternative methods for determining moisture content, such as heating the sample at about (103-105) °C until achieving constant weight.

Reported moisture determination ranged from 3.3 % to 7.1 %.

7.3 Cadmium

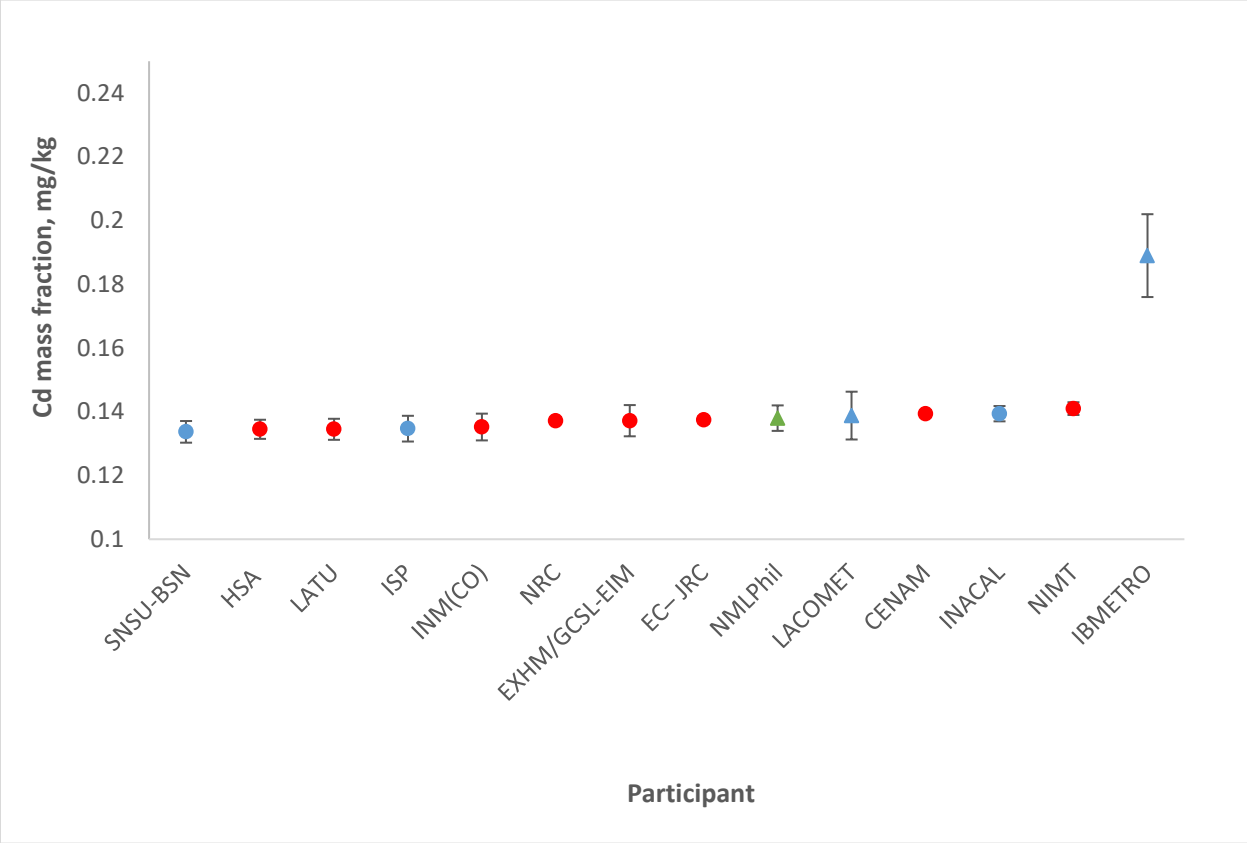
Fourteen laboratories reported values for mass fraction of cadmium. Results are presented in Table 10.

Table 10. Reported results for mass fraction of Cd and their associated combined and relative expanded uncertainties, with the coverage factor *k* as reported by the participants **in the order of increasing mass fraction value.**

Participant	Reported value (mg/kg)	u_c, (mg/kg)	Coverage factor *(k)*	*U* (mg/kg)	n	Degrees of Freedom	Analytical Method/ Instrument
SNSU-BSN	0.1337	0.0034	2	0.0068	6	5	Gravimetric SA-ICP-MS with IS
HSA	0.1345	0.0030	2.31	0.0069	8	8.26	ID-MS
LATU	0.1345	0.0033	2	0.0067	18	60	ID-MS
ISP	0.1347	0.00404	2	0.0081	10	4.2	Gravimetric SA-ICP-MS with IS
INM(CO)	0.1352	0.0042	2	0.0084	10	60	IDMS with Padé function
NRC	0.1372	0.001	2	0.0022	12	11	ID-MS
EXHM/GCSL-EIM	0.1372	0.0047	2	0.0094	5	25	Gravimetric SA ICP-MS
EC-JRC	0.13742	0.00117	2	0.0023	5	9.3	ID-MS
NMLPhil	0.138	0.004	2	0.008	5	12	GF-AAS
LACOMET	0.1388	0.0075	2	0.015	7	19406	SA- GF-AAS
CENAM	0.1394	0.0011	2.1	0.0024	7	15.7	ID-ICP-SFMS
INACAL	0.1394	0.0024	2	0.0048	5	33	SA-ICP-MS with IS
NIMT	0.141	0.002	2	0.005	5	9	ID-MS
IBMETRO	0.189	0.013	2.07	0.027	5	22	SA- GF-AAS

n: Number of independent replicates

Figure 3. Cadmium mass fraction as reported by the participants. Error bars denote the combined standard uncertainty (u_c, k=1).



Red: ID; Blue: SA, Green: EC; Circle: ICP-MS, Square: ICP-OES, Triangle: GF-AAS

7.4 Lead

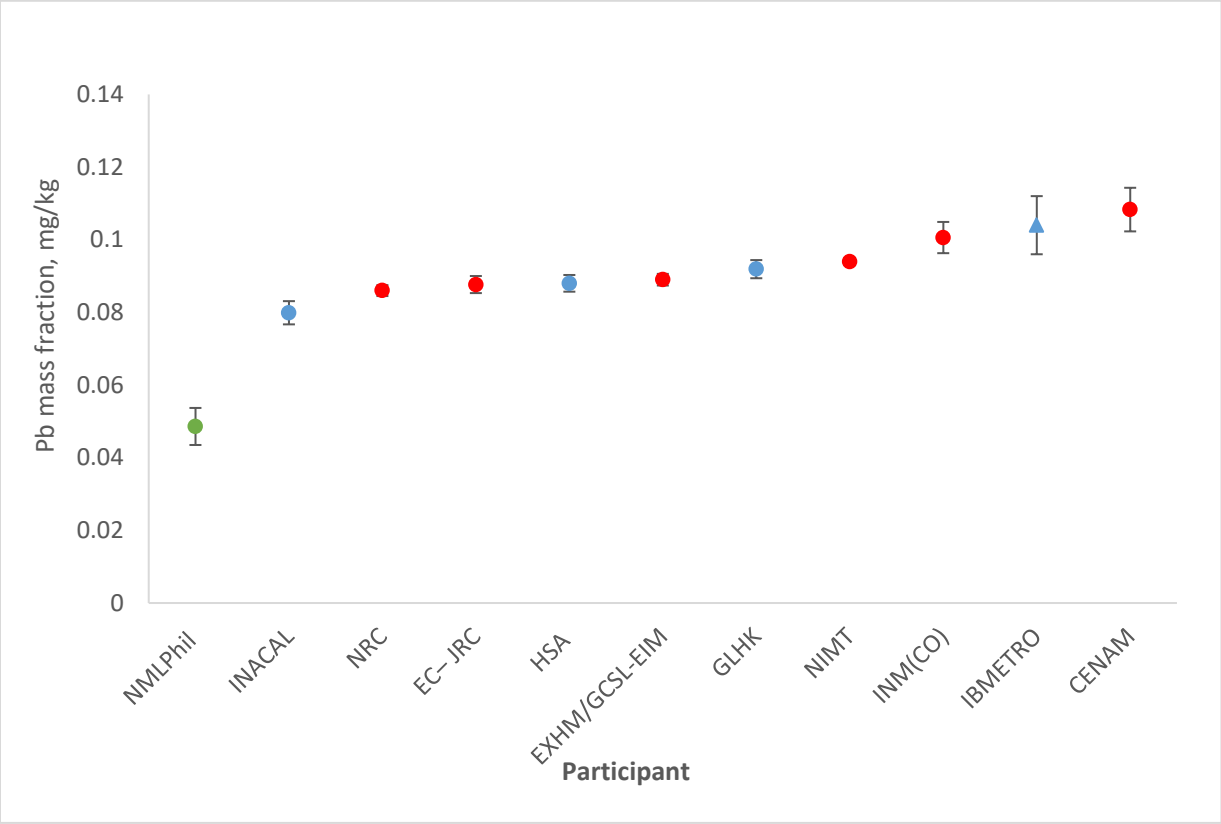
Eleven laboratories reported values for mass fraction of lead. Results are presented in Table 11.

Table 11. Reported Results for mass fractions of Pb, along with their associated combined uncertainties, relative expanded uncertainties, and the coverage factor *k*, in order of increasing mass fraction as reported by the participants**.**

Participant	Reported value (mg/kg)	u_c, (mg/kg)	Coverage factor *(k)*	*U* (mg/kg)	n	Degrees of Freedom	Analytical Method/ Instrument
NMLPhil	0.0486	0.0051	2	0.0102	5	7	gravimetric EC-ICP-MS with IS
INACAL	0.0799	0.0032	2	0.0064	5	13	SA-ICP-MS with IS
NRC	0.086	0.0015	2	0.003	13	13	ID-MS
EC– JRC	0.08766	0.00235	2	0.0047	5	7.4	ID-MS
HSA	0.0880	0.0023	2.26	0.0052	7	10	gravimetric SA-ICP-MS
EXHM/GC SL-EIM	0.089	0.0016	2	0.0032	5	30	gravimetric SA-ICP-MS
GLHK	0.0919	0.0025	2	0.0049	8	63	gravimetric SA-ICP-MS with IS
NIMT	0.094	0.001	2	0.002	5	9	ID-MS
INM(CO)	0.1006	0.0043	2	0.0087	10	60	ID-MS with Padé function
IBMETRO	0.104	0.008	2.13	0.016	5	15	SA- GF-AAS
CENAM	0.1083	0.006	2.4	0.014	7	7.4	ID-ICP-SF-MS

n: Number of independent replicates

Figure 4. Lead mass fraction as reported by the participants. Error bars denote the combined standard uncertainty (u_c, k=1).



Red: ID; Blue: SA, Green: EC; Circle: ICP-MS, Triangle: GF-AAS

8. Discussion

8.1 Supplementary Comparison Reference Values (SCRVs)

The compiled data for the SIM.QM-S18 Supplementary Comparison on trace elements in cacao powder were circulated to all participants on January 28, 2025 for checking any transcription and typographical errors. Participants were requested to review their data and provide comments by February 14, 2025, ensuring that results could be presented at the SIM WG8 meeting in March and IAWG meeting in early April 2025.

8.2 Screening the data for consistency and outlier rejection

No results were identified as outliers. Although the cadmium results reported by IBMETRO was higher than those submitted by the other participants, no technical reason was found to exclude the result.

8.3 Determination of the Supplementary Comparison Reference Values (SCRV), Degrees of equivalence and their associated uncertainties

The NIST decision tree was employed to calculate both SCRVs and the degrees of equivalence for each participant. The inputs to the NIST decision tree included the participant identification, reported results including uncertainty and degrees of freedom. Following hypothesis tests regarding homogeneity, symmetry and normality (Gaussian shape), the NIST decision tree recommends the most suitable statistical model for calculating both the SCRV and degrees of equivalence (D_i). Those values are listed in Tables 12 to 15 and presented in Figures 5 to 8.

8.3.1 Cadmium

Table 12 shows results of the decision tree hypothesis tests for cadmium in SIM.QM-S18. The NIST decision tree recommended using the Hierarchical Laplace-Gauss approach for the cadmium data.

Table 12. Decision tree hypothesis test results for cadmium in SIM.QM-S18

Decision tree hypothesis	**Results**	**Answers**
Cochran's test for homogeneity	*p*-value = 0.0186 Q = 25.71 (Reference Distribution: Chi-Square with 13 Degrees of Freedom) tau est. = 0.002112 tau/median(x) = 0.01538 tau/median(u) = 0.6306	Assume Homogeneity? no
Miao-Gel-Gastwirth test of Symmetry	*p* = 0.062	Assume Symmetry? Yes
Shapiro-Wilk test for Normality	*p* = 0.02	Assume Normality? no
Recommended Approach	Hierarchical Laplace-Gauss	
SCRV, mg/kg	0.1378	
Standard uncertainty (u), mg/kg	0.0007302	
Dark uncertainty (σ), mg/kg	0.0009481	

Figure 5 shows the participants' results relative to the SCRV estimation using the NIST decision tree (Hierarchical Laplace-Gauss). Degrees of equivalence and their uncertainties are listed in Table 16 and also presented in Figure 6.

Figure 5. SCRV estimation for cadmium in SIM.QM-S18 using the NIST decision tree (using Hierarchical Laplace-Gauss for SCRV estimation); the yellow band represents *u*(SCRV).

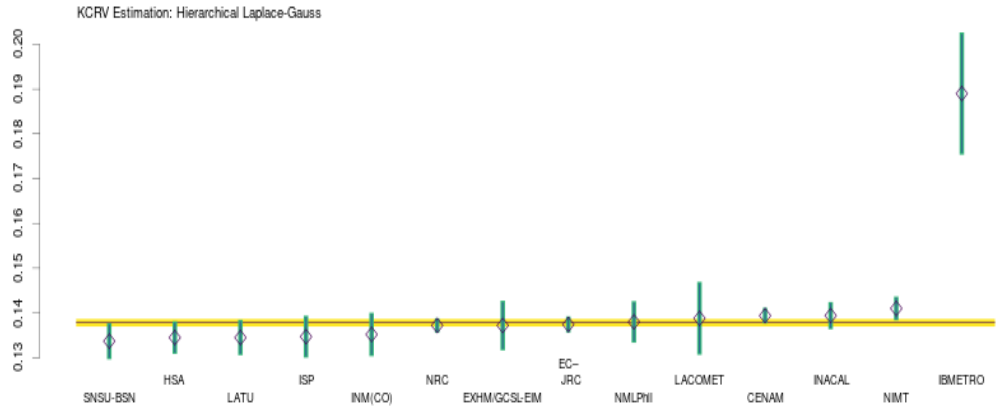
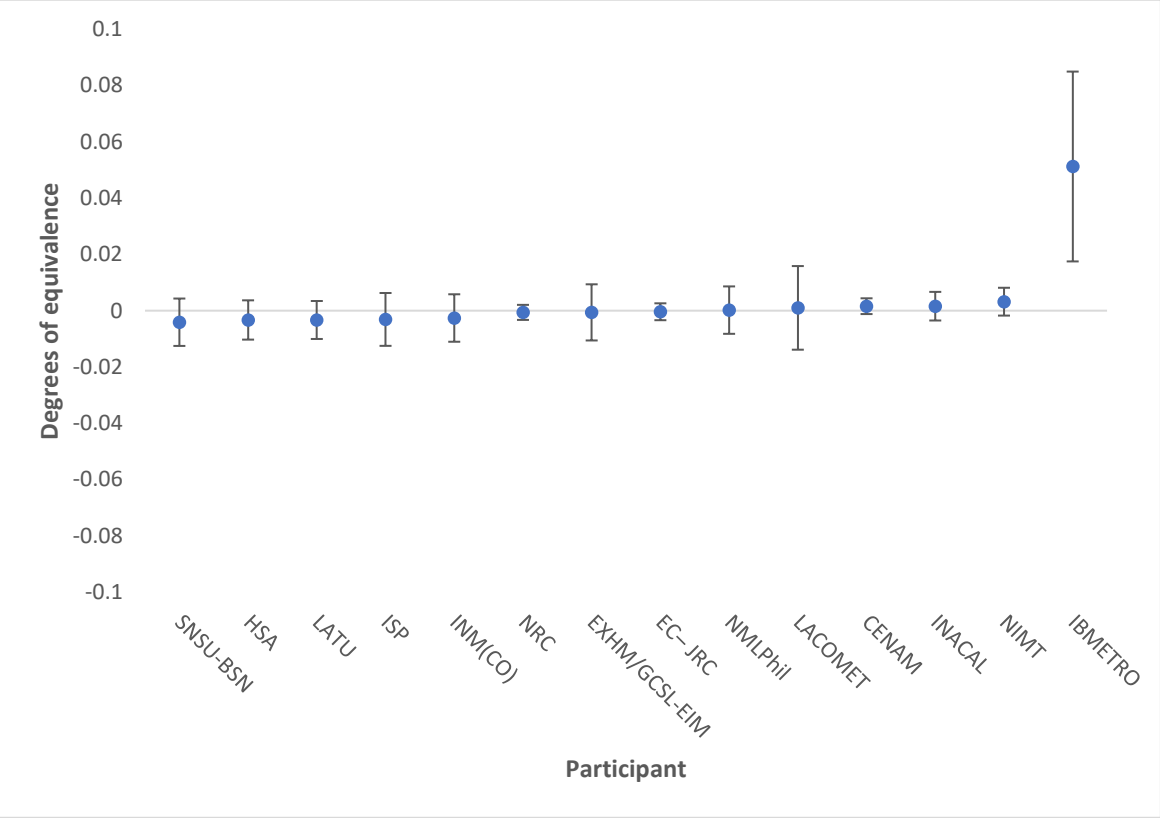


Table 13. Degrees of equivalence and their uncertainties (95 % CI) for cadmium in SIM.QM-S18 (using Hierarchical Laplace-Gauss for SCRV estimation).

Participant	Reported mass fraction, x_i (mg/kg)	Standard uncertainty, u_i (mg/kg)	Difference from SCRV, D_i (mg/kg)	Expanded uncertainty of the difference, $U(D_i)$ (mg/kg)	$D_i/U(D_i)$
SNSU-BSN	0.1337	0.0034	-0.0041	0.008416	-0.48764
HSA	0.1345	0.003	-0.0033	0.006975	-0.47369
LATU	0.1345	0.0033	-0.0033	0.006739	-0.49028
ISP	0.1347	0.00404	-0.0031	0.009386	-0.33071
INM(CO)	0.1352	0.0042	-0.0026	0.008429	-0.30893
NRC	0.1372	0.001	-0.0006	0.002673	-0.22593
EXHM/GCSL-EIM	0.1372	0.0047	-0.0006	0.009972	-0.06056
EC– JRC	0.13742	0.00117	-0.0004	0.002999	-0.12801
NMLPhil	0.138	0.004	0.0002	0.008419	0.023293
LACOMET	0.1388	0.0075	0.001	0.01485	0.067077
CENAM	0.1394	0.0011	0.0016	0.002801	0.569797
INACAL	0.1394	0.0024	0.0016	0.005078	0.314297
NIMT	0.141	0.002	0.0032	0.004941	0.646833
IBMETRO	0.189	0.01303*	0.0512	**0.03371***	1.518837

**Reported values and tau summed in quadrature*

Figure 6. Degrees of equivalence estimates for cadmium in SIM.QM-S18 (using Hierarchical Laplace-Gauss for SCRV estimation).



The dark uncertainty was combined in quadrature with the reported value for the results submitted by IBMETRO. Despite this adjustment, the results remain in disagreement with the SCRV value, as the degree of equivalence is still significantly distant from zero. Consequently, IBMETRO will not be able to use this comparison to support a CMC claim for Cd.

8.3.2 Lead

Table 14 shows results of the decision tree hypothesis tests for lead in SIM.QM-S18. The NIST decision tree recommended using the Hierarchical Gauss-Gauss approach for the lead data.

Table 14. Decision tree hypothesis test results for lead in SIM.QM-S18

Decision tree hypothesis	**Results**	**Answers**
Cochran's test for homogeneity	$p < 0.001$ Q = 120.1 (Reference Distribution: Chi-Square with 10 Degrees of Freedom) tau est. = 0.007352 tau/median(x) = 0.08261 tau/median(u) = 2.941	Assume Homogeneity? No
Miao-Gel-Gastwirth test of Symmetry	$p = 0.99$	Assume Symmetry? Yes
Shapiro-Wilk test for Normality	$p = 0.57$	Assume Normality? Yes
Recommended Approach	**Hierarchical Gauss-Gauss**	
SCRV, mg/kg	0.08902	
Standard uncertainty (u), mg/kg	0.003781	
Dark uncertainty (σ), mg/kg	0.01256	

Figure 7 illustrates the participants' results in relation to the SCRV estimation using the NIST decision tree (Hierarchical Gauss-Gauss). Figure 8 showcases the degrees of equivalence estimates for lead. Table 15 provides a detailed listing of the degrees of equivalence along their associated uncertainties.

Figure 7. SCRV estimation for lead in SIM.QM-S18 using the NIST decision tree (using Hierarchical Gauss-Gauss for SCRV estimation) ; the yellow band represents *u*(SCRV), and the skinny extensions on each laboratory's uncertainty bar represents the contribution of dark uncertainty.

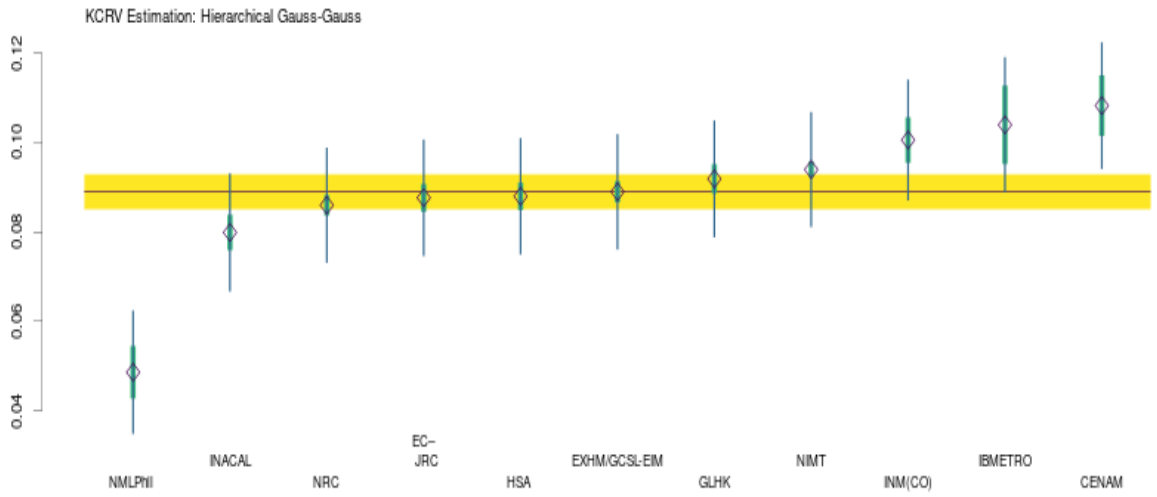
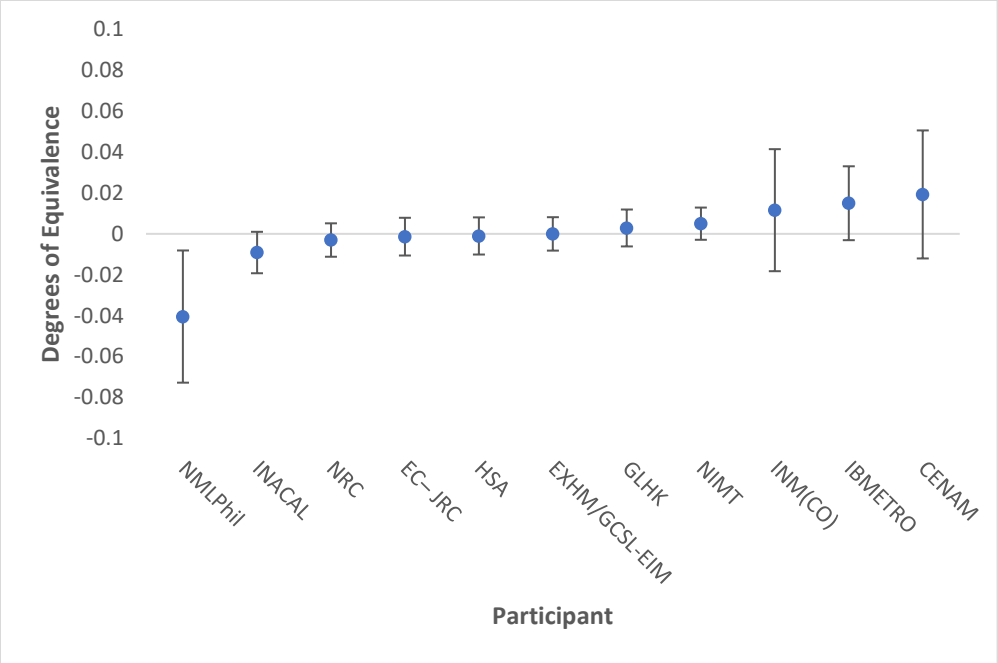


Table 15. Degrees of equivalence and their uncertainties (95 % CI) for lead in SIM.QM-S18 (using Hierarchical Gauss-Gauss for SCRV estimation).

Participant	Reported mass fraction, x_i (mg/kg)	Standard uncertainty, u_i (mg/kg)	Difference from SCRV, D_i (mg/kg)	Expanded uncertainty of the difference, $U(D_i)$ (mg/kg)	$D_i/U(D_i)$
NMLPhil	0.0486	0.01356*	- 0.04042	**0.03231***	-1.25101
INACAL	0.0799	0.0032	- 0.009116	0.01013	-0.89990
NRC	0.086	0.0015	- 0.003016	0.008164	-0.36943
EC– JRC	0.08766	0.00235	- 0.001356	0.009224	-0.14701
HSA	0.088	0.0023	- 0.001016	0.009082	-0.11187
EXHM/GCSL-EIM	0.089	0.0016	- 0.00001598	0.008169	-0.00196
GLHK	0.0919	0.0025	0.002884	0.009024	0.31959
NIMT	0.094	0.001	0.004984	0.007874	0.63297
INM(CO)	0.1006	0.01328*	0.01158	**0.02983***	0.38820
IBMETRO	0.104	0.008	0.01498	0.01806	0.82946
CENAM	0.1083	0.01392*	0.01928	**0.03129***	0.61617

**Reported values and tau summed in quadrature*

Figure 8. Degrees of equivalence estimates for lead in SIM.QM-S18 (using Hierarchical Gauss-Gauss for SCRV estimation).



For the Pb results submitted by INM(CO), CENAM and NMLPhil, the dark uncertainty was combined in quadrature with the reported value. With this adjustment, the results from INM(CO) and CENAM are now in agreement with the SCRV value. However, for NMLPhil, even after this adjustment, its result remains in disagreement with the SCRV value, as the degree of equivalence is still significantly distant from zero. Consequently, NMLPhil will not be able to use this comparison to support a CMC claim for Pb.

9. Demonstrated Core capabilities – How far the light shines

Successful participation in this supplementary comparison demonstrates the capability for the determination of trace elements in food matrices. According to the IAWG Core Capability Matrix, this material falls into the matrix challenge called “High organics content”. Consequently, this comparison supports broad scope CMC claims for transition elements in high organic content materials, at mass fraction levels above 50 µg/kg.

10. Conclusion

The SIM.QM-S18 supplementary comparison successfully assessed the capability of participating NMIs and DIs to measure trace levels of cadmium and lead in cacao powder, a challenging high organic content food matrix. The preparation and characterization of the study material met the requirements for homogeneity and stability, ensuring its suitability for the comparison.

Participants used a variety of analytical methods, with the majority utilizing ICP-MS, either via gravimetric SA or ID-MS. The SCRVs, along with their corresponding expanded uncertainties and degrees of equivalence, were calculated using the NIST decision tree approach.

The determination of lead proved more challenging than cadmium due to variations in isotopic composition of lead in the cacao powder when analyzed by ICP-MS technique. Despite this challenge, most participants achieved results in agreement with the SCRVs within their expanded uncertainties.

Overall, SIM.QM-S18 was a successful supplementary comparison, enabling participants to support CMC claims under the broad scope core capability approach for transition elements in high organic content.

11. Acknowledgments

The study coordinators extend their sincere thanks to all participating laboratories for providing the requested information used in this study. We also gratefully acknowledge the NRC ICM team for the preparation of the material and for providing invaluable logistical support throughout the comparison.

12. References

NIST decision tree (Version 1.0.4), https://decisiontree.nist.gov/ accessed October 2025

Possolo, A., Koepke, A., Newton, D. and Winchester, M. (2021), Decision Tree for Key Comparisons, Journal of Research (NIST JRES), National Institute of Standards and Technology, Gaithersburg, MD, [online], https://doi.org/10.6028/jres.126.007

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APPENDIX A

SIM.QM-S18/ SIM.QM-P27

Cd and Pb in Cacao Powder

Study Protocol

[January 2024]

Patricia Grinberg[1], Maria del Rocio Arvizu Torres[2], Melina Perez[2]

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1. INTRODUCTION

With annual global chocolate consumption of approximately 7.5 million metric tons last year and a global chocolate industry worth approximately $130 billion, the market for cacao-related products is a significant part of the global food economy.

Cacao beans are the main ingredient in chocolate production. It is well known that some dark chocolates currently available in the market are contaminated with toxic metals (Cd & Pb) and it is mainly due to the presence of these contaminants in the cacao beans used to produce the chocolates. In general, cacao powder has the highest concentration of heavy metals. It's made by essentially concentrating the solids of the cacao bean and removing the oils (known as cacao butter).

Over the past few years, food safety regulations around the world have been revising the maximum levels of toxic metals in cacao products such as chocolate and cocoa powder. For instance, as of 2019, in the European Union, products that exceed the maximum level cannot be placed on the market.

This proposal is for the determination of cadmium and lead in cacao powder. The matrix of cacao powder has not yet been tested before in CCQM and RMO studies.

This comparison is organized jointly by the National Research Council Canada (NRC) and National Metrology Institute of Mexico (CENAM). Evidence of successful participation in formal, relevant international comparisons is needed to document calibration and measurement capability claims (CMCs) made by national metrology institutes (NMIs) and designated institutes (DIs). Although this is organized as a SIM regional comparison, it is open to other participants of the MRA throughout all RMOs. A pilot study will be run in parallel with this comparison.

Results for this supplementary comparison will be registered on the BIPM Key comparison Database (KCDB).

2. PROPOSED SCHEDULE

The following table lists the timeline for the proposed study.

Table 1. Proposed schedule

Date	**Action**
April/ May 2023	Sample Preparation
May 2023	Send Questionnaire
May/ September 2023	Homogeneity & Stability Studies
June 2023	Deadline for submission of questionnaire
November 2023	Presentation of homogeneity and stability studies
December 2023	Call for participation
January 26, 2024	Deadline for registration
February 2024	Distribution of samples
September 2024	Deadline for submission of results
October 2024	Circulation of compile data among participants
November/ Dec 2024	First results discussion at SIM and CCQM IAWG meeting
Jan 2025	Draft A submitted to participants
Feb 2025	Breakout meeting with participants

3. MEASURANDS

The measurands and their expected mass fractions are listed in Table 2 (on a dry mass basis).

Table 2. Measurands and expected mass fraction range.

Element	**Expected mass fraction**	**Natural/Spiked**	**Description**
Cadmium (Cd)	(0.01-2) mg/kg	Natural	Toxic element
Lead (Pb)	(0.01-2) mg/kg	Natural	Toxic element

4. STUDY MATERIAL

4.1 Preparation

The source of the study material was commercially available cacao powder.

The material was sieved to pass an 850 µm nylon screen, blended and bottled in amber glass bottles. After bottling, the material was sterilized by subjecting it to a minimum dose of 25 kGy gamma irradiation. Following irradiation, the material was packaged in trilaminate bags. Each unit contains minimum 15 g of the material. Fat content is about 15 %.

4.2 Recommended Minimum Sample Amount

The recommended minimum sample amount for analysis is 0.25 g. Participating NMIs/DIs should take at least 5 subsamples for the measurement of measurands. The bottle contents should be well mixed by rotation and shaking prior to use.

4.3 Dry mass determination

The dry mass correction determination must be performed on a minimum of three separate portions of 1 g each. Sub-samples should be dried over anhydrous calcium sulphate (e.g. DRIERITE) or magnesium perchlorate in a desiccator for at least 10 days until constant mass is attained (as recommendation: successive weights should not differ more than 1 mg). Do not use the sample, which was used for the determination of moisture content, for analysis.

The elemental contents determined should be reported on the basis of dry mass.

4.4 Homogeneity and stability assessment of Study Material

Ten bottles of sample were randomly selected for homogeneity study. Three subsamples were taken from each bottle for analysis. Determination of Cd and Pb was performed by ICP-MS.

ANOVA at 95 % level of confidence was applied to assess the between-bottle homogeneity in accordance with ISO Guide 35:2017. The study material was found to be sufficiently homogeneous. The results are summarized in Table 3.

Table 3. Results of the homogeneity assessment for the measurands.

Measurand	ANOVA test		Relative standard uncertainty due to between-bottle (in)homogeneity, u_{bb} (%)
	F-statistics	Critical value	
Cadmium	1.17	2.29	0.4
Lead	1.23	2.29	0.9

The short-term stability of the measurands over a period of 6 weeks at 40 °C was assessed using isochronous approach. Two randomly selected sample bottles were transferred from the storage condition (-20 °C) to 40 °C on three occasions (2 weeks, 4 weeks, and 6 weeks) over the study period. Two subsamples were then taken from each bottle. Determination of Cd and Pb was performed by ICP-MS. Using Student's *t*-test on the slope of the linear regression at 95 % level of confidence, no significant instability of the measurands was observed upon exposure to 40 °C up to 6 weeks. The results are presented in Table 4.

Table 4. Results of the stability assessment for the measurands at 40oC over a period of 6 weeks.

Measurand	Student's *t*-test		*p*-value
	Calculated test statistics	Critical value	
Cadmium	-0.558	4.303	0.5880
Lead	-0.644	4.303	0.5326

The long-term stability of the measurands in the comparison material at -20 °C will be assessed. The testing will be carried out before sample dispatch and continuously monitored until completion of the supplementary comparison using the classical approach. For each occasion of the stability testing, at least two bottles will be randomly selected, and two subsamples will be taken from each bottle. Student's t-test on the slope of the linear regression at 95 % level of confidence will be used for the evaluation of instability of the measurands.

5 AVAILABLE CALIBRATION MATERIALS

In accordance with Section 3.1 of CIPM MRA-G-13 (CIPM MRA-G-13), participants may establish the metrological traceability of their results to the SI using a direct realization via a primary method or using certified reference materials (CRMs) from an NMI/DI having the required CMC claims. Participants may prepare their own calibrants from high-purity source materials that they have independently assayed for purity, but a full explanation of how this was done will be required when reporting measurement results. Table 5 lists examples of the matrix CRMs that are available for use as quality control material for this study.

Table 5. Examples of Matrix Certified Reference Materials Available for Use

CRM	**Provider**	**Measurand**
SRM 2384, baking chocolate	NIST	Cd, Pb
SRM 2386, avocado powder	NIST	Cd

CRM	Provider	Measurand
SRM 1577c, bovine liver	NIST	Cd, Pb
DORM-5, fish protein	NRC	Cd, Pb
ERM-BD512 dark chocolate	ERM	Cd
ERM- BD 513, Cd in Cocoa	BAM/ERM	Cd
ERM- BD 514, Cd in Cocoa	BAM/ERM	Cd
ERM- BD 515, Cd in Cocoa	BAM/ERM	Cd

Table 6 lists examples of primary standards available that could be used in this study, including both elemental calibration solutions and high-purity source materials available from NMIs/DIs that can be used to prepare one's own calibration solutions. Participants can also refer to the KCDB link (https://www.bipm.org/kcdb/cmc/advanced-search?area=8) to search for the analyte in the category of "Inorganic solutions" in order to find those calibration reference materials that fulfill the CIPM MRA requirement for key/supplementary comparisons.

Table 6. Examples of Primary Standards Available for Use

Provider	Primary standard
Cd	
NIST	SRM 3108 – Cadmium (Cd) Standard Solution
NIM	GBW08612, 1000 µg/mL
NMIJ	CRM 3609-a – Cadmium (Cd) Standard Solution (1000 mg/kg)
CENAM	CMR-6100085f Cadmium (Cd) Spectrometric Standard Solution (1000 mg/kg)
CENAM	DMR-461a, Cadmium (Cd) Spectrometric Standard Solution (1000 mg/kg).
Pb	
CENAM	CMR-62063f Lead (Pb) Spectrometric Standard Solution (1000 mg/kg).
CENAM	DMR-463a Lead (Pb) Spectrometric Standard Solution (1000 mg/kg).
NIST	SRM 3128 – Lead (Pb) Standard Solution

Provider	Primary standard
NIST	SRM 983 – Radiogenic Lead Isotopic Standard
NRC	HIPB-1- High Purity Lead CRM for Lead Mass fraction, Atomic Weight, Isotopic Composition and Elemental Impurities (requires digestion and dissolution) doi.org/10.4224/crm.2020.hipb-1
NRC	ALED-1 – Lead-206 and lead-207 double spike isotopic standard doi:10.4224/crm.2021.aled-1
NRC	BLED-1 – Lead-204 and lead-207 double spike isotopic standard doi:10.4224/crm.2021.bled-1
NRC	CLED-1 – Lead-206 and lead-208 double spike isotopic standard doi:10.4224/crm.2021.cled-1
NRC	ELED-1 – Equal atom lead isotopic standard doi:10.4224/crm.2021.eled-1
NIM	GBW08619, 1000 µg/mL
BAM	Pb BAM Y004 high purity lead (requires digestion and dissolution)
NMIJ	CRM 3608-a – Lead (Pb) Standard Solution (1000 mg/kg)
NMIJ	CRM 3681-a – Lead Isotopic Standard Solution

6 INSTRUCTIONS AND SAMPLE DISTRIBUTION

Each participant will receive one vial of the sample containing at least 15 g of sample. If more sample is required, please inform us at the time of registration.

The samples will be distributed by courier to the participants (monitored by a temperature strip). Participants will be informed and provided with the tracking number after samples dispatch. Upon receipt, the samples should be stored at -20 °C (due to the fat content). A Sample Receipt Form will be provided to the participating NMIs/DIs for completion. The completed form should be sent to CENAM and NRC at your earliest convenience.

Prior to use, the material should be allowed to warm to room temperature and the contents of the vial should be thoroughly mixed by gentle shaking and rolling of the container. After use, the vials should be tightly closed and returned to the freezer.

7 CHOICE OF METHOD / PROCEDURE

Participants may use any method of their choice. Calibrations should be carried out using standards with metrological traceability in accordance with section 3 in CIPM MRA-G-13 (https://www.bipm.org/documents/20126/43742162/CIPM-MRA-G-13.pdf/f8b8c429-42e0-4cf1-dc6c-bc60ab7f371a).

8 REPORTING OF RESULTS

A reporting template will be supplied to all participants by email before sample dispatch.

Please use the supplied reporting template when submitting the results and include:

-Results for each measurand should be reported in minimum five independent replicate measurements as the element content mass fraction (mass/mass, mg/kg) on test aliquots drawn from the bottle.

- A detailed uncertainty budget

-A detailed description of the sample preparation methods, analytical techniques, calibration approach, calibration standards, reference material used, and any corrections applied (such as interference elimination method). If calibration standards were prepared in-house, please include a detailed description of the preparation procedure.

- Source of traceability

- Participants are encouraged to provide any results obtained for matrix CRMs used as QC.

- Results of all participating NMIs/DIs will be evaluated against the supplementary comparison reference value (SCRV). The SCRV and associated uncertainty will only be determined from results of NMIs/DIs that participate in the supplementary comparison using methods with demonstrated metrological traceability. The document “CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence” shall be referenced for SCRV and Degree of Equivalence (DoE) calculations.

If the participant decides to report the individual results from different methods, one of the results must be declared as the “best value” for inclusion in SIM.QM-S18 and any others will be included in SIM.QM-P27. The method that will be used to obtain this “best value” must be stated by the participant during registration. Only the “best value” will be used for the calculation of the SCRV.

9 USE OF SIM.QM-S18/SIM.QM-P27 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

9.1 How Far the Light Shines

Successful participation in this supplementary comparison will help demonstrate capabilities for determination of elements in food matrices. Considering the IAWG Core Capability Matrix, this material falls into the matrix challenge called “High organics content”, and so will support CMCs for the following analyte groups

- Cadmium and Lead: Transition elements at mass fraction levels above 50 µg/kg, except mercury.

Participation is open to all NMIs/DIs as listed in the CIPM MRA (https://www.bipm.org/en/cipm-mra/participation). Thank you very much for your participation!

10 CONTACT DETAILS

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Melina Perez Urquiza

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11 REFERENCES

CIPM MRA-G-13 “Calibration and measurement capabilities in the context of the CIPM MRA, Guidelines for their review, acceptance and maintenance”, Version 1.1, 30/03/2021.

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

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Appendix B

SIM.QM-S18/ SIM.QM-P27: Cd and Pb in Cacao Powder

Registration Form

This invitation to participate is extended to National Metrology Institutes (NMIs) and Designated Institutes (DIs) in all RMOs

Participant's Name	
Name of the Institute	
NMI/DI	☐ National Metrology Institute (NMI) ☐ Designated Institute (DI)
Country	
Address	
Postal code	
E-Mail:	
Tel.-Number	
Fax-Number	

Canada

Indicate the element(s) for which you will be submitting results by inserting an **X** under the heading of the appropriate comparison. Also please include the methods of analysis that you will be using.

Measurand	**SIM.QM-S18 Supplementary Comparison**	**SIM.QM-P27 Pilot**	**Methods of analysis***
Cd	☐	☐	
Pb	☐	☐	

**If more than one method used, please indicate the method that should be used for the calculation of the SCRV*

Number of vials required	

Shipping instructions:

Please indicate any special instructions (local customs/special permits) for importation and the full shipping address and telephone number of a contact.

Please send the completed form by e-mail before January 26, 2024 to:

Patricia Grinberg
National Research Council Canada
patricia.grinberg@nrc-cnrc.gc.ca

Maria del Rocio Arvizu Torres
National Metrology Institute of Mexico, Mexico
marvizu@cenam.mx

If you do not receive an acknowledgement of your registration from us within 5 working days, please send us an email.

We look forward to your participation in this comparison.

Yours sincerely,

Dr. Patricia Grinberg	**M.Sc. Maria del Rocio Arvizu Torres**
NRC	**CENAM**

Appendix C

Core Capability Information

European Commission – Joint Research Centre (EC-JRC), Belgium

For ID-ICP-MS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	For Pb, procedural blanks are higher than desired. Sample preparation and drying of acid washed vessels took place on clean benches (HEPA filtered laminar airflow). However, a clean room was not available.
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.	
Digestion/dissolution of inorganic matrices	*N/A*
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.	
Digestion/dissolution of organic matrices	No specific challenges.
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	
Volatile element containment	*N/A*
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	*N/A*
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.	
Vapor generation	*N/A*
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.	
Matrix separation	*N/A*

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	
Spike equilibration with sample	No specific challenges.
The mixing and equilibration of the enriched isotopic spike with the sample	
Signal detection	The instrumental method for Pb ratio measurement required improvement. Variance on ratio measurement for the Pb molar mass determination was higher than desired.
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.	
Memory effect	No specific challenges.
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Correction or removal of isobaric/ polyatomic interferences	The sample contained a comparitively large amount of W. For the molar mass determination of Pb in the sample, the influence of WO+ formation on the m/z 202 was quantified to allow correction of the Hg content and its influence on the m/z 204 signal. For Cd measurement, Mo was present in sample digests, but the influence of MoO+ formation on 113/111 ratios was found to be insignificant.
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	
Detector deadtime correction	No specific challenges.
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	For Cd mass bias determination, blends are run in sequence with bracketing unspiked sample digests. For this series of measurments there was an unexplained outlier in a measurement of an unspiked sample, which was discarded.
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	No specific challenges. (Certified values of CRMs were used).
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

Instituto Boliviano de Metrología (IBMETRO), Bolivia

For ICP-MS (without ID), ICP-OES or ETAAS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	Standards and samples were prepared using ultra-pure water and distilled nitric acid. Blanks were measured at the beginning and the end of the measurement of each analyte.
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.	
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.	
Digestion/dissolution of organic matrices	*Acid digestion with 4 mL of with Nitric acid and 1 mL of hydrogen peroxide in 2 cycles of digestion at 190 °C*
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 or ETAAS	
Volatile element containment	
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	
Techniques and procedures used to increase the concentration of the analyte introduced to the ICP or ETAAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	
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/ETAAS.	
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	

Hydride preconcentration/ matrix separation of volatile species.	
Coupling of a hydride system to the ICP or ETAAS and optimization of conditions.	
Calibration of analyte concentration	External calibration with single point standard addition was used to measure each analyte. A 0,2% HNO3 solution was used to prepare standards and to dilute samples.
The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.	
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.	
Memory effect	
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Optimization of the furnace temperature program (for ETAAS)	*Optimizations of furnace program for each analyte were done.* *For Cd: recommended conditions from manufacturer (Perkin Elmer PinAAcle 900T) with the following changes:* *Pyrolysis temperature: 500 °C* *Atomization temperature: 1600 °C* *For Pb: recommended conditions from manufacturer (Perkin Elmer PinAAcle 900T) with the following changes:* *Pyrolysis temperature: 900 °C* *Atomization temperature: 1700 °C*
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.	
Correction or removal of isobaric/ polyatomic interferences (for ICP)	
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	
Correction or removal of matrix effects or interferences	Matrix modifiers were used for measurement of analytes:

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.	As: 5 µg Pd + 3 µg $Mg(NO_3)_2$, modifier volume: 10 µL, sample volume: 20 µL Cd and Pb: 50 µg $NH_4H_2PO_4$ + 3 µg $Mg(NO_3)_2$, modifier volume: 10 µL, sample volume: 20 µL No background correction was used.
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.	
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.	
Detector deadtime correction	
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

National Research Council Canada (NRC), Canada

For ID-ICP-MS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	Samples were prepared in the clean room to avoid contamination. In addition, process blanks were carried out, which were used for the final correction of results.
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.	
Digestion/dissolution of inorganic matrices	*N/a*
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.	
Digestion/dissolution of organic matrices	*A subsample of 0.25g was taken from each bottle, spiked with proper amount of isotopic solution and digested in a Multivawe PRO using 7mL of sub-boiled HNO3 and 0.5mL of Optima grade H2O2. Sample solutions were transfered to tefflon tube and evaporated to 0.5-1mL, and reconstituted in 25 mL with DIW to have a final acid concentration of roughly 2%.*
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	
Volatile element containment	*n/a*
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	*n/a*
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.	
Vapor generation	*n/a*
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.	
Matrix separation	*n/a*

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	
Spike equilibration with sample	Microwave digestion was employed to ensure spike equilibration prior to analysis by ICP-MS.
The mixing and equilibration of the enriched isotopic spike with the sample	
Signal detection	Mass fractions of analytes are high enough, no difficulty to record the signals.
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.	
Memory effect	*Between samples, it was rinse with 2% HNO3 to the blank level.*
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Correction or removal of isobaric/ polyatomic interferences	The instrument software auto-correct the signal of Cd113 = -0.0449*In115. In115=-0.0149*Sn118
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	
Detector deadtime correction	Yes
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	Yes, it was corrected
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	Reverse ID was applied
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

Health Public Institute of Chile (ISP), Chile

For ICP-MS (without ID), ICP-OES or ETAAS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	rigorous cleaning procedures for labware (e.g., soaking in 20% HNO_3 for 24 hours and rinsing with reactive-grade water).
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.	
Digestion/dissolution of inorganic matrices	*Complete dissolution of inorganic matrices using microwave digestion with HNO_3 and H_2O_2 under controlled conditions*
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.	
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 or ETAAS	
Volatile element containment	
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	
Techniques and procedures used to increase the concentration of the analyte introduced to the ICP or ETAAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	
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/ETAAS.	
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	
Hydride preconcentration/ matrix separation of volatile species.	
Coupling of a hydride system to the ICP or ETAAS and optimization of conditions.	
Calibration of analyte concentration	
The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.	
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.	
Memory effect	
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Optimization of the furnace temperature program (for ETAAS)	
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.	
Correction or removal of isobaric/ polyatomic interferences (for ICP)	
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	

Correction or removal of matrix effects or interferences	Viscosity differences and matrix composition affecting ionization efficiency. Mitigated with internal standards and gravimetric standard addition.
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.	
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.	
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.	
Detector deadtime correction	
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

Instituto Nacional de Metrología de Colombia (INM(CO)), Colombia

For ID-ICP-MS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	Blank evaluation in each batch. Use of doubly subdestilled nitric acid and ultrapure water. Cleaning procedures for plastic labware and the interface cones of the ICP-MS.
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.	
Digestion/dissolution of inorganic matrices	Not tested
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.	
Digestion/dissolution of organic matrices	*Microwave assisted acid digestion.*
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	
Volatile element containment	Not tested
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	Not tested
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.	
Vapor generation	Not tested
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.	
Matrix separation	Not tested
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.	
Spike equilibration with sample	Samples were digested after spiking with enriched isotopes. After digestion, solutions were thoroughly mixed in vortex.
The mixing and equilibration of the enriched isotopic spike with the sample	
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.	Setting of 80 sweeps per reading and 10 replicates for each isotope signal detection.
Memory effect	*Tubing cleaning with diluted nitric acid between samples.*
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Correction or removal of isobaric/ polyatomic interferences	Not tested
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	
Detector deadtime correction	Not tested
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	Standard-sample bracketing with lead isotopic reference material (NIST SRM 981) during the confirmation of the similar isotopic composition of lead in samples and calibrants.
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	Reverse isotope dilution was used to determine the analyte concentration in the enriched spike solutions.
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

Laboratorio Costarricense de Metrología (LACOMET), Costa Rica

For ICP-MS (without ID), ICP-OES or ETAAS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	A reagent blank was included for the analysis of the SIM.QM-S18 samples and the IQC NIST 2384 to account for potential contamination
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.	
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.	
Digestion/dissolution of organic matrices	The samples and the IQC were digested using the same acids and microwave-assisted acid digestion. The residual acid from the digestion process was evaporated under controlled conditions
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 or ETAAS	
Volatile element containment	
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	Controlled acid evaporation reduced the residual acid content and allowed the definition of an appropriate dissolution mass for the measurement technique used.
Techniques and procedures used to increase the concentration of the analyte introduced to the ICP or ETAAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	
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/ETAAS.	
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	

Hydride preconcentration/ matrix separation of volatile species.	
Coupling of a hydride system to the ICP or ETAAS and optimization of conditions.	
Calibration of analyte concentration	Calibration was conducted using the standard addition method to mitigate matrix effects in the samples
The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.	
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.	
Memory effect	A cleaning step was performed during each measurement, and a sequential measurement approach was applied as follows: SIM.QM-S18 P27 sample, IQC NIST 2384 sample, SIM.QM-S18 P27 sample, IQC NIST 2384 sample, and so on. This strategy minimized memory effects between measurements.
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Optimization of the furnace temperature program (for ETAAS)	A matrix modifier consisting of a mixture of Pd and $Mg(NO_3)_2$ was used to enhance the sensitivity of the technique.
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.	
Correction or removal of isobaric/ polyatomic interferences (for ICP)	
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	
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.	The Zeeman effect correction was applied in all measurements to eliminate matrix interferences.
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.	
Correction or removal of matrix-induced signal suppression or enhancement	The residual acid from the digestion process was evaporated under controlled conditions
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.	
Detector deadtime correction	
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

National Chemical Metrology Laboratory (EXHM/GCSL-EIM), Greece

For ID-ICP-MS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	Blank & RM analysis in every Batch
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.	
Digestion/dissolution of inorganic matrices	4 mL up trace metal grade HNO_3 + 0.5 mL up H_2O + 0.5 mL H_2O_2
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.	
Digestion/dissolution of organic matrices	Microwave digestion with Antoon Paar Multiwave 7000
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	
Volatile element containment	none
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	none
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.	
Vapor generation	none
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.	
Matrix separation	none
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	

Spike equilibration with sample	overnight
The mixing and equilibration of the enriched isotopic spike with the sample	
Signal detection	none
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.	
Memory effect	blanks between each sample measured
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Correction or removal of isobaric/ polyatomic interferences	ICP MS/MS in He and O_2 mode measurement in high resolution mode
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	
Detector deadtime correction	none
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	none
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	none
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	
For ICP-MS (without ID), ICP-OES or ETAAS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	Blank & RM analysis in every Batch

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.	
Digestion/dissolution of inorganic matrices	4 mL up trace metal grade HNO_3 + 0.5 mL up H_2O + 0.5 mL H_2O_2
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.	
Digestion/dissolution of organic matrices	Microwave digestion with Antoon Paar Multiwave 7000
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 or ETAAS	
Volatile element containment	none
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	none
Techniques and procedures used to increase the concentration of the analyte introduced to the ICP or ETAAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	
Vapor generation	none
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/ETAAS.	
Matrix separation	none
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	
Hydride preconcentration/ matrix separation of volatile species.	none
Coupling of a hydride system to the ICP or ETAAS and optimization of conditions.	
Calibration of analyte concentration	

The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.	external CC with internal standards & Standard Addition experiments
Signal detection	none
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.	
Memory effect	blanks between each sample measured
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Optimization of the furnace temperature program (for ETAAS)	none
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.	
Correction or removal of isobaric/ polyatomic interferences (for ICP)	ICP MS/MS in He and O_2 mode measurement in high resolution mode
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	
Correction or removal of matrix effects or interferences	standard additions
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.	
Complex spectral backgrounds	none

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.	
Correction or removal of matrix-induced signal suppression or enhancement	Analysis in different instrumental modes (MS, MS/MS & HR MS) & Isotope Ratios CC & matrix Match CC for differnet isotopes, standard addition
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.	
Detector deadtime correction	none
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	*none*
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	none
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

Government Laboratory, Hong Kong (GLHK)

For ICP-MS (without ID), ICP-OES or ETAAS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	Nil
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.	
Digestion/dissolution of inorganic matrices	Residue remained when only HNO_3 and H_2O_2 were used for digestion. HF was required for the complete digestion of the sample.
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.	
Digestion/dissolution of organic matrices	Nil
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 or ETAAS	
Volatile element containment	Nil
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	NA
Techniques and procedures used to increase the concentration of the analyte introduced to the ICP or ETAAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	
Vapor generation	NA
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/ETAAS.	
Matrix separation	NA
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	

Hydride preconcentration/ matrix separation of volatile species.	NA
Coupling of a hydride system to the ICP or ETAAS and optimization of conditions.	
Calibration of analyte concentration	Nil
The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.	
Signal detection	Nil
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.	
Memory effect	Nil
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Optimization of the furnace temperature program (for ETAAS)	NA
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.	
Correction or removal of isobaric/ polyatomic interferences (for ICP)	Nil
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	
Correction or removal of matrix effects or interferences	Nil

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.	
Complex spectral backgrounds	NA
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.	
Correction or removal of matrix-induced signal suppression or enhancement	Nil
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.	
Detector deadtime correction	NA
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	Nil
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	Nil
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

National Measurement Standards, National Standardization Agency of Indonesia (SNSU-BSN), Indonesia

For ICP-MS (without ID), ICP-OES or ETAAS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	The sample was poured into a cleaned centrifuge tube prior to preparation to avoid contamination directly to the bottle sample. The blank reagent was measured to check for any contamination 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.	
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.	
Digestion/dissolution of organic matrices	The sample was digested using microwave assisted digestion system, added with HNO_3, H_2O_2, and HF. The digested sample was a clear solution. No specific challenges encountered.
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 or ETAAS	
Volatile element containment	-
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	-
Techniques and procedures used to increase the concentration of the analyte introduced to the ICP or ETAAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	
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/ETAAS.	
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	
Hydride preconcentration/ matrix separation of volatile species.	-
Coupling of a hydride system to the ICP or ETAAS and optimization of conditions.	
Calibration of analyte concentration	All calibration standards were prepared gravimetrically using a calibrated analytical balance. The calibration performed using an standard addition technique for Cd and Pb determination. The standard addition was set in 3-4 different level of concentration added into the samples
The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.	
Signal detection	*The low concentration of Pb in the matrix CRM used make it difficult to get a satisfactory results of accuracy (large % recovery) . Similar condition in the sample, make repeatability of measurement larger.*
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.	
Memory effect	*Wash the sequence using HNO_3 and also measure only HNO_3 in between standards, blanks, samples, and CRM.*
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Optimization of the furnace temperature program (for ETAAS)	-
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.	
Correction or removal of isobaric/ polyatomic interferences (for ICP)	In order to remove possibility of polyatomic interference, the measurement of Cd and Pb

Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	were performed in KED mode. The internal standard were using to monitor the instrument drift and calculated as ratio with the analytes. The internal standard used were 115In for Cd and 209Bi for Pb.
Correction or removal of matrix effects or interferences	The matrix effect interferences were eliminated by using standard addition technique, and the results were confirmed by external calibration techniques.
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.	
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.	
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.	
Detector deadtime correction	-
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	-
correction	

Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	-
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

Centro Nacional de Metrología (CENAM), Mexico

For ID-ICP-MS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	The water was purified by double subdistillation) to reduce potential contamination of samples as well as blank correction procedures.
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.	
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.	
Digestion/dissolution of organic matrices	*In order to put the sample in solution a extra steps of digestion was applied, the the following sample preparation is described: Pre-digestion and two steps of digestion procedure was applied to avoid high pressure in the vessels due to the fat of the sample, also between the last two steps HF was added to samples and control CRM*
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	
Volatile element containment	
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	*Not necesary, as ICP-SFMS in low resolution mode was used*
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.	
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.	
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	*anion-exchange method separation using a strong base type I anion resin (Dowex 1-X8) was used to isolate the analyte Cd from the sample matrix to avoid interferences and matrix effects; also analyte Pb to avoid matrix effects caused by the matrix.*
Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample*	Enriched isotope was spiked before the microwave digestion. Samples were subject to rigorous digestion procedures (microwave) to ensure complete dissolution of the sample enabling equilibrationof the enriched isotope spike with the sample.
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.*	Samples where prepared in a clean room to take care of cross contamination mainly with Pb. Also an adequate sample preparation was applied in order to obtain an adequate sensitivity in a low resolution mode in ICP-SFMS
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.*	Rigorous rinsed between each measurement of samples with 2 % HNO3 solution. Before analysis, a washing time was optimized for minimizing memory effect. Consequently, two minutes washing was performed.
Correction or removal of isobaric/ polyatomic interferences *Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.*	Due the source of Hg and Sn from acid and water, minimous correction was applied for: ^{204}Pb caused by mass overlap of ^{204}Hg, ^{112}Sn caused by mass overlap of ^{112}Cd, ^{114}Sn caused by mass overlap of ^{114}Cd isobaric interference.
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	
Mass bias/fractionation control and correction	Mathematical correction used to correct for mass bias for Pb

Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	The enrriched 111Cd was caracterized using ICP-SFMS The source of the enrriched 206Pb used was a CRM from NRC
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

National Institute for Quality (INACAL), Perú

For ICP-MS (without ID), ICP-OES or ETAAS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	*Method blank was used for the measurement.*
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.	
Digestion/dissolution of inorganic matrices	*Using MRC as a control sample for the digestion process*
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.	
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 or ETAAS	
Volatile element containment	
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	
Techniques and procedures used to increase the concentration of the analyte introduced to the ICP or ETAAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	
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/ETAAS.	
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	
Hydride preconcentration/ matrix separation of volatile species.	
Coupling of a hydride system to the ICP or ETAAS and optimization of conditions.	
Calibration of analyte concentration	*Measurements were made by standard addition with Internal standard*
The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.	
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.	
Memory effect	
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Optimization of the furnace temperature program (for ETAAS)	
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.	
Correction or removal of isobaric/ polyatomic interferences (for ICP)	
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	

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.	
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.	
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.	
Detector deadtime correction	
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

National Metrology Laboratory of the Philippines (NMLPhil), Philippines

For ICP-MS (without ID), ICP-OES or ETAAS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	*Sample tubes used were acid-washed prior to use. Water, reagents, and acid's responses to instruments were monitored for possible contaminations. Trace amounts of Pb were found on blank samples, and the corrective action was to subject the labware to acid-washing including the pipette tips and use freshly distilled acid. However, the distillation of nitric acid was halted due to the break-down of the chiller. The analysts were able to use the acid distillation system again after the repair of chiller was done.*
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.	
Digestion/dissolution of inorganic matrices	*None*
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.	
Digestion/dissolution of organic matrices	*None*
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 or ETAAS	
Volatile element containment	*None*
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	*None*
Techniques and procedures used to increase the concentration of the analyte introduced to the ICP or ETAAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	
Vapor generation	*None*
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/ETAAS.	
Matrix separation	*Not applicable*

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	
Hydride preconcentration/ matrix separation of volatile species.	*Not applicable*
Coupling of a hydride system to the ICP or ETAAS and optimization of conditions.	
Calibration of analyte concentration	*None*
The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.	
Signal detection	*In Pb analysis using ICP-MS, the signal of the sample blank is very high.*
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.	
Memory effect	*None*
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Optimization of the furnace temperature program (for ETAAS)	*None*
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.	
Correction or removal of isobaric/ polyatomic interferences (for ICP)	*In Pb analysis using ICP-MS, KED mode was used to remove isobaric/polyatomic interferences. However, we ran out of ultrahigh purity helium gas which is important for mitigating polyatomic interferences and enhancing the accuracy and reliability of elemental analysis. And we also ran out of ultrahigh purity argon gas which is the source for the plasma generation.*
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	

Correction or removal of matrix effects or interferences	*None*
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.	
Complex spectral backgrounds	*Not conducted*
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.	
Correction or removal of matrix-induced signal suppression or enhancement	*Not conducted*
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.	
Detector deadtime correction	*None*
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	*Not monitored*
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	*Not conducted*
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

Health Sciences Authority (HSA), Singapore

For ID-ICP-MS

Capabilities/Challenges	*Specific challenges encountered*
Contamination control and correction	*Samples were prepared in class 100 low laminar flow fumehood or 10,000 clean room and high purity reagents were used. All labwares were pre-cleaned by soaking in acid.*
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 .	
Digestion/dissolution of inorganic matrices	*Microwave assisted acid digestion was used.*
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.	
Digestion/dissolution of organic matrices	*Microwave assisted acid digestion was used.*
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	
Volatile element containment	*NA*
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage .	
Pre-concentration	*NA*
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.	
Vapor generation	*NA*
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.	
Matrix separation	*NA*
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	

Spike equilibration with sample *The mixing and equilibration of the enriched isotopic spike with the sample*	*Microwave assisted acid digestion gave a clear digest.*
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.*	*The instrument sensitivity for cadmium analysis was adequate.*
Memory effect *Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples .*	*NA*
Correction or removal of isobaric/ polyatomic interferences *Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.*	*Helium collision gas was used to remove polyatomic interferences. Isobaric interference from tin was corrected by applying mathematical correction.*
Detector deadtime correction *Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.*	*Sample and calibration blends intensities were matched to reduce the significance of this effect.*
Mass bias/fractionation control and correction *Techniques used to determine, monitor, and correct for mass bias/fractionation.*	*Sample and calibration blends were bracketed with a standard solution with known isotopic composition to correct for mass bias.*
Spike calibration *Techniques used to determine the analyte concentration in the enriched isotopic spike solution .*	*Exact-matching IDMS was used.*

For ICP-MS (without ID), ICP-OES or ETAAS

Capabilities/Challenges	*Specific challenges encountered*
Contamination control and correction	*Samples were prepared in class 100 low laminar flow fumehood or 10,000 clean room and high purity reagents were used. All labwares were pre-cleaned by soaking in acid.*
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.	
Digestion/dissolution of inorganic matrices	*Microwave assisted acid digestion was used.*
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.	
Digestion/dissolution of organic matrices	*Microwave assisted acid digestion was used.*
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 or ETAAS	
Volatile element containment	*NA*
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
Pre-concentration	*NA*
Techniques and procedures used to increase the concentration of the analyte introduced to the ICP or ETAAS. Includes evaporation, ion-exchange, extraction, precipitation procedures, but not vapor generation procedures.	
Vapor generation	*NA*
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/ETAAS .	
Matrix separation	*NA*
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	
Hydride preconcentration/ matrix separation of volatile species.	*NA*
Coupling of a hydride system to the ICP or ETAAS and optimization of conditions .	

Calibration of analyte concentration	
The preparation of calibration standards and the strategy for instrument calibration. Includes external calibration and standard additions procedures.	*Standard addition was used.*
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 .	*A larger amount of sample (0.5 g) was digested for the analysis of lead.*
Memory effect	
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	*NA*
Optimization of the furnace temperature program (for ETAAS)	
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.	*NA*
Correction or removal of isobaric/ polyatomic interferences (for ICP)	
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	*Helium collision gas was used to remove polyatomic interferences. Isobaric interference from mercury was corrected by applying mathematical correction.*
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.	*NA*

National Institute of Metrology (Thailand) (NIMT), Thailand

For ID-ICP-MS	
Capabilities/Challenges	***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.	
Digestion/dissolution of inorganic matrices	*The sample was digested clearly by microwave digestion system (Antom paar Multiwave 7000).*
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.	
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	
Volatile element containment	-
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
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.	
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.	
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	

Spike equilibration with sample	-
The mixing and equilibration of the enriched isotopic spike with the sample	
Signal detection	The isotope composition of Pb in SIM.QM-S18 sample differs from the used standard solution (SRM3128). Therefore, determination of Pb isotope composition is required. SRM981 is used as an isotopic reference material.
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.	
Memory effect	-
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Correction or removal of isobaric/ polyatomic interferences	-
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	
Detector deadtime correction	Method of the measurement employed triple detection mode (pulse & analog & faraday), therefore correction of deadtime is required for low signal.
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	SRM3108 and SRM3128 were used for Cd and Pb mass bias correction, respectively. SRM981 was used for isotope ratio measurement of Pb.
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	^{111}Cd and ^{206}Pb from Oak Ridge
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	

Laboratorio Tecnológico del Uruguay (LATU), Uruguay

For ID-ICP-MS	
Capabilities/Challenges	***Specific challenges encountered***
Contamination control and correction	

All techniques and procedures employed to reduce potential contamination of samples as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and also present at very low concentrations in the sample.	All plastic materials in contact used (bottles, tips, spoons, tubes, etc.) were new and decontaminated by soaking overnight with HNO3 20 % and ultrapure water. Microwave vessels were decontaminated using a microwave cleaning method with HNO3 and ultrapure water.
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.	
Digestion/dissolution of organic matrices	*Samples were digested using microwave digestion system.*
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	
Volatile element containment	-
All techniques and procedures used to prevent the loss of potentially volatile analyte elements during sample treatment and storage.	
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.	
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.	
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	
Spike equilibration with sample	Enriched isotopes were added prior to microwave digestion, and equilibration was assumed.
The mixing and equilibration of the enriched isotopic spike with the sample	
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.	
Memory effect	-
Any techniques used to avoid, remove or reduce the carry-over of elemental species between consecutively measured standards and/or samples.	
Correction or removal of isobaric/ polyatomic interferences	Cd111 and Cd114 signals were mathematically corrected for Sn120 and Mo98 isobaric interference. The correction factor was determined each day of measurement.
Any techniques used to remove, or reduce, interferences caused by mass overlap of analyte isotopes with isobaric or polyatomic species, which may lead to high baseline signals. Includes collision cell techniques, high resolution mass spectrometry, or chemical separations. The relative concentrations and sensitivities of the analyte isotopes and the interfering species will affect the degree of difficulty.	
Detector deadtime correction	-
Measurement of, and correction for, ion detector deadtime. Importance increases in situations where high ion count rates are encountered.	
Mass bias/fractionation control and	Mass bias determination was performed each day of analysis using Calibration Standard: NIST SRM 3108 Cadmium.
correction	
Techniques used to determine, monitor, and correct for mass bias/fractionation.	
Spike calibration	Samples and standards were spiked with the same Cd-111 enriched isotope solution. The concentration of the enriched isotopic spike solution was determined according to the concentration of the calibration standard.
Techniques used to determine the analyte concentration in the enriched isotopic spike solution.	