APMP.QM-S19: Toxic elements in seafood

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APMP.QM-S19
Toxic Elements in Seafood

Supplementary Comparison

Final Report

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SUMMARY

Seafood is one of the major food resources for human consumption in the world. The CODEX Alimentarius Commission and many jurisdictions have set maximum levels of metallic contaminants in seafood. The use of reliable methods for measurement of metallic contaminants is important in safeguarding the quality of these products and the public health.

The Supplementary Comparison and parallel Pilot Study APMP.QM-S19 & P40 (Toxic Elements in Seafood) covered arsenic (0.2 mg/kg – 50 mg/kg), cadmium (0.04 mg/kg – 10 mg/kg), mercury (0.02 mg/kg – 5 mg/kg) and lead (0.04 mg/kg – 10 mg/kg) in seafood. The last CCQM or RMO key comparison / supplementary comparison in the area of metallic contaminants in seafood was organized by the Government Laboratory, Hong Kong, China (GLHK) in 2011 (APMP.QM-S5 Essential and Toxic Elements in Seafood). Hence, it was timely to organize another comparison that covers different measurands. This Supplementary Comparison (APMP.QM-S19) offers different analytical challenges (e.g. in analysis of mercury and different range of measurands) as compared to the previous comparison. Moreover, it enabled National Metrology Institutes / Designated Institutes (NMIs/DIs) that did not participate in the previous comparisons to demonstrate their measurement competencies. 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).

Nineteen National Metrology Institutes and Designated Institutes participated in the Supplementary Comparison APMP.QM-S19 Toxic Elements in Seafood. Participants were requested to evaluate the mass fractions, expressed in mg/kg on dry mass basis, of arsenic, cadmium, mercury and lead in a seafood matrix (dried shrimp). Results of all participating NMIs/DIs were evaluated against the supplementary comparison reference value (SCRV). The SCRV and associated uncertainty were determined from results of NMIs/DIs that participated in the supplementary comparison using methods with demonstrated metrological traceability. Most participating NMIs/DIs employed microwave-assisted acid digestion for sample dissolution. Inductively coupled plasma mass spectrometry (ICP-MS), including triple quadrupole and sector field, were the most commonly used instrumental techniques. For arsenic, the SCRV was 1.342 mg/kg calculated as the median from 15 participating NMIs/DIs. For arsenic, cadmium, mercury and lead, the SCRVs were 1.342 mg/kg, 0.3630 mg/kg, 0.1230 mg/kg and 0.4101 mg/kg, respectively; the SCRVs were calculated as the median from 15, 14, 13 and 11 participating NMIs/DIs, respectively.

Successful participation in APMP.QM-S19 demonstrates measurement capabilities in determining inorganic elements, in a mass fraction range from 0.02 mg/kg to 50 mg/kg in high organic content matrix, including seafood of animal origin and high protein food.

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ACRONYMS

APMP TCQM: Asia Pacific Metrology Programme Technical Committee for Amount of Substance: Metrology in Chemistry and Biology
As: Arsenic
CCQM IAWG: Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology Inorganic Analysis Working Group
Cd: Cadmium
CMC: Calibration and Measurement Capability
CRM: Certified Reference Material
CVAAS: Cold Vapor Atomic Absorption Spectroscopy
DI: Designated Institute
DoE: Degrees of Equivalence
GFAAS: Graphite Furnace Atomic Absorption Spectroscopy
GSA: Gravimetric Standard Addition
H_2O_2: Hydrogen peroxide
HCl: Hydrochloric acid
HF: Hydrofluoric acid
Hg: Mercury
HNO_3: Nitric acid
HR-ICP-MS: High Resolution Inductively Coupled Plasma Mass Spectrometry
IC: Ion Chromatography
ICP-MS: Inductively Coupled Plasma Mass Spectrometry
ICP-QQQ-MS: Triple Quadrupole Inductively Coupled Plasma Mass Spectrometry
IDMS: Isotope Dilution Mass Spectrometry
INAA: Instrumental Neutron Activation Analysis
n: Number of Replicates
NMI: National Metrology Institute
Pb: Lead
PS: Pilot Study
SC: Supplementary Comparison
SCRV: Supplementary Comparison Reference Value
SRM: Standard Reference Material

INTRODUCTION

Seafood is one of the major food resources for human consumption in the world. Metals such as arsenic, cadmium and mercury occur naturally in the earth's crust. They can be released into the aquatic environment through various natural processes or human activities and then taken up by aquatic animals. Different regions around the world have established relevant guidelines and regulations to safeguard the safety of consumers.

The ability to perform complete digestion of high organic content matrix, such as seafood of animal origin and high protein food, and determine mass fraction of transition elements and metalloids/semi-metals in such matrices are important challenges for metrology institutes. 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).

At the APMP meeting in November 2018, the Government Laboratory, Hong Kong, China (GLHK) initially proposed to organize an Asia Pacific Metrology Programme (APMP) supplementary comparison (suggested measurands: total arsenic, cadmium, mercury, lead and inorganic arsenic) in 2021. The proposal was also presented at the CCQM IAWG meetings in April & September 2019. After discussion, the working group supported running an APMP supplementary comparison for total elements in seafood, with a separate CCQM pilot study for arsenic speciation in seafood. In December 2019, the Technical Committee for Amount of Substance: Metrology in Chemistry and Biology (TCQM) approved the Supplementary Comparison (SC) APMP.QM-S19 "Toxic Elements in Seafood". In November 2021, the TCQM approved the parallel-run Pilot Study (PS) numbered APMP.QM-P40.

APMP.QM-S19 was designed to assess participating NMIs/DIs' capabilities for determination of mass fraction of transition elements and metalloids/semi-metals, in mass fraction range from as low as 0.02 mg/kg to as high as 50 mg/kg in high organics content matrix, including seafood of animal origin and high protein food. Arsenic, cadmium, mercury and lead were covered since their maximum levels are stated under the CODEX Alimentarius and/or limited by many countries/regions. The last CCQM or RMO key comparison / supplementary comparison in the area of metallic contaminants in seafood, APMP.QM-S5 "Essential and Toxic Elements in Seafood", was organized by GLHK in 2011.

The analytical challenges and competencies of this study include complete dissolution of high organic content material (seafood) and accurate determination of mass fraction of inorganic elements (arsenic, cadmium, mercury and lead) by minimising the effect of spectral interference, sample loss or carry over, etc. Most participating NMIs/DIs employed microwave-assisted acid digestion for sample dissolution. Inductively coupled plasma mass spectrometry (ICP-MS), including triple quadrupole and sector field, were the most commonly used instrumental techniques.

The following sections of this report document the timeline of APMP.QM-S19, the measurands, study material, participants, results, and the measurement capability claims that participation in APMP.QM-S19 can support. The Appendices reproduce the official communication materials.

TIMELINE

Table 1 lists the timeline for APMP.QM-S19.

Table 1: Timeline for APMP.QM-S19

Date	Action
November 2018	Proposal presented to APMP TCQM
April 2019	Proposal presented to CCQM IAWG
September 2019	CCQM IAWG agreed to run an APMP supplementary comparison
December 2019	APMP TCQM authorized APMP.QM-S19
July 2021	Call for participation to APMP TCQM and CCQM IAWG members
September 2021	Deadline of registration
October – November 2021	Distribution of samples
April 2022	Original deadline for submission of results
July 2022	Extended deadline for submission of results
September 2022	Initial Results Summary
April 2023	Draft A Report (version A1)
September 2023	Draft A Report (version A2)
October 2023	Draft B Report
January 2024	Final Report approved by CCQM IAWG

MEASURANDS

The comparison covered arsenic, cadmium, mercury and lead in a seafood matrix. The expected mass fractions of the measurands (on a dry mass basis) are given in Table 2.

Table 2: Measurands and expected mass fraction

Measurand	Expected mass fraction (mg/kg)
Arsenic	0.2 – 50
Cadmium	0.04 – 10
Mercury	0.02 – 5
Lead	0.04 – 10

STUDY MATERIALS

Dried shrimps were purchased from the local market in Hong Kong. The shrimps were soaked in a spike solution containing the target analytes for several hours, freeze-dried, blended into powder, and subjected to a sieving process through two calibrated sieves (200 μm and 100 μm, respectively). The sieved powder (particle size: 100 μm – 200 μm) was thoroughly homogenized in a 3-dimensional mixer for 5 days. The material was irradiated using a gamma source at a dose of about 10 kGy for disinfection. The irradiated material was packed into high-density polyethylene bottles, each of about 30 g. The bottles were purged with nitrogen and stored at room temperature (20 °C ± 5 °C).

Each participant received two bottles of sample, each containing approximately 30 g of dried shrimp powder. The recommended minimum sample amount for analysis was at least 0.5 g. Measurement results were to be reported on a dry-mass basis.

Dry Mass Determination

Dry mass determination shall be carried out, at the same time as the test portions were analyzed, by placing three separate portions (about 1 g each) of sample over anhydrous calcium sulphate (e.g. DRIERITE®) in a desiccator for at least 10 days until constant mass was reached. The sample which was used for the determination of moisture content shall not be used for analysis. All participants were required to follow the method outlined in the protocol.

Homogeneity Assessment of Study Material

Ten bottles of sample were randomly selected for homogeneity study. Two test portions of 0.5 g each were taken from each bottle for analysis. The test portions were digested using microwave-assisted acid digestion and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) with gravimetric standard additions. ANOVA at 95 % level of confidence was applied to assess the between-bottle homogeneity in accordance with ISO Guide 35:2017, the comparison 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	
Arsenic	1.50	3.02	0.7
Cadmium	0.93	3.02	0.6
Mercury	1.95	3.02	1.6
Lead	0.59	3.02	1.0

Stability Assessment of Study Material

In total, two rounds of short-term stability studies were conducted for the comparison sample.

Initially, before the call of participation, the short-term stability of the measurands over a period of 4 weeks at 40 °C was accessed using an isochronous approach. The analytical procedures were the same as those for the homogeneity study. Two randomly selected sample bottles were transferred from the storage condition (20 °C ± 5 °C) to 40 °C on three occasions (1 week, 2 weeks, and 4 weeks) over the study period. Two subsamples were then taken from each bottle. 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 4 weeks. The results are summarized in Table 4 and graphically represented in Figure 1.

Table 4. Results of the stability assessment (at 40 °C for 4 weeks) for the measurands

Measurand	Student's *t*-test		*p*-value
	Calculated test statistics	Critical value	
Arsenic	0.201	4.303	0.859
Cadmium	0.864	4.303	0.479
Mercury	0.232	4.303	0.838
Lead	0.709	4.303	0.552

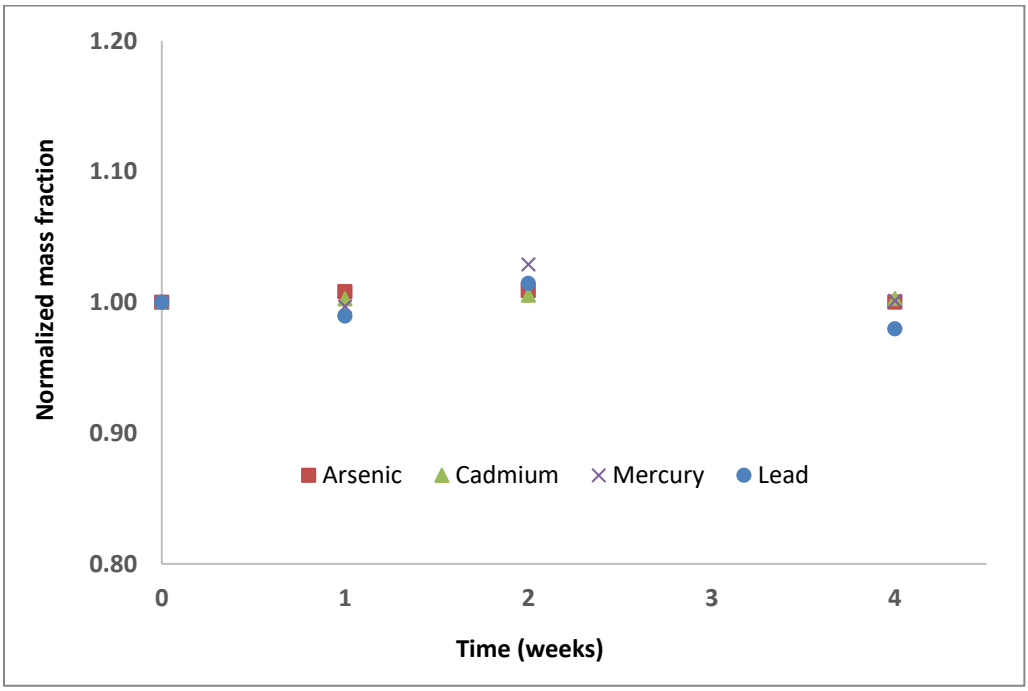

Figure 1. Short-term stabilities of the measurands at 40 °C for 4 weeks.

Due to delayed logistics and/or customs clearance, it took more than 4 weeks for the samples to reach INACAL (4 weeks 2 days) and JSI (5 weeks 3 days). Therefore, to ensure the validity of the study, the short-term stability study was repeated for an extended period of 6 weeks after the deadline of results submission. The overall procedures were similar to those described above, except that selected sample bottles were transferred from the storage condition (20 °C ± 5 °C) to 40 °C on three occasions (*2 weeks, 4 weeks, and 6 weeks*). Again, no significant instability of the measurands was observed upon exposure to 40 °C up to 6 weeks. The results are summarized in Table 5 and graphically represented in Figure 2.

Table 5. Results of the stability assessment (at 40 °C for 6 weeks) for the measurands

Measurand	Student's *t*-test		*p*-value
	Calculated test statistics	Critical value	
Arsenic	0.999	4.303	0.423
Cadmium	1.815	4.303	0.211
Mercury	0.727	4.303	0.543
Lead	1.918	4.303	0.195

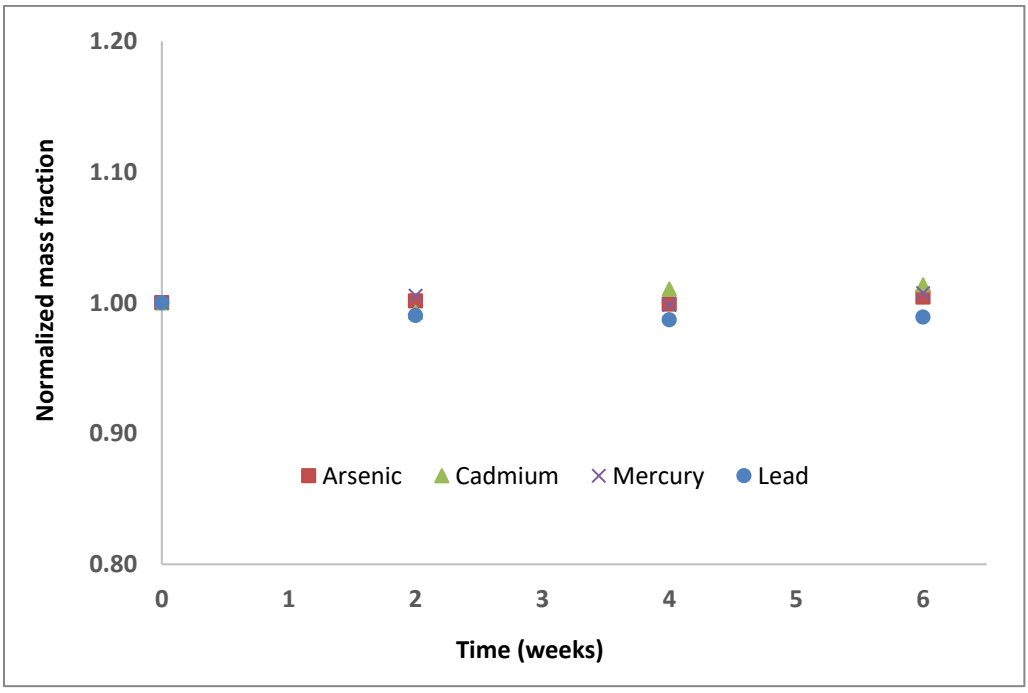

Figure 2. Short-term stabilities of the measurands at 40 °C for 6 weeks.

The long-term stability of the measurands in the comparison material at 20 °C ± 5 °C was assessed using the same analytical procedures as for the homogeneity study. The tests were carried out on four occasions over the study period of about 90 weeks using the classical approach. On each occasion of the stability testing, at least two bottles were randomly selected and at least two subsamples were taken from each bottle. Student's *t*-test on the slope of the linear regression at 95 % level of confidence was used for the evaluation of instability of the measurands. No instability was observed during the duration of the comparison at the recommended storage temperature (20 °C ± 5 °C). The results are summarized in Table 6 and graphically represented in Figure 3.

Table 6. Results of the stability assessment (at 20 ± 5 °C for about 90 weeks) for the measurands

Measurand	Student's *t*-test		*p*-value
	Calculated test statistics	Critical value	
Arsenic	0.718	4.303	0.547
Cadmium	3.299	4.303	0.081
Mercury	1.242	4.303	0.340
Lead	1.207	4.303	0.351

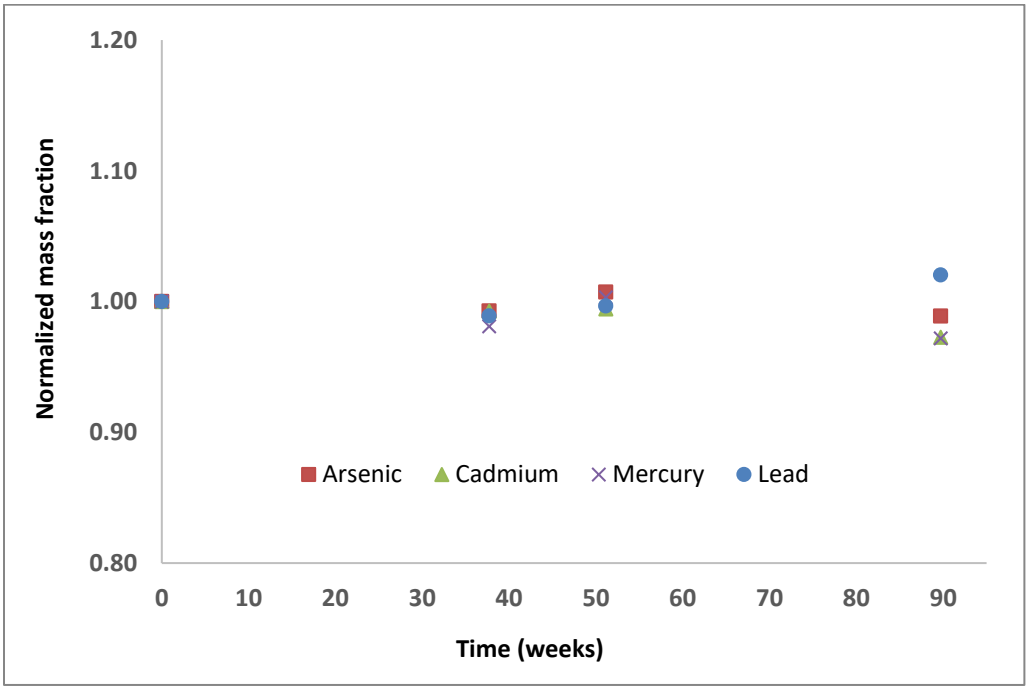

Figure 3. Long-term stabilities of the measurands at 20 °C ± 5 °C for about 90 weeks.

PARTICIPANTS, INSTRUCTIONS AND SAMPLE DISTRIBUTION

The call for participation was distributed in July 2021 with the intent of distributing samples in October 2022. Due to the COVID-19 pandemic, the result submission deadline was extended from April 2022 to July 2022. See Table 1 for a detailed study timeline. Appendix A and Appendix B reproduce the Study Protocol and the Registration Form, respectively.

A total of 19 institutes registered for the APMP.QM-S19 supplementary comparison. Table 7 lists the participating NMIs/DIs in alphabetical order of the countries / economies.

Table 7: Institutes registered for APMP.QM-S19

Member state / Associate	NMI or DI	Code	Contact
Bangladesh	Bangladesh Reference Institute for Chemical Measurements	BRiCM	Mala Khan
Chile	Instituto de Salud Pública de Chile	ISP	Soraya Sandoval Riquelme / Javier Vera
China	National Institute of Metrology	NIM	Mr. Li Xiao / Dr. Lu Hai
Colombia	Instituto Nacional de Metrología de Colombia	INMC	Ronald Orlando Cristancho Amaya
Greece	National Laboratory of Chemical Metrology, EXHM/GSCL-EIM	EXHM	Elias Kakoulides
Hong Kong, China	Government Laboratory	GLHK	Alvin Wai-hong Fung / Kelvin Chun-wai Tse
Indonesia	National Standardization Agency of Indonesia	SNSU-BSN	Christine Elishian / Isna Komalasari
Italy	National Institute of Metrological Research	INRIM	Luigi Bergamaschi / Giancarlo D'Agostino / Marco di Luzio
Japan	National Metrology Institute of Japan	NMIJ	Shin-ichi Miyashita
Mexico	Centro Nacional de Metrología	CENAM	Maria-del-Rocio Arvizu-Torres
Monaco	International Atomic Energy Agency / Environment Laboratories	IAEA	Emilia Vasileva-Veleva
Perú	National Institute for Quality/Instituto Nacional de Calidad	INACAL	Elmer Carrasco
Philippines	Department of Science and Technology – Industrial Technology Development Institute	DOST-ITDI	Alleni T. Junsay
Poland	Central Office of Measures	GUM	Michał Strzelec

Member state / Associate	NMI or DI	Code	Contact
Singapore	Health Sciences Authority	HSA	Richard Shin
Slovenia	Jožef Stefan Institute / Department of Environmental Sciences	JSI	Radojko Jaćimović
South Africa	National Metrology Institute of South Africa	NMISA	Angelique Botha / Maré Linsky
Thailand	National Institute of Metrology (Thailand)	NIMT	Nunnapus Laitip
Uruguay	Laboratorio Tecnológico del Uruguay	LATU	Ramiro Pérez Zambra / Romina Napoli

The study samples were transported at ambient temperature. A temperature strip was pasted inside each box to monitor the temperature during transportation. A Sample Receipt Form was provided to the participating NMIs/DIs for completion. Appendix C reproduces the Sample Receipt Form. The study sample dispatched to NMISA in October 2022 was exposed to 42 °C during transportation, exceeding the 40 °C covered by the short-term stability study. Hence, a second study sample was sent to NMISA in November 2022 and it was satisfactorily transported at not more than 34 °C. Due to delayed logistics and/or customs clearance, it took more than 4 weeks for the samples to reach INACAL (4 weeks 2 days) and JSI (5 weeks 3 days). Additional short-term stability study (*vide supra*) was conducted to ensure the samples were fit for purpose in this supplementary comparison.

A Report Form was provided to the participating NMIs/DIs for completion. The participating NMIs/DIs were expected to report their results based on at least four subsamples for each measurand. The participating NMIs/DIs were requested to report only one result, calculated from the average of the measurements, for each measurand. The results were reported on a dry-mass basis in the unit of mg/kg, and included standard and expanded uncertainties (95 % level of confidence) for the mean of the replicate determinations.

The participating NMIs/DIs were reminded to establish the metrological traceability of their results to the SI using a direct realization via a primary method, certified reference materials (CRMs) from a NMI/DI having the required CMC claims, or by preparing their own calibration standards using commercially available high purity materials for which they have determined the purity themselves.

The participating NMIs/DIs were also asked to include information on the measurement procedure (including the sample dissolution method, the calibration method, the internal standard, the quality control, the analytical instrument(s) used, etc), the calculation of the results, and the estimation of measurement uncertainty in the Report Form. The completed form was to be sent to GLHK on or before the scheduled deadline. Appendix D reproduces the Report Form.

To facilitate in-depth performance evaluation, participating NMIs/DIs were requested to clearly identify and quantify those factors that were considered to contribute to the measurement uncertainty of the analysis.

RESULTS

APMP.QM-S19 results were received from all of the 19 institutes that registered and received study samples.

Methods Used by Participants

Table 8 summarizes the measurement methods and reference materials (for calibration) used by the participating NMIs/DIs for APMP.QM-S19.

Table 8: Summary of measurement methods and reference materials (for calibration) used

Institute code	Measurand	Sample preparation method	Calibration method	Analytical instruments	Reference material used for calibration (traceability)
BRiCM	As, Cd, Hg, Pb	As, Cd, Pb: Microwave assisted digestion (HNO_3/H_2O_2) Hg: Direct analysis	As, Cd, Pb: Multi Point Calibration curve Hg: Standard Sample Calibration Curve	As, Cd, Pb: ICP-MS Hg: Direct mercury analyser	As, Cd, Pb: Agilent multi-element calibration standard 2A Hg: Sigma Aldrich mercury standard
ISP	As, Cd	Microwave assisted digestion (HNO_3/H_2O_2)	Standard addition	ICP-MS	As: NIST SRM 3103a Cd: NIST SRM 3108
NIM	As, Cd, Hg, Pb	As, Cd, Pb: Microwave assisted digestion (HNO_3) Hg: Microwave assisted digestion (HNO_3/HCl)	As: Standard addition Cd: Double IDMS ($^{113}Cd/^{111}Cd$) Hg: Double IDMS ($^{201}Hg/^{202}Hg$) Pb: Double IDMS ($^{206}Pb/^{207}Pb$)	As: ICP-QQQ-MS (O_2 mode) Cd, Hg, Pb: ICP-MS	As: GBW08667 Cd: GBW08612 Hg: GBW08617 Pb: GBW08619
INMC	As, Hg	Microwave assisted digestion (HNO_3/H_2O_2)	As: Standard addition Hg: Standard addition and external bracketing calibration	As: ICP-MS Hg: ICP-MS and CVAAS	As: SMU B03 Hg: NIST SRM 3133
EXHM	As, Cd, Hg, Pb	Microwave assisted digestion (HNO_3)	Standard addition	HR-ICP-MS	As: NIST SRM 3103a Cd: NIST SRM 3108 Hg: NIST SRM 3133 Pb: NIST SRM 3128

Institute code	Measurand	Sample preparation method	Calibration method	Analytical instruments	Reference material used for calibration (traceability)
GLHK	As, Cd, Hg, Pb	Microwave assisted digestion (HNO_3/H_2O_2)	As: Standard addition Cd: Double IDMS ($^{114}Cd/^{111}Cd$) Hg: Double IDMS ($^{200}Hg/^{202}Hg$) Pb: Double IDMS ($^{208}Pb/^{206}Pb$)	ICP-MS	As: NIST SRM 3103a Cd: NIST SRM 3108 Hg: NIST SRM 3133 Pb: NIST SRM 3128
SNSU-BSN	As, Cd, Pb	Microwave assisted digestion ($HNO_3/HF/H_2O_2$)	As, Cd: Standard addition Pb: Double IDMS ($^{208}Pb/^{206}Pb$)	ICP-MS	As: NIST SRM 3103a Cd: NIST SRM 3108 Pb: NIST SRM 3128
INRIM	As	Pressing at 15 bar to form a cylindrical tablet	Relative-INAA (^{75}As)	INAA	NIST SRM 3103a
NMIJ	As, Cd, Hg	Microwave assisted digestion (HNO_3)	As: Standard addition Cd: Double IDMS ($^{114}Cd/^{111}Cd$) Hg: Double IDMS ($^{202}Hg/^{200}Hg$)	ICP-MS	As: JCSS 01805-1B Cd: JCSS 07993-1B Hg: JCSS 25828-1B
CENAM	Hg	Microwave assisted digestion (HNO_3/H_2O_2)	Double IDMS ($^{201}Hg/^{202}Hg$)	CV-ICP-QMS	DMR-438b
IAEA	Cd, Hg, Pb	Microwave assisted digestion (HNO_3/H_2O_2)	Cd: IDMS ($^{110}Cd/^{111}Cd$) Hg: IDMS ($^{200}Hg/^{202}Hg$) Pb: IDMS ($^{208}Pb/^{206}Pb$)	ICP-MS	Cd: IRMM-622 Hg: ERM-AE640 Pb: NIST SRM 981
INACAL	As, Cd, Hg, Pb	Microwave assisted digestion (HNO_3/H_2O_2)	Standard addition	As, Cd, Pb: ICP-MS Hg: CVAAS	As: NIST SRM 3103a Cd: NIST SRM 3108 Hg: NIST SRM 3133 Pb: NIST SRM 3128
ITDI	As, Cd, Hg, Pb	As, Cd, Pb: Microwave assisted digestion (HNO_3/H_2O_2) Hg: Direct analysis	As: Standard addition Cd, Hg, Pb: External calibration	As: ICP-MS Cd, Pb: GFAAS Hg: Direct mercury analyser	As: NIST SRM 3103a Cd: NIST SRM 3108 Hg: NIST SRM 3133 Pb: NIST SRM 3128

Institute code	Measurand	Sample preparation method	Calibration method	Analytical instruments	Reference material used for calibration (traceability)
GUM	As, Cd, Hg, Pb	Microwave assisted digestion ($HNO_3/H_2O_2/HCl$)	Standard addition	ICP-MS	As: SMU B03 Cd: SMU B08 Hg: SMU B15 Pb: SMU B26
HSA	As, Cd, Hg, Pb	Microwave assisted digestion ($HNO_3/HF/H_2O_2$)	As: Standard addition Cd: Double IDMS ($^{114}Cd/^{111}Cd$) Hg: Double IDMS ($^{202}Hg/^{201}Hg$) Pb: Double IDMS ($^{208}Pb/^{206}Pb$)	As: HR-ICP-MS Cd, Hg, Pb: ICP-MS	As: NIST SRM 3103a Cd: NIST SRM 3108 Hg: NIST SRM 3133 Pb: NIST SRM 3128
JSI	As, Cd, Hg, Pb	As, Hg: Microwave assisted digestion (HNO_3) Cd, Pb: Microwave assisted digestion (HNO_3/H_2O_2)	External Calibration	As: ICP-QQQ-MS (O_2 mode) Cd, Pb: ICP-MS Hg: ICP-QQQ-MS (He mode)	As: NIST SRM 3103a Cd: NIST SRM 3108 Hg: NIST SRM 3133 Pb: NIST SRM 3128
NMISA	As, Cd, Hg, Pb	Microwave assisted digestion ($HNO_3/HF/H_2O_2$)	As: Standard addition Cd: Double IDMS ($^{114}Cd/^{111}Cd$) Hg: Double IDMS ($^{202}Hg/^{198}Hg$) Pb: Double IDMS ($^{208}Pb/^{206}Pb$)	As: ICP-QQQ-MS (H_2 mode) Cd, Hg, Pb: HR-ICP-MS	As: NIST SRM 3103a Cd: NIST SRM 3108 Hg: NIST SRM 3133 Pb: NIST SRM 3128
NIMT	As, Cd, Hg, Pb	Microwave assisted digestion (HNO_3)	As: Standard addition Cd: Double IDMS ($^{112}Cd/^{111}Cd$) Hg: Double IDMS ($^{202}Hg/^{201}Hg$) Pb: Double IDMS ($^{208}Pb/^{206}Pb$)	As: ICP-QQQ-MS (O_2 mode) Cd, Pb: ICP-MS Hg: HR-ICP-MS	As: NIST SRM 3103a Cd: NIST SRM 3108 Hg: NIST SRM 3133 Pb: NIST SRM 3128
LATU	As, Cd, Hg, Pb	As, Cd, Pb: Microwave assisted digestion (HNO_3/HF) Hg: Microwave assisted digestion (HNO_3/H_2O_2)	As: Standard addition Cd: Double IDMS ($^{114}Cd/^{111}Cd$) Hg: Double IDMS ($^{202}Hg/^{199}Hg$) Pb: Double IDMS ($^{208}Pb/^{206}Pb$)	As: HR-ICP-MS Cd, Hg, Pb: ICP-MS	As: NIST SRM 3103a Cd: NIST SRM 3108 Hg: NIST SRM 3133 Pb: NIST SRM 3128

Calibration Materials Used by Participants

Participating NMIs/DIs of APMP.QM-S19, except BRiCM and IAEA, established the metrological traceability of their results using CRMs with stated traceability. Most of the participating NMIs/DIs used the following standard solutions from NIST: SRM 3103a Arsenic, SRM 3108 Cadmium, SRM 3133 Mercury and SRM 3128 Lead. INMC used SMU B03 for arsenic analysis. NMIJ used JCSS As, Cd and Hg calibration solutions. NIM used the following standard solutions: GBW08667 Arsenic, GBW08612 Cd, GBW08617 Hg and GBW08619 Pb. GUM used the following standard solutions: SMU B03 As, SMU B08 Cd, SMU B15 Hg and SMU B26 Pb. CENAM used DMR-438b for mercury analysis.

BRiCM used the Agilent multi-element calibration standard 2A for As, Cd and Pb analysis and the Sigma Aldrich mercury standard for Hg analysis. These commercial standards were considered to have insufficient metrological traceability. Therefore, the results of BRiCM cannot be used for SCRV calculations.

IAEA used IRMM-622 Cd, ERM-AE640 Hg and NIST SRM 981 Pb as the primary calibrants in IDMS experiments. These isotopic standards are not supported by CMCs in the BIPM Key Comparison Database (KCDB) and therefore do not fulfil the requirements of CIPM MRA-G-13. Consequently, the results of IAEA cannot be used for SCRV calculations neither.

Participant Results for Arsenic, Cadmium, Mercury and Lead

The results for APMP.QM-S19 for the determination of arsenic, cadmium, mercury and lead are detailed in Tables 9 to 12 and graphically presented in Figures 4 to 7.

Table 9. Reported results for arsenic

Participating NMI/DI	Reported mass fraction (mg/kg)	Number of subsamples	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)
BRiCM	0.899	5	0.0262	1.96	0.0515
INMC	1.29	5	0.0278	1.97	0.0547
GUM	1.31	9	0.07	2	0.14
EXHM	1.32	4	0.04	2	0.08
NIM	1.32	7	0.02	2	0.04
NMISA	1.325	4	0.032	2	0.064
INRIM	1.3336	9	0.0148	1.98	0.0293
NIMT	1.34	8	0.027	2	0.055
GLHK	1.342	4	0.021	2	0.042
JSI	1.342	14	0.047	2	0.094
INACAL	1.3429	4	0.0375	2	0.075
LATU	1.349	6	0.0165	2	0.033
HSA	1.356	6	0.013	2	0.026
NMIJ	1.36	4	0.01	2	0.02
ISP	1.365	9	0.0628	2	0.124
ITDI	1.57	4	0.06	1.96	0.11
SNSU-BSN	1.919	13	0.0585	2	0.117

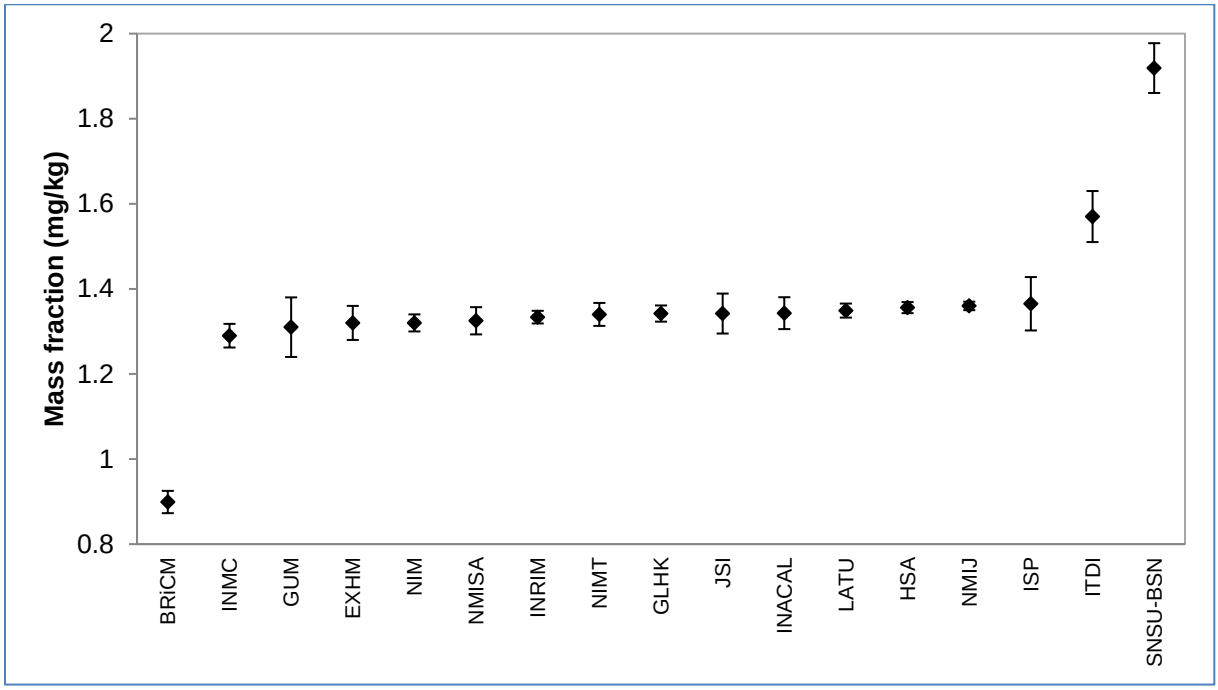

Figure 4. Reported results for arsenic in mg/kg. Error bars represent the standard uncertainties.

Table 10. Reported results for cadmium

Participating NMI/DI	Reported mass fraction (mg/kg)	Number of subsamples	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)
BRiCM	0.255	5	0.0093	1.96	0.0182
SNSU-BSN	0.3515	9	0.0116	2	0.0231
JSI	0.358	4	0.011	2	0.022
NMISA	0.359	5	0.013	2	0.026
HSA	0.3607	8	0.0018	2	0.0035
GLHK	0.3615	5	0.0058	2	0.0116
INACAL	0.3616	4	0.0106	2	0.0212
EXHM	0.362	4	0.011	2	0.022
NMIJ	0.364	4	0.003	2	0.006
GUM	0.365	10	0.039	2	0.078
NIM	0.366	9	0.003	2	0.007
IAEA	0.368	6	0.005	2	0.009
LATU	0.369	6	0.0055	2	0.011
ISP	0.372	9	0.0174	2	0.0347
ITDI	0.384	4	0.010	2.02	0.020
NIMT	0.409	11	0.007	2	0.015

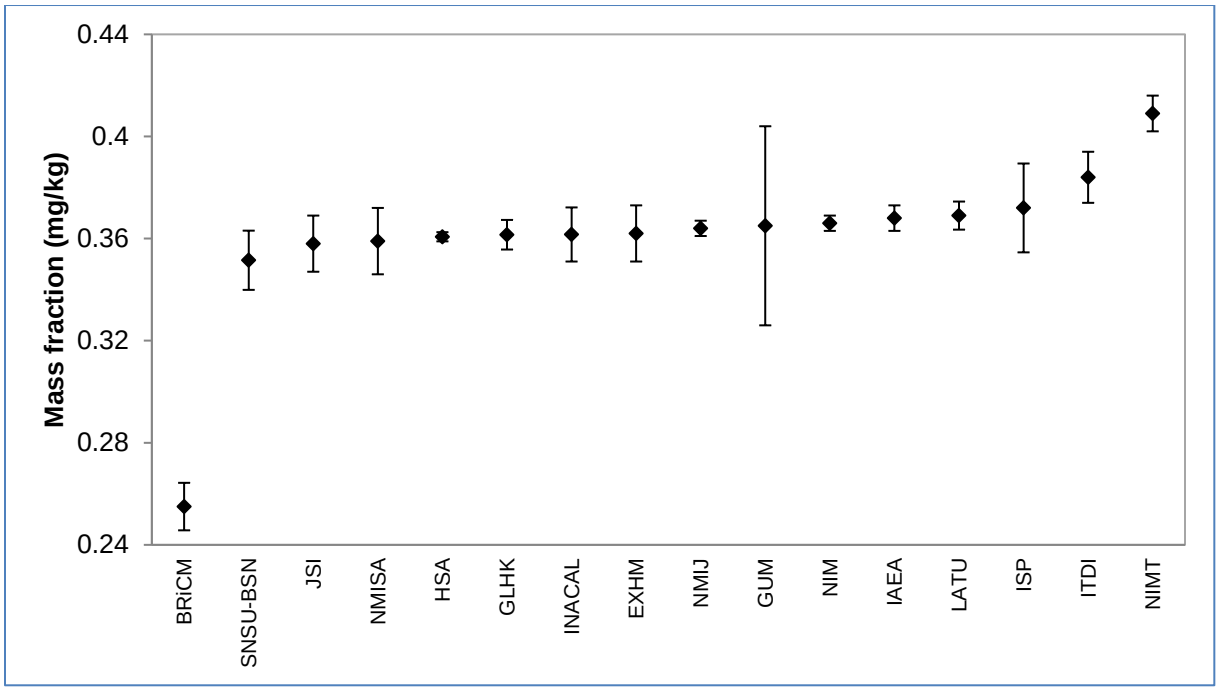

Figure 5. Reported results for cadmium in mg/kg. Error bars represent the standard uncertainties.

Table 11. Reported results for mercury

Participating NMI/DI	Reported mass fraction (mg/kg)	Number of subsamples	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)
NMISA	0.1091	4	0.0026	2	0.0052
GUM	0.118	8	0.006	2.13	0.012
JSI	0.119	14	0.008	2	0.016
GLHK	0.1195	4	0.0036	2	0.0072
NIMT	0.121	6	0.002	2	0.004
NIM	0.122	4	0.002	2	0.004
HSA	0.123	8	0.0016	2.36	0.0038
IAEA	0.124	6	0.001	2	0.003
NMIJ	0.125	4	0.002	2	0.004
INACAL	0.12559	4	0.00343	2	0.00687
LATU	0.1261	6	0.0020	2	0.0040
BRiCM	0.127	4	0.00131	1.96	0.00257
CENAM	0.12776	7	0.00212	2.4	0.00519
ITDI	0.130	4	0.007	1.96	0.013
EXHM	0.1381	4	0.0071	2	0.0141
INMC	0.167	5	0.00735	1.97	0.0144

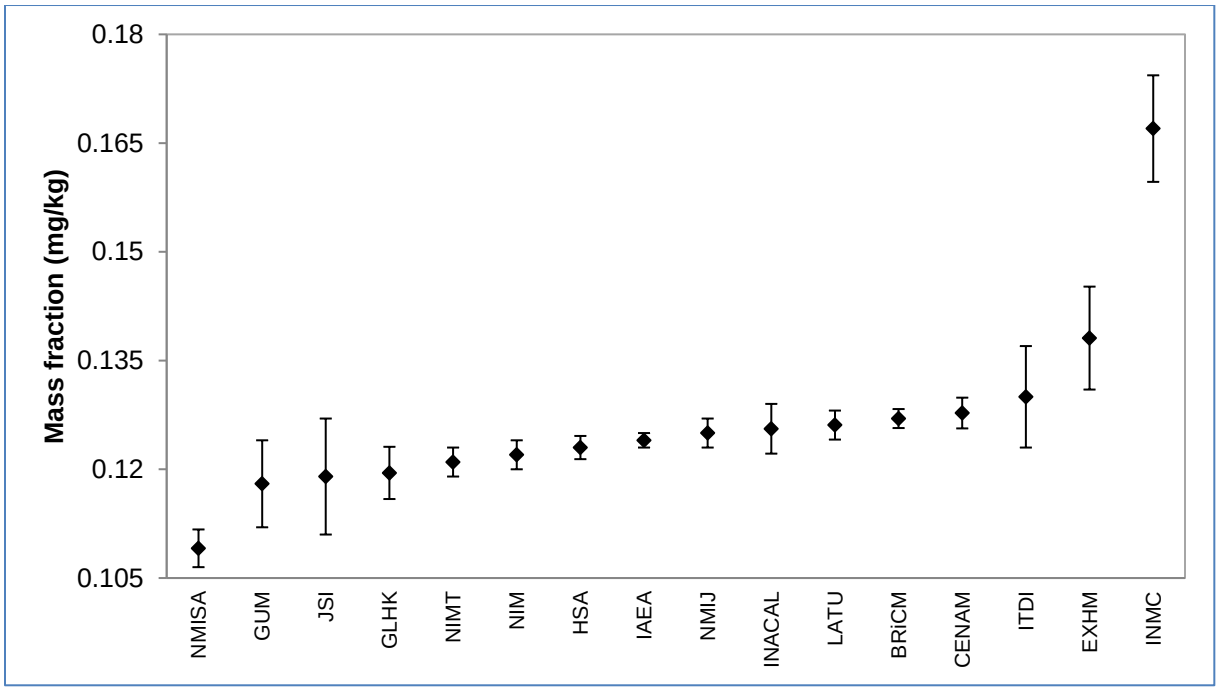

Figure 6. Reported results for mercury in mg/kg. Error bars represent the standard uncertainties.

Table 12. Reported results for lead

Participating NMI/DI	Reported mass fraction (mg/kg)	Number of subsamples	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)
BRiCM	0.234	5	0.0709	1.96	0.139
INACAL	0.3742	4	0.0131	2	0.0262
IAEA	0.376	6	0.004	2	0.007
ITDI	0.402	4	0.011	1.98	0.022
NMISA	0.408	4	0.008	2	0.016
HSA	0.408	8	0.010	2	0.020
JSI	0.410	4	0.011	2	0.022
GLHK	0.4101	5	0.0054	2	0.0108
GUM	0.411	9	0.027	2	0.054
LATU	0.413	6	0.0075	2	0.015
NIMT	0.415	10	0.006	2	0.013
NIM	0.4197	7	0.0042	2	0.009
EXHM	0.426	4	0.028	2	0.055
SNSU-BSN	0.4684	6	0.00913	2	0.0183

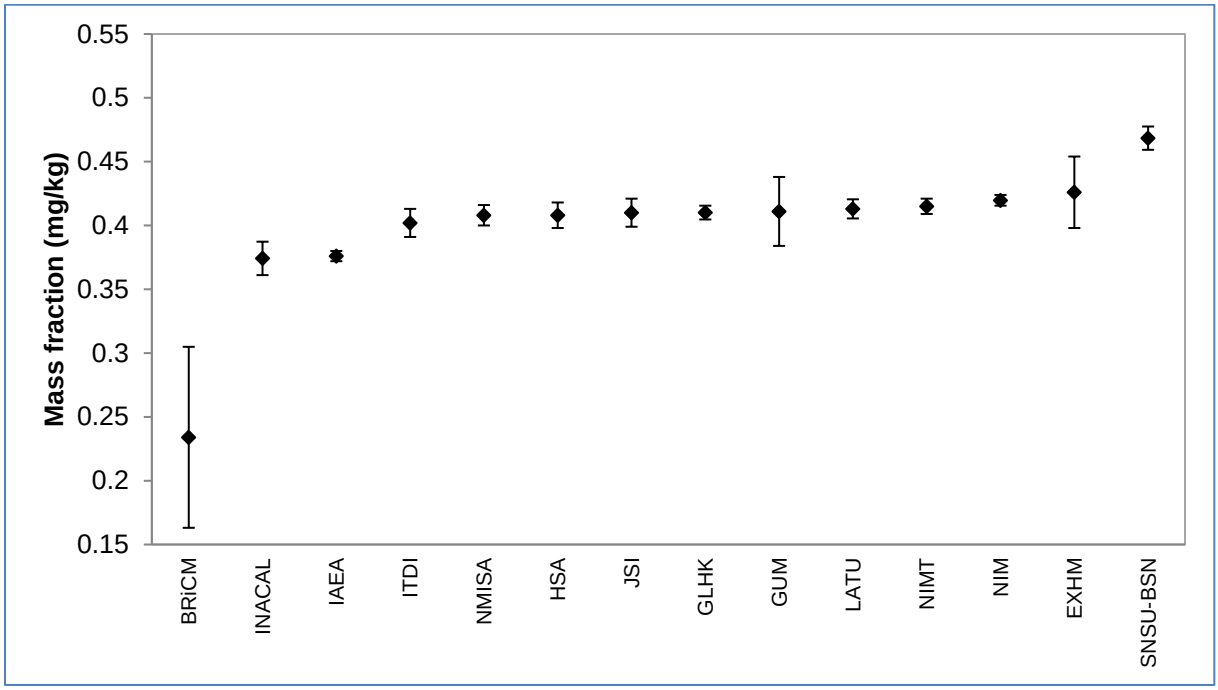

Figure 7. Reported results for lead in mg/kg. Error bars represent the standard uncertainties.

Discussion of Results

Most of the institutes used a microwave-assisted digestion method for sample dissolution. ICP-MS, including triple quadrupole and sector field, were the most commonly used instrumental techniques. Other techniques used included INAA for arsenic, GFAAS for cadmium and lead, and CVAAS and direct mercury analyzer for mercury. Standard addition was used by most institutes for the measurement of arsenic. For cadmium, mercury and lead, IDMS and standard addition were the two most commonly used calibration techniques.

The Initial Results Summary was issued on 20 September 2022. Each participating NMI/DI was only identified anonymously by a code. Participating NMIs/DIs were requested to notify the coordinator for any error in the transcription of results and/or provide any comments by 7 October 2022.

The results of BRiCM and IAEA were excluded from subsequent analysis in this report, due to insufficient metrological traceability as described above.

According to the CCQM Guidance note, the data reported by participants were preliminarily inspected for any anomalous values. Data points that deviate substantially from the median, med(x), relative to their reported uncertainties were identified by plotting [x_i – med(x)] against $u(x_i)$. The results are summarized in Table 13 and the plots are shown in Figure 8.

Most reported data give rise to [x_i – med(x)]/$u(x_i)$ values in between –3 and 3. Several data giving values outside of this range were identified as anomalous and highlighted in red.

Table 13. Results on preliminary inspection for anomalous values

	Arsenic	Cadmium	Mercury	Lead
Median (mg/kg)	1.342	0.3640	0.1240	0.4101
Institute	**$[x_i - \text{med}(x)]/\ u(x_i)$**			
INACAL	0.0	-0.1	0.5	-2.8
LATU	0.4	1.1	1.1	0.3
NMISA	-0.5	-0.3	-5.7	-0.3
INRIM	-0.6	-	-	-
ISP	0.4	0.5	-	-
INMC	-1.9	-	5.9	-
NIMT	-0.1	6.6	-1.5	0.7
HSA	1.1	-1.3	-0.6	-0.3
EXHM	-0.6	-0.1	2.0	0.6
GLHK	0.0	-0.3	-1.3	-0.1
SNSU-BSN	9.9	-1.0	-	6.3
NMIJ	1.8	0.3	0.5	-
NIM	-1.1	1.0	-1.0	2.2
GUM	-0.5	0.1	-1.0	0.0
JSI	0.0	-0.5	-0.6	0.0
CENAM	-	-	1.8	-
ITDI	3.8	2.1	0.9	-0.8

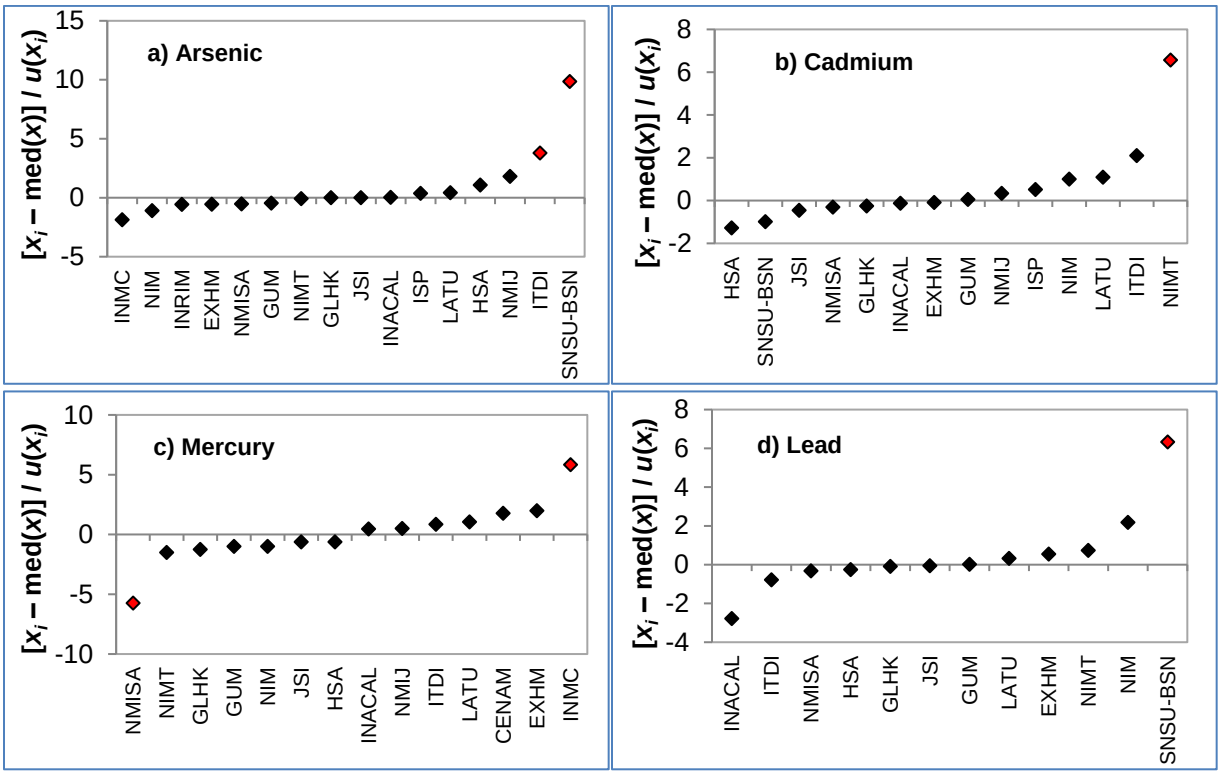

Figure 8. Plots of $[x_i - \text{med}(x)]$ against $u(x_i)$ for a) arsenic, b) cadmium, c) mercury and d) lead.

At the 22nd APMP TCQM meeting (online) held on 14th November 2022, the preliminary results were presented and discussed without disclosing the identity of participating NMIs/DIs (i.e. each institute was assigned with an anonymous code such as S1, S2, and etc.). Concerns were raised on whether any possible problems or mistakes were identified in the measurement procedures by institutes with anomalous values. To address this concern, NMISA (for Hg), INMC (for Hg), NIMT (for Cd), SNSU-BSN (for As and Pb) and ITDI (for As) were invited by email on 23rd November 2022 to check the submitted results including quality control data. All invited institutes provided response by 9th December 2022.

NMISA replied that the CRM used for mercury was DOLT-5 from NRC and the results were 2 % biased on the lower side of the certified value. The mass fraction of mercury in this CRM was considerably higher than the level found in the comparison sample, but the precision found for the CRM and comparison sample using IDMS method were comparable. A technical reason could not be offered for the biased result (for mercury in the comparison sample) at the moment.

INMC replied that the reported value for mercury was the combination obtained from the measurement by two different techniques: ICP-MS and CV-AAS. The value obtained by the ICP-MS method was 0.167 mg/kg ± 0.005 mg/kg while the value obtained by the CV-AAS was 0.138 mg/kg ± 0.010 mg/kg. They concluded that the high value in the measurement results by ICP-MS was due to the memory effect, which was not sufficiently controlled at a low concentration of mercury.

NIMT replied that raw data and calculation throughout the experiment were checked and found to be alright. Recovery of CRM was in the acceptable range. Dry mass correction factor was in the right factor. A technical reason could not be identified.

SNSU-BSN replied that regarding arsenic, the most probable reason came from wrong calculation of reagent blank. In their investigation, they recalculated the values and obtained a result that is close to the proposed SCRV. Regarding lead, they did not perform any experiment to determine the isotope amount ratio for the sample (R_x) and this was suspected to be the cause of bias.

ITDI replied that the QC material used was DORM-4 from NRC. The results obtained for the analysis of arsenic in DORM-4 were 6.84 mg/kg and 6.88 mg/kg (equivalent to 99.6 % and 100.2 %, respectively). The moisture content determined for the comparison sample was 4.8 %. Even before applying dry mass correction, the mass fraction obtained for the comparison sample (ranging from 1.39 mg/kg to 1.59 mg/kg) was way above the majority of participants. However, a technical reason could not be identified.

Based on the above findings, it was considered that there is sufficient technical ground to exclude the reported results of INMC (for Hg) and SNSU-BSN (for As and Pb) from the candidate set for SCRV calculations (while keeping them in the calculation of degree of equivalence). The reported results of NMISA (for Hg), NIMT (for Cd) and ITDI (for As) were kept in the candidate set for SCRV calculations, since no obvious technical issues could be identified.

With reference to the CCQM Guidance note, the chi-squared test was applied to the reduced data set as a consistency check. The results are summarized in Table 14. For arsenic, cadmium and mercury where $\chi^2_{\text{obs}} > \chi^2_{0.05,m-1}$, the data sets were considered mutually inconsistent. For lead where $m - 1 < \chi^2_{\text{obs}} < \chi^2_{0.05,m-1}$, the data provide no strong evidence that the reported uncertainties are inappropriate, but it remains a risk that additional factors are contributing to the dispersion.

Table 14. Summary of consistency check on the data sets for SCRV calculation

Measurand	*m*	χ^2_{obs}	$\chi^2_{0.05,m-1}$	Data set consistency
As	15	24.3	23.7	inconsistent
Cd	14	52.0	22.4	inconsistent
Hg	13	46.2	21.0	inconsistent
Pb	11	13.6	18.3	No evidence of significant inconsistency

For reference purpose, the consistency check was also tested if all of the anomalous values identified in Table 13 were excluded. The results are summarized in Table 15. For arsenic and cadmium where $\chi^2_{\text{obs}} < m - 1$, it is normally safe to proceed with the assumption that the results are mutually consistent and that the uncertainties account fully for the observed dispersion of values. For mercury and lead where $m - 1 < \chi^2_{\text{obs}} < \chi^2_{0.05,m-1}$, the data provide no strong evidence that the reported uncertainties are inappropriate, but it remains a risk that additional factors are contributing to the dispersion.

Overall, it could be concluded that no significant inconsistency was observed in the majority of results.

Table 15. Summary of consistency check on the data sets with anomalous values excluded

Measurand	*m*	χ^2_{obs}	$\chi^2_{0.05,m-1}$	Data set consistency
As	14	10.3	22.4	Mutually consistent
Cd	13	10.0	21.0	Mutually consistent
Hg	12	16.0	19.7	No evidence of significant inconsistency
Pb	11	13.6	18.3	No evidence of significant inconsistency

SUPPLEMENTARY COMPARISON REFERENCE VALUE (SCRV)

Table 16 lists the SCRVs, X, and standard uncertainties, $u(X)$, calculated using the relevant equations for the median and arithmetic mean. The MADe values were calculated by multiplying the median absolute deviation (MAD) values with 1.483. The MAD values were calculated using Equation 1. The median standard uncertainties in Table 16 were calculated using Equation 2. The arithmetic mean standard uncertainties in Table 16 were calculated using Equation 3. The approximate 95 % expanded uncertainties, $U_{95}(X)$, on the median and mean are estimated as: $U_{95}(X) = t_s \times u(X)$, where t_s is the Student's t two-tailed expansion factor for 95 % coverage.

$$MAD = median\ (|x_i - x^*|_{i-1,2,\ldots,n}) \quad (1)$$

$$Standard\ uncertainty = 1.25 \times \frac{MADe}{\sqrt{n}} \quad (2)$$

$$Standard\ uncertainty = \frac{Standard\ deviation}{\sqrt{n}} \quad (3)$$

where:

n = the number of participating NMIs/DIs' results included in the calculation
x_i = the participating NMI/DI's result (mg/kg)
x^* = the median (mg/kg)

Table 16: Supplementary Comparison Reference Values for arsenic, cadmium, mercury and lead

	Arsenic, mg/kg				Cadmium, mg/kg			
Estimator	X	$u(X)$	$U_{95}(X)$[a]	U (%)	X	$u(X)$	$U_{95}(X)$[a]	U (%)
Median	**1.3420**	**0.0081**	**0.0175**	**1.3**	**0.3630**	**0.0017**	**0.0037**	**1.0**
Mean	1.3510	0.0165	0.0353	2.6	0.3674	0.0038	0.0082	2.2

	Mercury, mg/kg				Lead, mg/kg			
Estimator	X	$u(X)$	$U_{95}(X)$[a]	U (%)	X	$u(X)$	$U_{95}(X)$[a]	U (%)
Median	**0.1230**	**0.0018**	**0.0039**	**3.2**	**0.4101**	**0.0016**	**0.0036**	**0.9**
Mean	0.1234	0.0019	0.0042	3.4	0.4088	0.0040	0.0088	2.2

a) $U_{95}(X) = t_s \cdot u(X)$, where t_s is the appropriate two-tailed Student's t critical value for 95 % coverage. The values of t_s are 2.145, 2.16, 2.179 and 2.228, for arsenic, cadmium, mercury and lead respectively.

For all measurands, good agreement was observed between the arithmetic mean and the median. The number of participating NMIs/DIs' results included in the calculation was at least eight ($n \geq 8$). Hence, the median was used as estimators of the SCRVs since it is a simple and robust estimator. Figures 9 to 12 display the application of the SCRVs to the reported data to be included in degrees of equivalence calculations. Dots in red were not included in the SCRV calculations.

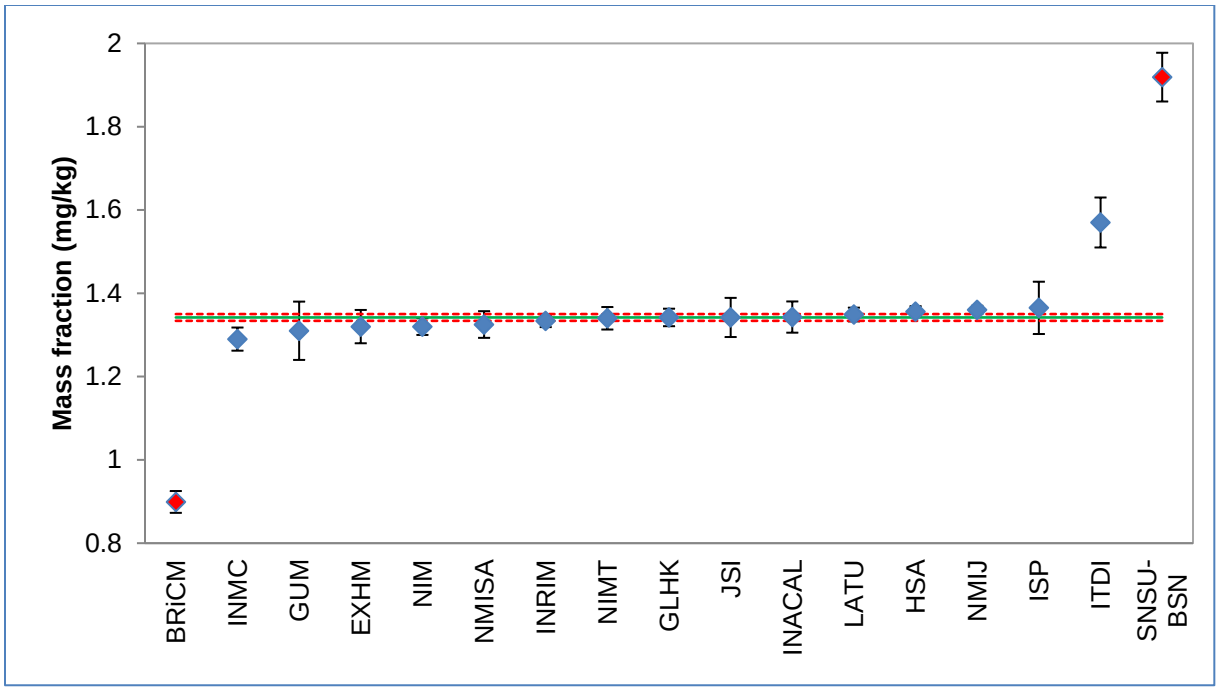

Figure 9. Results for arsenic. Green solid line is the SCRV. Red dashed lines are the standard uncertainty of the SCRV, *u*(SCRV). Error bars represent the reported standard uncertainties.

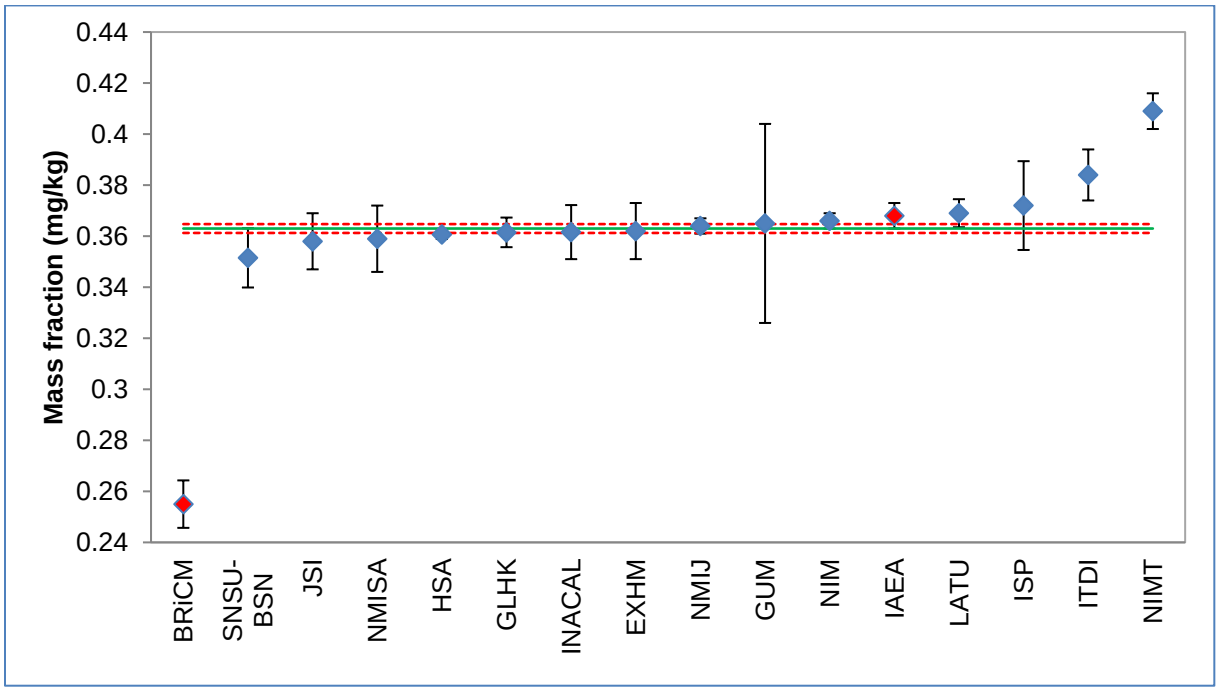

Figure 10. Results for cadmium. Green solid line is the SCRV. Red dashed lines are the standard uncertainty of the SCRV, *u*(SCRV). Error bars represent the reported standard uncertainties.

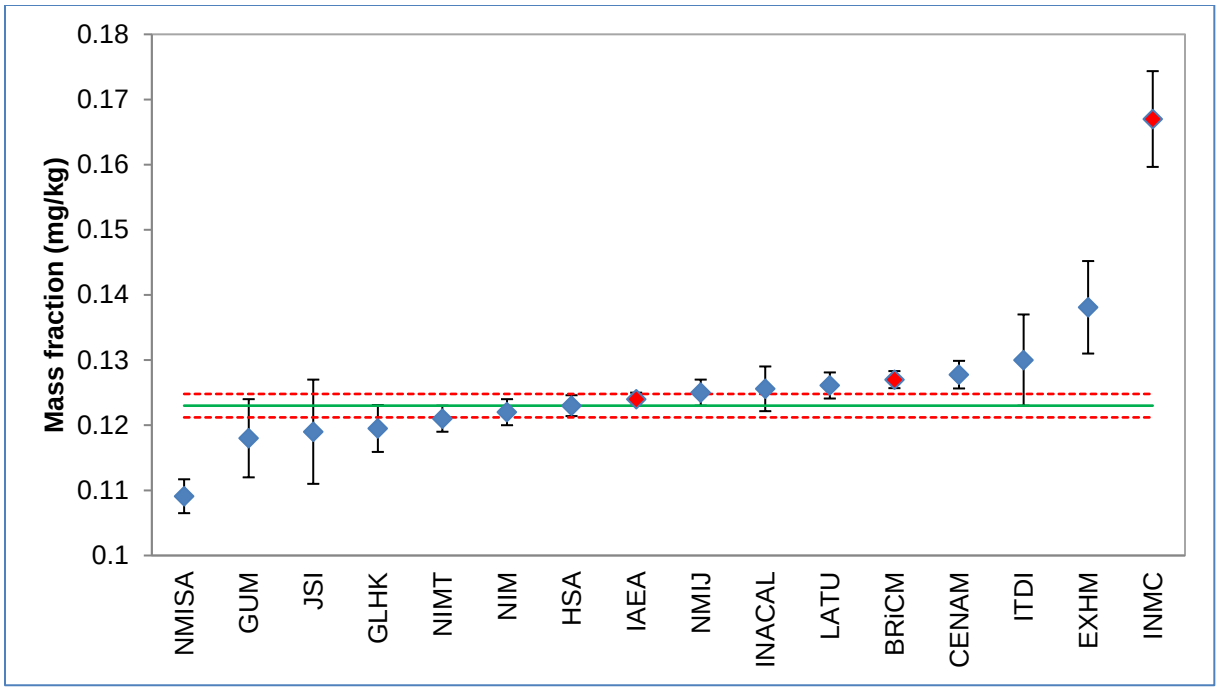

Figure 11. Results for mercury. Green solid line is the SCRV. Red dashed lines are the standard uncertainty of the SCRV, *u*(SCRV). Error bars represent the reported standard uncertainties.

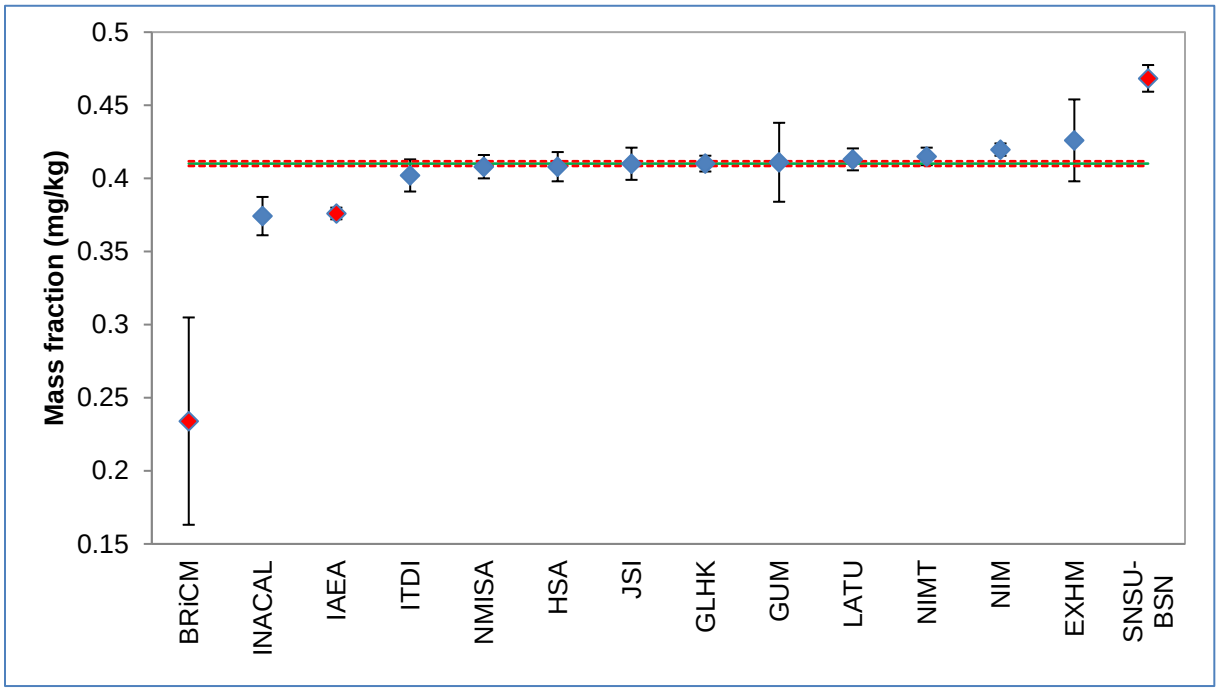

Figure 12. Results for lead. Green solid line is the SCRV. Red dashed lines are the standard uncertainty of the SCRV, *u*(SCRV). Error bars represent the reported standard uncertainties.

At the 22nd APMP TCQM meeting (online) held on 14th November 2022, enquiries were raised on whether the pilot institute had considered using the NIST Decision Tree (NDT) approach to evaluate the results. Representatives of GLHK presented the results of each measurand evaluated using the NDT approach and gave a brief background of the ongoing discussion of the NDT within the CCQM IAWG, particularly on how the dark uncertainty might influence CMC claims. As the adoption of the NDT had not been finalized in the CCQM IAWG, the pilot institute preferred to use the classical estimators to avoid any significant delay of this comparison. This proposal was supported by member(s) in the APMP TCQM. Nevertheless, the results evaluation using the NDT was included in the Draft A1 Report as reference. For all elements, the SCRVs calculated as median was found in good agreement with the estimation of the NDT. At the CCQM IAWG meeting held on 26th April 2023, the Draft A1 Report was presented and discussed, and it was agreed to use median as the estimator of SCRVs for this Supplementary Comparison.

DEGREES OF EQUIVALENCE (DoE)

The absolute degrees of equivalence (DoE) for the participating NMIs/DIs in APMP.QM-S19 and its uncertainty based on the reported measurement results with respect to the SCRV were calculated using Equations 4 and 5, respectively.

$$d_i = (x_i - \mathrm{SCRV}) \tag{4}$$

$$U(d_i) = \sqrt{k_i^2 \times u(x_i)^2 + t_s^2 \times u(\mathrm{SCRV})^2} \tag{5}$$

where:

x_i	=	the reported result from the i^{th} participating institute (i = 1 to n)
k_i	=	the reported coverage factor of the uncertainty of the result from the i^{th} participating institute (i = 1 to n)
d_i	=	the difference between the reported result and the SCRV
$U(d_i)$	=	the expanded uncertainty of the difference d_i at 95 % confidence level

To enable comparison with the degrees of equivalence estimates from other studies, the d_i and $U(d_i)$ were also expressed as percentages relative to the SCRV: $\%d_i = 100 \cdot d_i/\mathrm{SCRV}$ and $\%U(d_i) = 100 \cdot U(d_i)/\mathrm{SCRV}$.

Tables 17 to 20 below list the numeric values of d_i, $U(d_i)$, $\%d_i$, $\%U(d_i)$ and $d_i/U(d_i)$ for participating NMIs/DIs in APMP.QM-S19 for arsenic, cadmium, mercury and lead.

Figures 13 to 16 below graphically illustrate both the absolute and relative DoEs for arsenic, cadmium, mercury and lead using the median as SCRVs. All results are sorted by increasing x. The y-axis to left edge of each graph displays the absolute DoE, d_i, in mg/kg. The y-axis to right edge of each graph displays the relative DoE, $\%d_i$ (i.e. $100 \cdot d_i/\mathrm{SCRV}$), as percent. Dots represent the d_i, bars their expanded uncertainties at 95 % confidence level, $U(d_i)$. The horizontal line denotes perfect agreement with the SCRV.

Table 17: Degrees of Equivalence for arsenic

Participating NMI/DI	Reported mass fraction, x_i (mg/kg)	Reported standard uncertainty, $u(x_i)$ (mg/kg)	Difference from SCRV, d_i (mg/kg)	Expanded uncertainty of the difference, $U(d_i)$ (mg/kg)	$\%d_i$	$\%U(d_i)$	$\frac{d_i}{U(d_i)}$
BRiCM	0.899*	0.0262	-0.443	0.054	-33.0	4.0	-8.17
INMC	1.29	0.0278	-0.052	0.057	-3.9	4.3	-0.90
GUM	1.31	0.07	-0.032	0.141	-2.4	10.5	-0.23
EXHM	1.32	0.04	-0.022	0.082	-1.6	6.1	-0.27
NIM	1.32	0.02	-0.022	0.044	-1.6	3.3	-0.50
NMISA	1.325	0.032	-0.017	0.066	-1.3	4.9	-0.26
INRIM	1.3336	0.0148	-0.008	0.034	-0.6	2.5	-0.25
NIMT	1.34	0.027	-0.002	0.057	-0.1	4.2	-0.04
GLHK	1.342	0.021	0.000	0.045	0.0	3.4	0.00
JSI	1.342	0.047	0.000	0.096	0.0	7.1	0.00
INACAL	1.3429	0.0375	0.001	0.077	0.1	5.7	0.01
LATU	1.349	0.0165	0.007	0.037	0.5	2.8	0.19
HSA	1.356	0.013	0.014	0.031	1.0	2.3	0.45
NMIJ	1.36	0.01	0.018	0.027	1.3	2.0	0.68
ISP	1.365	0.0628	0.023	0.127	1.7	9.4	0.18
ITDI	1.57	0.06	0.228	0.119	17.0	8.9	1.92
SNSU-BSN	1.919**	0.0585	0.577	0.118	43.0	8.8	4.88

*: Reported value was not included in the calculation of SCRV and shall not underpin CMC.
**: Reported value was not included in the calculation of SCRV.

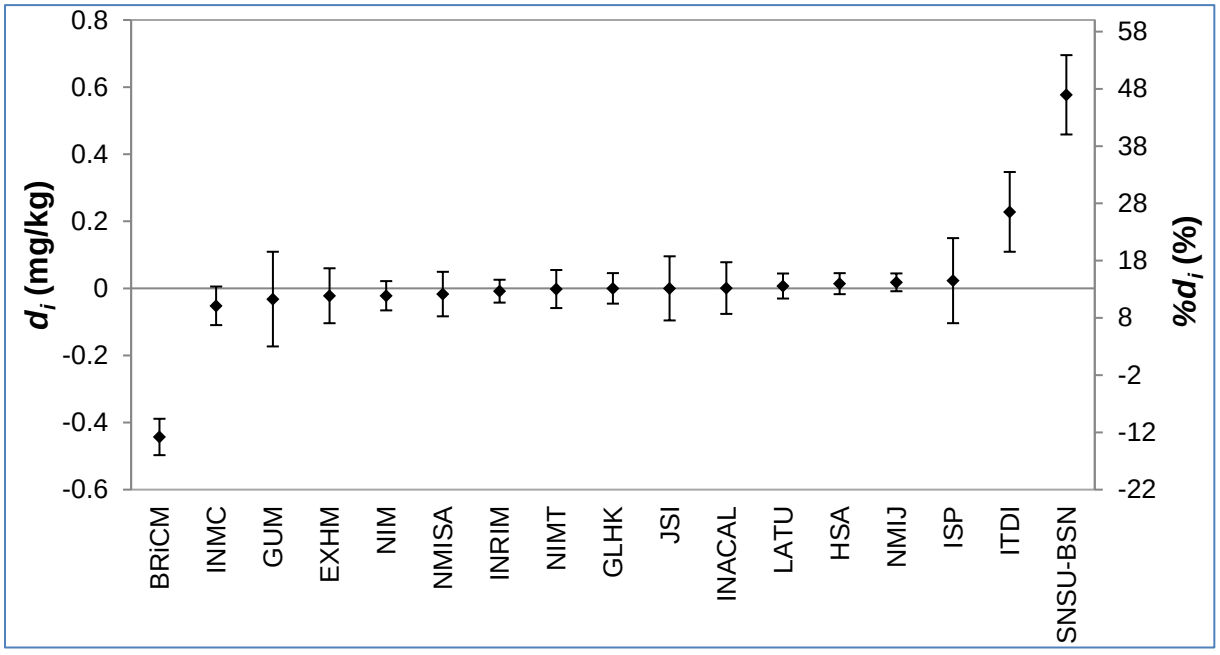

Figure 13. Degrees of Equivalence (DoE) for arsenic.

Table 18: Degrees of Equivalence for cadmium

Participating NMI/DI	Reported mass fraction, x_i (mg/kg)	Reported standard uncertainty, $u(x_i)$ (mg/kg)	Difference from SCRV, d_i (mg/kg)	Expanded uncertainty of the difference, $U(d_i)$ (mg/kg)	$\%d_i$	$\%U(d_i)$	$\frac{d_i}{U(d_i)}$
BRiCM	0.255*	0.009	-0.108	0.019	-29.8	5.1	-5.80
SNSU-BSN	0.3515	0.0116	-0.012	0.024	-3.2	6.5	-0.49
JSI	0.358	0.011	-0.005	0.022	-1.4	6.1	-0.22
NMISA	0.359	0.013	-0.004	0.026	-1.1	7.2	-0.15
HSA	0.3607	0.0018	-0.002	0.005	-0.6	1.4	-0.44
GLHK	0.3615	0.0058	-0.002	0.012	-0.4	3.4	-0.12
INACAL	0.3616	0.0106	-0.001	0.022	-0.4	5.9	-0.07
EXHM	0.362	0.0110	-0.001	0.022	-0.3	6.1	-0.04
NMIJ	0.364	0.003	0.001	0.007	0.3	1.9	0.14
GUM	0.365	0.039	0.002	0.078	0.6	21.5	0.03
NIM	0.366	0.003	0.003	0.007	0.8	1.9	0.42
IAEA	0.368*	0.005	0.005	0.011	1.4	2.9	0.47
LATU	0.369	0.0055	0.006	0.012	1.7	3.2	0.52
ISP	0.372	0.0174	0.009	0.035	2.5	9.6	0.26
ITDI	0.384	0.010	0.021	0.021	5.8	5.7	1.02
NIMT	0.409	0.007	0.046	0.014	12.7	4.0	3.17

*: Reported values were not included in the calculation of SCRV and shall not underpin CMC.

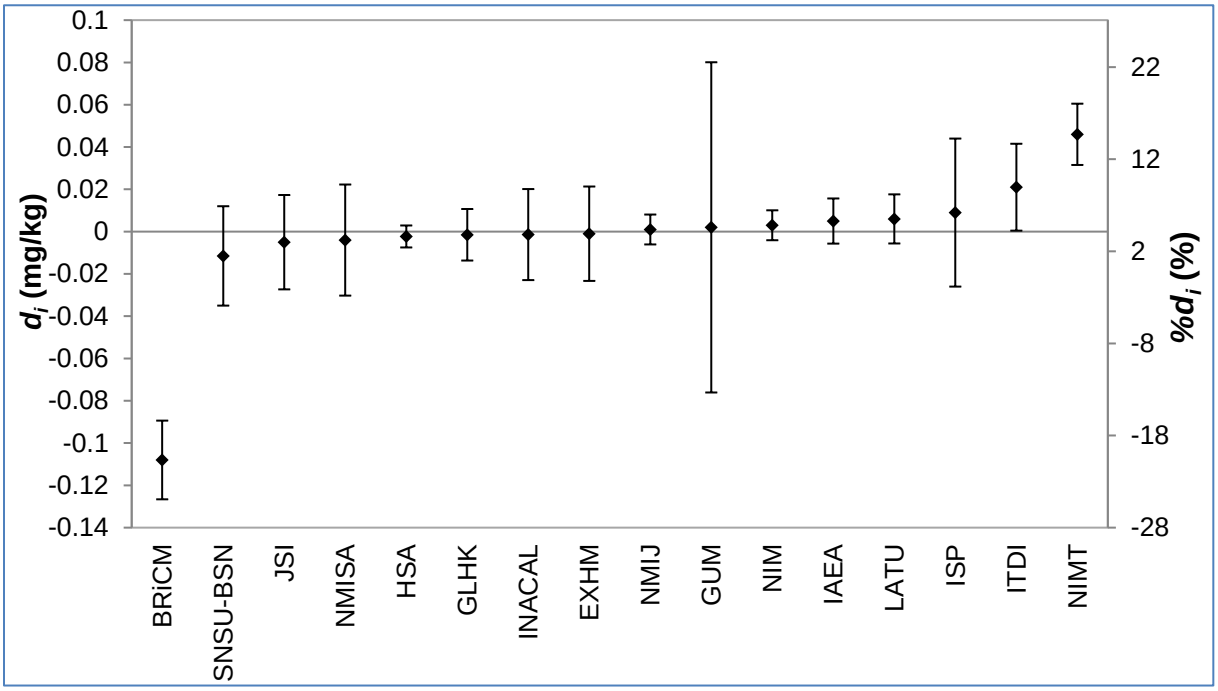

Figure 14. Degrees of Equivalence (DoE) for cadmium.

Table 19: Degrees of Equivalence for mercury

Participating NMI/DI	Reported mass fraction, x_i (mg/kg)	Reported standard uncertainty, $u(x_i)$ (mg/kg)	Difference from SCRV, d_i (mg/kg)	Expanded uncertainty of the difference, $U(d_i)$ (mg/kg)	$\%d_i$	$\%U(d_i)$	$\frac{d_i}{U(d_i)}$
NMISA	0.1091	0.0026	-0.014	0.007	-11.3	5.3	-2.13
GUM	0.118	0.006	-0.005	0.013	-4.1	10.9	-0.37
JSI	0.119	0.008	-0.004	0.016	-3.3	13.4	-0.24
GLHK	0.1195	0.0036	-0.004	0.008	-2.8	6.7	-0.43
NIMT	0.121	0.002	-0.002	0.006	-1.6	4.6	-0.36
NIM	0.122	0.002	-0.001	0.006	-0.8	4.6	-0.18
HSA	0.123	0.0016	0.000	0.005	0.0	4.4	0.00
IAEA	0.124*	0.0010	0.001	0.004	0.8	3.6	0.23
NMIJ	0.125	0.002	0.002	0.006	1.6	4.6	0.36
INACAL	0.12559	0.00343	0.003	0.008	2.1	6.4	0.33
LATU	0.1261	0.002	0.003	0.006	2.5	4.6	0.55
BRiCM	0.127*	0.001	0.004	0.005	3.3	3.8	0.85
CENAM	0.12776	0.00212	0.005	0.006	3.9	5.2	0.74
ITDI	0.130	0.007	0.007	0.014	5.7	11.6	0.49
EXHM	0.1381	0.0071	0.015	0.015	12.3	12.0	1.03
INMC	0.167**	0.00735	0.044	0.015	35.8	12.2	2.93

*: Reported values were not included in the calculation of SCRV and shall not underpin CMC.
**: Reported value was not included in the calculation of SCRV.

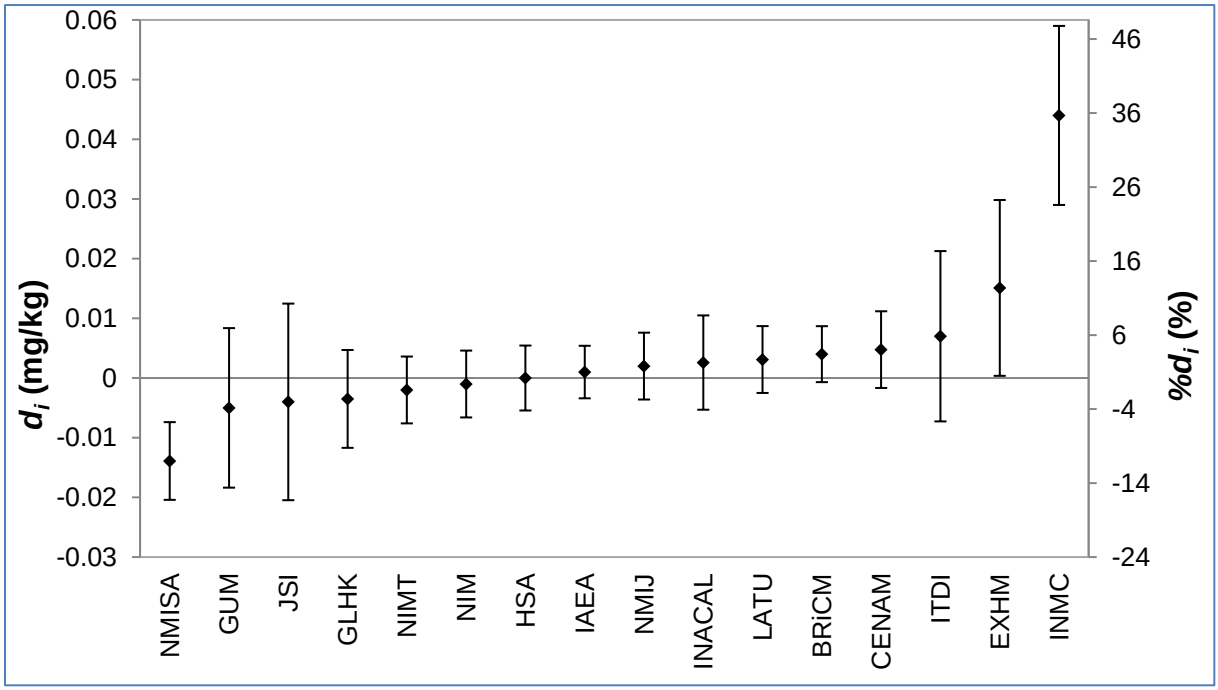

Figure 15. Degrees of Equivalence (DoE) for mercury.

Table 20: Degrees of Equivalence for lead

Participating NMI/DI	Reported mass fraction, x_i (mg/kg)	Reported standard uncertainty, $u(x_i)$ (mg/kg)	Difference from SCRV, d_i (mg/kg)	Expanded uncertainty of the difference, $U(d_i)$ (mg/kg)	$\%d_i$	$\%U(d_i)$	$\frac{d_i}{U(d_i)}$
BRiCM	0.234*	0.0709	-0.176	0.139	-42.9	33.9	-1.27
INACAL	0.3742	0.0131	-0.036	0.026	-8.8	6.4	-1.36
IAEA	0.376*	0.0040	-0.034	0.009	-8.3	2.1	-3.88
ITDI	0.402	0.011	-0.008	0.022	-2.0	5.4	-0.37
NMISA	0.408	0.008	-0.002	0.016	-0.5	4.0	-0.13
HSA	0.408	0.010	-0.002	0.020	-0.5	5.0	-0.10
JSI	0.410	0.011	0.000	0.022	0.0	5.4	0.00
GLHK	0.4101	0.0054	0.000	0.011	0.0	2.8	0.00
GUM	0.411	0.027	0.001	0.054	0.2	13.2	0.02
LATU	0.413	0.0075	0.003	0.015	0.7	3.8	0.19
NIMT	0.415	0.006	0.005	0.013	1.2	3.1	0.39
NIM	0.4197	0.0042	0.010	0.009	2.3	2.2	1.05
EXHM	0.426	0.028	0.016	0.056	3.9	13.7	0.28
SNSU-BSN	0.4684**	0.00913	0.058	0.019	14.2	4.5	3.13

*: Reported values were not included in the calculation of SCRV and shall not underpin CMC.
**: Reported value was not included in the calculation of SCRV.

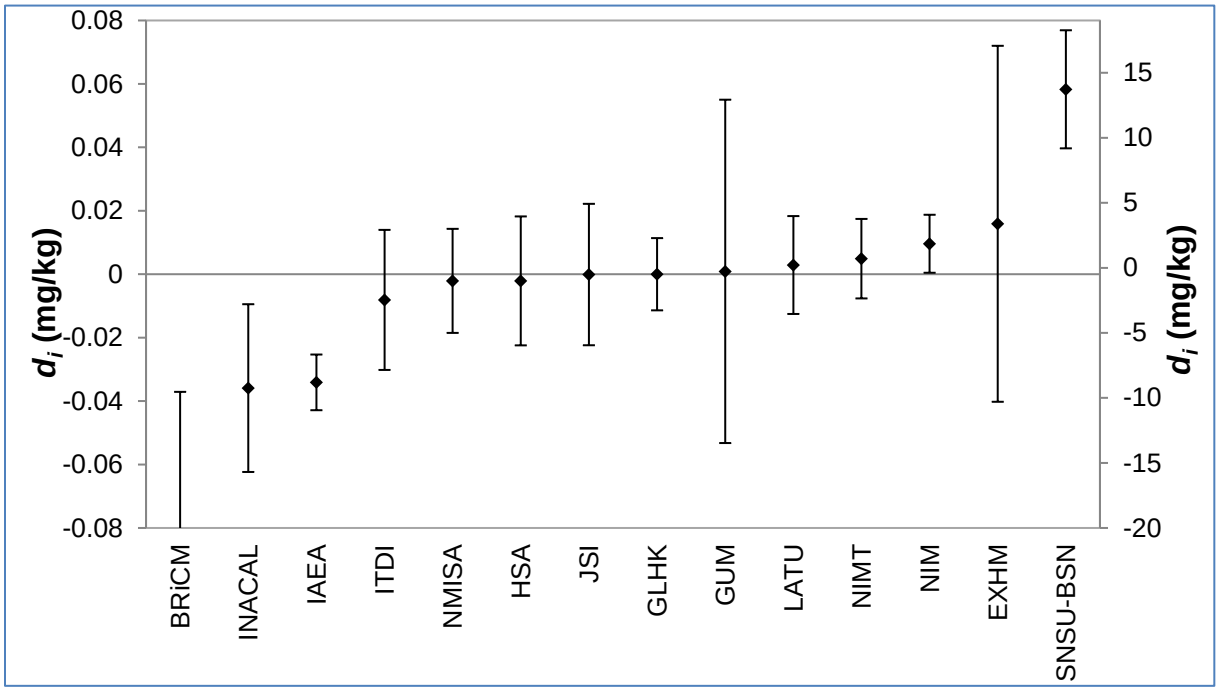

Figure 16. Degrees of Equivalence (DoE) for lead.

USE OF APMP.QM-S19 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

How Far the Light Shines, Core Capability Statements and CMC support

Successful participation in APMP.QM-S19 demonstrates the following measurement capabilities in determining mass fraction of transition elements and metalloids/semi-metals, in mass fraction range from 0.02 mg/kg to 50 mg/kg in a high organics content matrix, including seafood of animal origin and high protein food. Table 21 shows the Core Capability Table.

Table 21. Core Capability Table

Analyte groups	Matrix challenges					
	Water	High Silica content (e.g. Soils, sediments, plants, ...)	High salts content (e.g. Seawater, urine, ...)	High organics content (e.g. high carbon) (e.g. Food, blood/serum, cosmetics, ...)	Difficult to dissolve metals (Autocatalysts, ...)	High volatile matrices (e.g. solvents, fuels, ...)
Group I and II: Alkali and Alkaline earth (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba)						
Transition elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ag, Cd, Ta, W, Au, Hg, Al, Ga, In, Tl, Pb, Po)						
				Cd, Hg, Pb		
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)						
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)						
				As		
Non-metals (P, S, C, N, O)						
Halogens (F, Cl, Br, I)						
Rare Earth Elements (Lanthanides, Actinides)						

Low level (e.g. below 50 µg/kg)

High level (e.g. above 50 µg/kg)

CONCLUSIONS

Most participating NMIs/DIs employed microwave-assisted acid digestion for sample dissolution. Inductively coupled plasma mass spectrometry (ICP-MS), including triple quadrupole and sector field, were the most commonly used instrumental techniques.

The majority of participating NMIs/DIs in APMP.QM-S19 demonstrated their capability on the determination of toxic elements (arsenic, cadmium, mercury and lead) in a seafood matrix. Participating NMIs/DIs, with two exceptions, established the metrological traceability of their results using CRMs with stated traceability.

ACKNOWLEDGEMENTS

GLHK would like to thank the participating NMIs/DIs for their support and providing the requested information used in this study.

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[3] 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.

[4] ISO/IEC Guide 98-3:2008 “Uncertainty of measurement Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)”, 2008, Geneva, Switzerland.

[5] CCQM Guidance note: Estimation of a consensus KCRV and associated Degree of Equivalence, Version: 10, 2013-04-12.

[6] 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.

APPENDIX A: Study Protocol

APMP.QM-S19/P40
Toxic Elements in Seafood

APMP Supplementary Comparison / Pilot Study

Study Protocol (Revised)
[November 2021]

Alvin Wai-hong FUNG and Kelvin Chun-wai TSE
Government Laboratory, Hong Kong (GLHK)
Hong Kong, China

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INTRODUCTION

Seafood is one of the major food resources for human consumption in the world. CODEX Alimentarius Commission [12.1] and many jurisdictions have set maximum levels of metallic contaminants in seafood. The use of reliable methods for measurement of metallic contaminants is important in safeguarding the quality of these products and the public health.

The last CCQM or RMO key comparison / supplementary comparison in the area of metallic contaminants in seafood was organized by the Government Laboratory, Hong Kong, China (GLHK) in 2011 (APMP.QM-S5 Essential and Toxic Elements in Seafood). Hence, it is timely to organize another comparison that covers different measurands. This APMP supplementary comparison (APMP.QM-S19) offers different analytical challenges (e.g. in analysis of mercury and different range of measurands) as compared to the previous comparison. Moreover, this will be a good opportunity for the National Metrology Institutes / Designated Institutes (NMIs/DIs) which did not participate in the previous comparison to demonstrate their measurement competencies.

The supplementary comparison aims to enable participating NMIs/DIs to demonstrate their competence in the determination of toxic elements at mg/kg levels in seafood matrix. It will also enable NMIs/DIs with the relevant services, upon successful completion, to submit Calibration and Measurement Capabilities (CMCs) claims under the Mutual Recognition Arrangement of the International Committee for Weights and Measures (CIPM MRA).

TIMELINE

Table 1 lists the timeline for the proposed study.

Table 1. Programme Schedule.

Action	**Date**	
	APMP.QM-S19	**APMP.QM-P40**
Call for participation	July 2021	16 November 2021
Deadline for registration	30 September 2021	30 November 2021
Distribution of samples	October 2021	By end November 2021
Deadline for submission of results	1 April 2022	
Presentation of first report in APMP TCQM meeting	Nov/Dec 2022	

MEASURANDS

The comparison will cover arsenic, cadmium, mercury and lead in a seafood matrix. The expected mass fractions of the measurands (on a dry mass basis) are given in Table 2.

Table 2. Measurands and expected mass fraction.

Measurand	Expected mass fraction (mg/kg)
Arsenic	0.2 – 50
Cadmium	0.04 – 10
Mercury	0.02 – 5
Lead	0.04 – 10

STUDY MATERIALS

Dried shrimps were purchased from the local market in Hong Kong. The shrimps were soaked in a spike solution containing the target analytes for several hours, freeze-dried, blended into powder, and subjected to a sieving process through two calibrated sieves (200 and 100 μm respectively). The sieved powder (particle size: 100–200 μm) was thoroughly homogenized in a 3-dimensional mixer for 5 days. The material was irradiated using a gamma source at a dose of about 10 kGy for disinfection. The irradiated material was packed into high-density polyethylene bottles, each of about 30 g. The bottles were purged with nitrogen and stored at room temperature (20 ± 5 °C).

Each participant will receive with **TWO** bottles of sample, each containing approximately 30 g of dried shrimp material. Measurement results are to be reported on a dry-mass basis.

Homogeneity Assessment of Study Material

Ten bottles of sample were randomly selected for homogeneity study. Two test portions of 0.5 g each were taken from each bottle for analysis. The test portions were digested using microwave-assisted acid digestion and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) with gravimetric standard additions. ANOVA at 95% level of confidence was applied to assess the between-bottle homogeneity in accordance with ISO Guide 35:2017 [12.2], the comparison 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	
Arsenic	1.50	3.02	0.7
Cadmium	0.93	3.02	0.6
Mercury	1.95	3.02	1.6
Lead	0.59	3.02	1.0

The graphical representation of the homogeneity data for individual measurand(s) are provided in Figures 1 to 4.

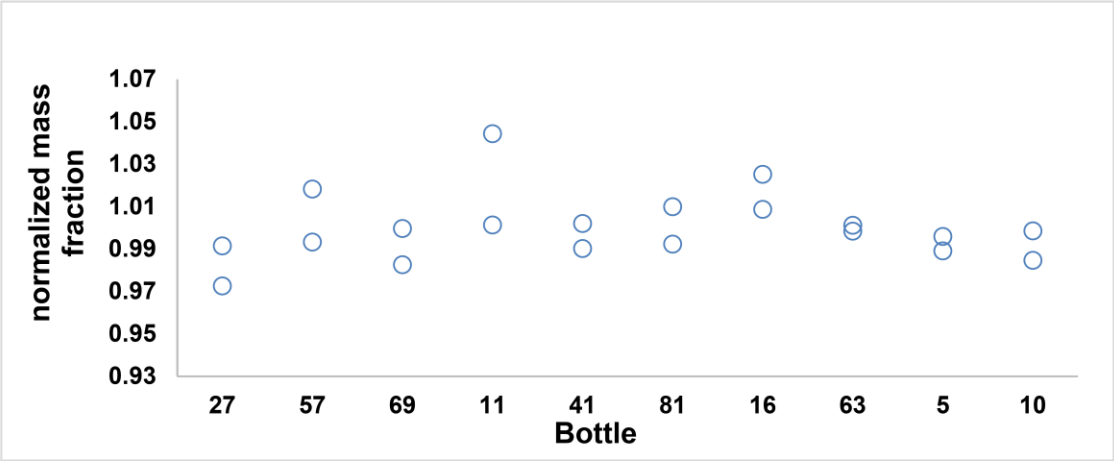

Figure 1. Homogeneity evaluation for Arsenic.

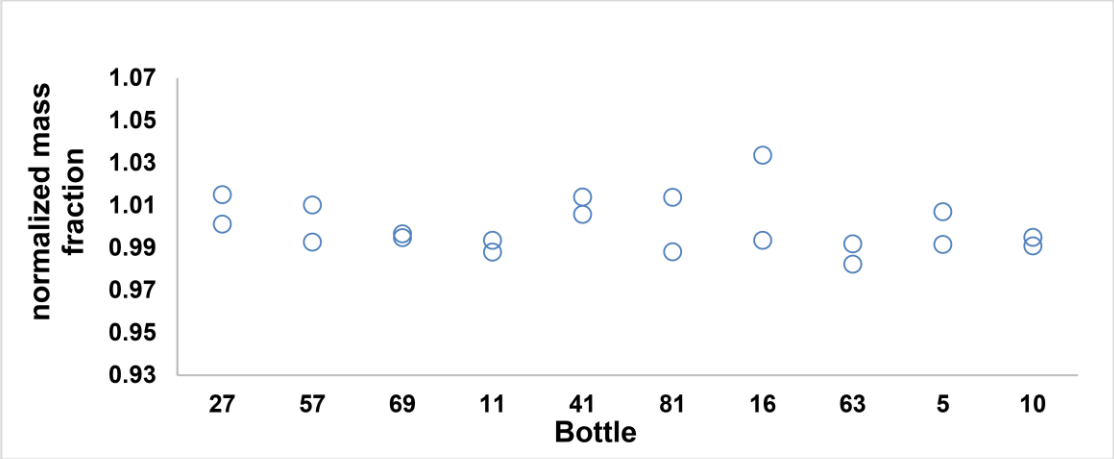

Figure 2. Homogeneity evaluation for Cadmium.

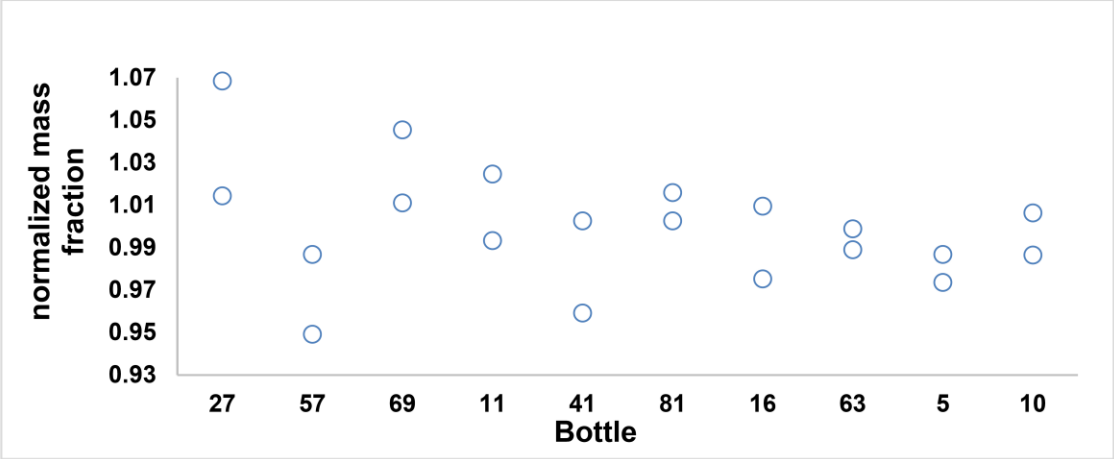

Figure 3. Homogeneity evaluation for Mercury.

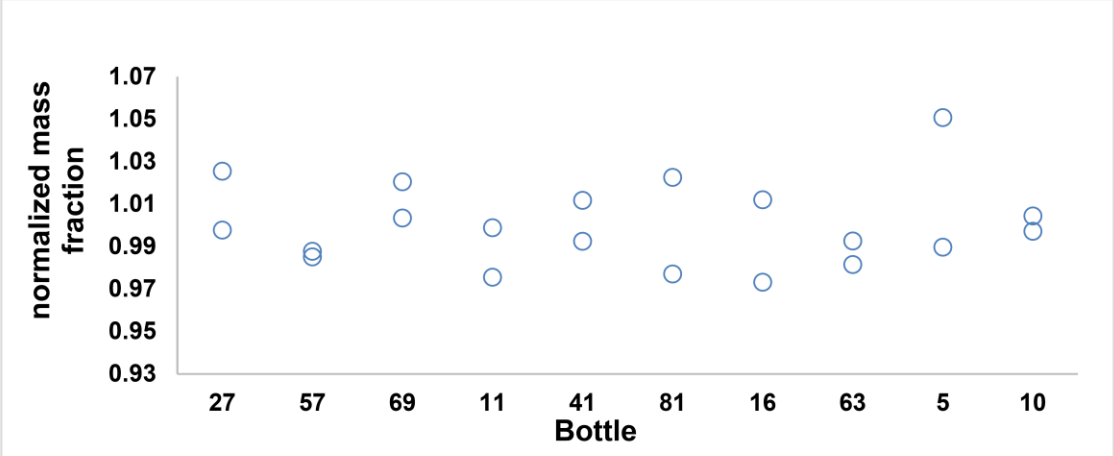

Figure 4. Homogeneity evaluation for Lead.

Stability Assessment of Study Material

The short-term stability of the measurands over a period of 4 weeks at 40 °C was accessed using isochronous approach, using the same analytical procedures as for the homogeneity study. Two randomly selected sample bottles were transferred from the storage condition (20 ± 5 °C) to 40 °C on three occasions (1, 2 and 4 weeks) over the study period. Two subsamples were then taken from each bottle. 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 4 weeks. The results are summarized in Table 4 and graphically represented in Figure 5.

Table 4. Results of the stability assessment (at 40 °C for 4 weeks) for the measurands.

Measurand	Student's *t*-test		*p*-value
	Calculated test statistics	Critical value	
Arsenic	0.201	4.303	0.859
Cadmium	0.864	4.303	0.479
Mercury	0.232	4.303	0.838
Lead	0.709	4.303	0.552

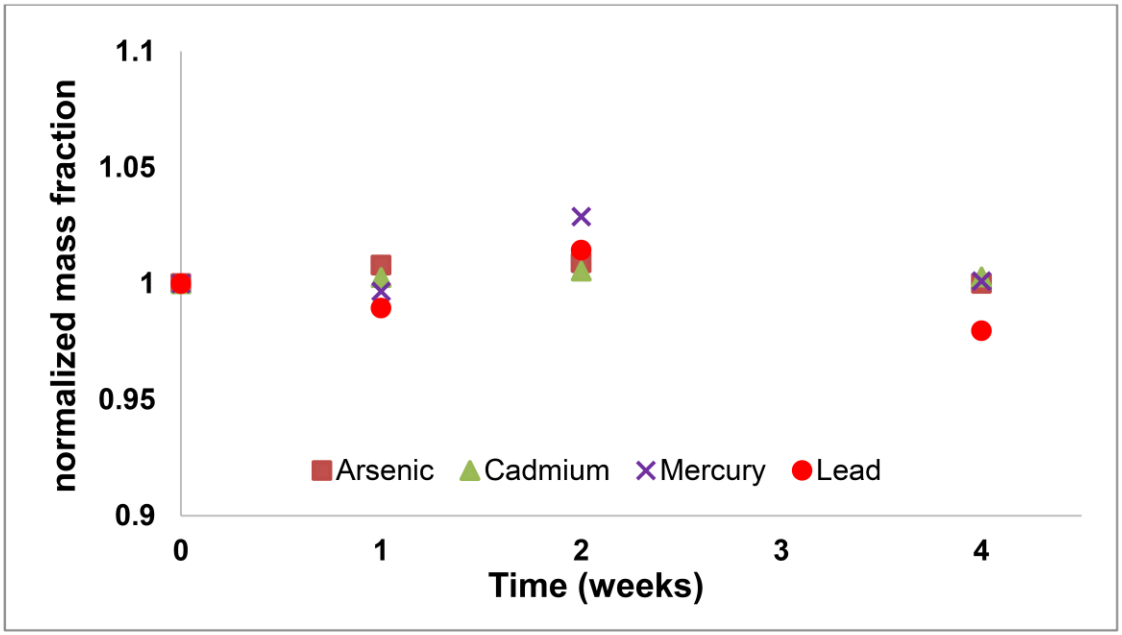

Figure 5. Short-term stabilities of the measurands at 40 °C for 4 weeks.

The long-term stability of the measurands in the comparison material at 20 ± 5 °C will be assessed using the same analytical procedures as for the homogeneity study. 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.

Calibration Materials

Participants may establish the metrological traceability of their results to the SI using a direct realization via a primary method, certified reference materials (CRMs) from a NMI/DI having the required CMC claims, or by preparing their own calibration standards using commercially

available high purity materials for which they have determined the purity themselves. Commercial standards should not be employed if a supplementary comparison is to be used to support CMCs claims (See section 3 in CIPM MRA-G-13 for more information: https://www.bipm.org/utils/common/documents/CIPM-MRA/CIPM-MRA-G-13.pdf) [12.3].

INSTRUCTIONS AND SAMPLE DISTRIBUTION

The samples will be transported at room temperature (monitored by a temperature strip). Upon receipt, the samples should be stored at 20 ± 5 °C. A Sample Receipt Form will be provided to the participating NMIs/DIs for completion. The completed form should be sent to GLHK at your earliest convenience.

Recommended Minimum Sample Amount

The recommended minimum sample amount for analysis is at least 0.5 g. Participating NMIs/DIs should take at least 4 subsamples for the measurement of measurands. The bottle contents should be well mixed by rotation and shaking prior to use.

Dry Mass Determination

Dry mass determination shall be carried out, at the same time as the test portions are analyzed, by placing three separate portions (about 1 g each) of sample over anhydrous calcium sulphate (e.g. DRIERITE®) in a desiccator for at least 10 days until constant mass is reached. Do not use the sample, which was used for the determination of moisture content, for analysis.

RESULTS

Reporting and submission of results

A Report Form will be provided to the participating NMIs/DIs for completion. The participating NMIs/DIs are expected to report their results based on at least four subsamples for each measurand. Only one result, calculated from the average of the measurements, should be reported for each measurand. The results should be reported on a dry-mass basis in the unit of mg/kg, and should include standard and expanded uncertainties (95% level of confidence) for the mean of the replicate determinations.

Information on the measurement procedure (including the sample dissolution method, the calibration method, the internal standard, the quality control, the analytical instrument(s) used, etc), the calculation of the results, and the estimation of measurement uncertainty should be included in the Report Form. The completed form should be sent to GLHK on or before the scheduled deadline (1 April 2022). The submitted results will be considered as final.

To facilitate in-depth performance evaluation, participating NMIs/DIs shall clearly identify and quantify those factors that are considered to contribute to the measurement uncertainty of the analysis [12.4].

Evaluation of results

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 NIST Decision Tree approach (https://doi.org/10.6028/jres.126.007) [12.5] may be used for SCRV and Degree of Equivalence (DoE) calculations.

USE OF APMP.QM-S19 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

How Far the Light Shines

The comparison enables NMIs/DIs to demonstrate their capabilities in analyzing inorganic elements between the mass fraction range of 0.02 mg/kg to 50 mg/kg in seafood. The comparison will support CMCs for transition elements and metalloids/semi-metals in high organics content matrix, including seafood of animal origin and high protein food in category 11 (food).

Core Capability table

Analyte groups	Matrix challenges					
	Water	High Silica content (e.g. Soils, sediments, plants, ...)	High salts content (e.g. Seawater, urine, ...)	High organics content (e.g. high carbon) (e.g. Food, blood/serum, cosmetics, ...)	Difficult to dissolve metals (Autocatalysts, ...)	High volatile matrices (e.g. solvents, fuels, ...)
Group I and II: Alkali and Alkaline earth (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba)						
Transition elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ag, Cd, Ta, W, Au, Hg, Al, Ga, In, Tl, Pb, Po)						
				Cd, Hg, Pb		
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)						
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)						
				As		
Non-metals (P, S, C, N, O)						
Halogens (F, Cl, Br, I)						
Rare Earth Elements (Lanthanides, Actinides)						

Low level (e.g. below 50 µg/kg)
High level (e.g. above 50 µg/kg)

REGISTRATION AND CONTACT DETAILS

The supplementary comparison is co-ordinated by the Government Laboratory, Hong Kong, China (GLHK) (Address: 7/F., Ho Man Tin Government Offices, 88 Chung Hau Street, Homantin, Kowloon, Hong Kong).

Participation is open to all NMIs/DIs under the APMP as listed in the CIPM MRA (https://www.bipm.org/en/cipm-mra/participation). NMIs/DIs from other RMOs are also welcome to join this supplementary comparison. Interested NMIs/DIs should complete the Registration Form and return it to Dr. Alvin W.H. Fung and Dr. Kelvin C.W. Tse before the deadline for registration on 30 September 2021.

Participation in the pilot study is open to 1) all laboratories eligible to join the supplementary comparison and 2) guest laboratories upon invitation. Interested NMIs/DIs/laboratories should complete the Registration Form and return it to Dr. Alvin W.H. Fung and Dr. Kelvin C.W. Tse before 30 November 2021.

For enquiries, you may wish to contact the co-ordinating laboratory as follows:

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APPENDIX B: Registration Form

APMP.QM-S19/P40
APMP Supplementary Comparison / Pilot Study
Toxic Elements in Seafood

Registration Form

Name of Institute / Laboratory : ||

NMI / DI (Please specify) : ||

Country/Economy : ||

Name of Contact Person(s) : ||

Designation(s) : ||

Email Address(es) : ||

Telephone Number(s) : ||

Postal Address : ||

Postal Code : ||

Date : ||

Remarks or special requests (e.g. any particular local customs requirements / special permits required for import of the comparison sample).

Please note that any import taxes or charges imposed on the comparison samples during transportation shall be borne by the participating laboratory.

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APMP.QM-S19/P40
APMP Supplementary Comparison / Pilot Study
Toxic Elements in Seafood

Please select the measurand(s) by checking the appropriate box(es).

Our Laboratory would like to register for participation in the following:

Measurand	APMP.QM-S19	APMP.QM-P40
Arsenic	☐	☐
Cadmium	☐	☐
Mercury	☐	☐
Lead	☐	☐

Please complete this form and return it to Dr. Alvin Wai-hong FUNG (E-mail: whfung@govtlab.gov.hk) and Dr. Kelvin Chun-wai TSE (E-mail: cwtse@govtlab.gov.hk) on or before the deadline (30 November 2021) for registration. An email reply will be sent within 5 working days to confirm the registration. If you do not receive an acknowledgement of your registration from us within 5 working days, please send us an email.

APPENDIX C: Sample Receipt Form

APMP.QM-S19/P40

APMP Supplementary Comparison / Pilot Study

Toxic Elements in Seafood

Sample Receipt Form

Institute/ Laboratory: _____

Postal address: _____

Authorised person: _____ _____ _____

Title Given name Surname

E-mail: _____

Print name/ Signature: _____

Date: _____

Confirmation of Package Contents (Please tick the appropriate boxes)

I hereby acknowledge the receipt of the sealed shipping box for the APMP Supplementary Comparison / Pilot Study (APMP.QM-S19/P40). The box contains:

☐ One bottle of sample with a bottle number of _____.

☐ The sample is *Intact & Sealed / Broken / Missing** and should be *Suitable / Not Suitable** for analysis (* Please delete as appropriate).

☐ The temperature recording strip indicated that the maximum temperature experienced during the transport was:

☐< 29°C ☐ 29 °C ☐ 33 °C ☐ 34 °C ☐ 37 °C ☐ 40 °C ☐ 42 °C

☐ The Material Safety Data Sheet for the sample.

Other comments: _____

Upon receipt of the sample, please complete this form and return it to Dr. Kelvin Chun-wai TSE (cwtse@govtlab.gov.hk).

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APPENDIX D: Report Form

APMP.QM-S19/P40

APMP Supplementary Comparison / Pilot Study

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REPORT FORM

Institute/
Laboratory: _____

Contact person: _____ _____ _____

Title Given name Surname

E-mail: _____

Print name /
Signature: _____

Date: _____

1. Analytical results and measurement uncertainties

Measurand	Arsenic (As)	Cadmium (Cd)	Mercury (Hg)	Lead (Pb)
Overall mean of results (mg/kg)				
Number of subsamples (n)				
Combined standard uncertainty (mg/kg)				
Coverage factor, *k* (95% confidence level)				
Expanded uncertainty (mg/kg)				

Notes: (i) Report the analytical results and associated uncertainty on dry-mass basis in mg/kg;
(ii) Report values with 3 significant figures.

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2 Technical Information on Methodology Used for the Quantification of the Measurands (please provide details, where appropriate)

2.1 Calibration and Internal Standards

Measurand	Calibration standard	Isotope spike / Internal Standard (if any)	Calibration method*	Instrument used
e.g. Arsenic	NIST SRM 3103a Arsenic standard solution	^{72}Ge	Gravimetric standard addition (^{75}As)	ICP-MS
e.g. Cadmium	NIST SRM 3108 Cadmium standard solution	^{111}Cd (96.44%) isotopic spike	Exact-matching IDMS (^{111}Cd /^{114}Cd)	ICP-MS
Arsenic				
Cadmium				
Lead				
Mercury				

* Please indicate the ions monitored

2.2 Sample Treatment (Please give details of sample preparation procedure including reagents and quality controls used, apparatuses and their operating conditions).

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2.3 Measurement Equation(s) Used to Determine the Mass Fraction(s) of the Measurand(s)

2.4 Uncertainty Budget (Please list and describe components of the final uncertainty budget and the magnitude of their contribution.)

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2.5 Other Information

Please complete and return this form to Dr. Alvin Wai-hong FUNG (whfung@govtlab.gov.hk) and Dr. Kelvin Chun-wai TSE (cwtse@govtlab.gov.hk) on or before the deadline (**30 April 2022**). We will acknowledge receipt of the Report Form within 5 working days.