LABORATORIO TECNOLÓGICO DEL URUGUAY

SIM.QM-S11
Supplementary Comparison for elements in Yerba mate (*Ilex paraguariensis*)

Final Report

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SUMMARY

Yerba mate is a native plant found in subtropical South American regions (Paraguay, Brazil, Argentina, and Uruguay), where is commonly consumed as an infusion and worldwide as tea. The safety of yerba mate involves continuous monitoring of arsenic and cadmium levels, and the product's labeling also includes measurement of nutrient content such as sodium and phosphorus.

The Supplementary Comparison and parallel Pilot Study SIM.QM-S11 & P25 Elements in Yerba mate (Ilex paraguariensis) covered arsenic (0.0575 mg/kg), cadmium (0.7526 mg/kg), sodium (33.46 mg/kg) and phosphorus (1.738 mg/g). The last CCQM or RMO key comparison / supplementary comparison of elements in plants matrices was organized by the Government Laboratory, Hong Kong, China (GLHK) in 2011 and results were published in 2013 (CCQM-K89 Trace and essential elements in Herba Ecliptae, including arsenic, calcium, cadmium, lead and zinc). Hence, it was timely to organize another comparison that could cover different measurands in high silica content matrix. Moreover, it enabled National Metrology Institutes / Designated Institutes (NMIs/DIs) that did not participate in 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).

Fifteen National Metrology Institutes and Designated Institutes participated in the Supplementary Comparison SIM.QM-S11 (Elements in Yerba mate (Ilex paraguariensis)).

Participants were asked to assess the mass fractions of arsenic, cadmium, and sodium in mg/kg, along with the mass fraction of phosphorus in mg/g on a dry mass basis in yerba mate matrix.

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 preparation. Inductively coupled plasma mass spectrometry (ICP-MS), sector field ICP-MS (SF-ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-OES) were the most commonly used instrumental techniques.

Successful participation in SIM.QM-S11 demonstrates measurement capabilities in determining mass fraction of transition elements (except Hg), alkali and alkaline earth, non-metals (exp: C, N, and O) and metalloids/ semi-metals in mass fraction range from 0.02 mg/kg to 5000 mg/kg in high silica content matrixes.

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INTRODUCTION

Yerba mate (Ilex paraguariensis, Aquilfoliaceae) is a native plant which grows in the subtropical regions of South America: Paraguay, Brazil, Argentina and Uruguay. It is consumed as an infusion called “mate” in the beforementioned countries as well as all around the world as tea.

Due to safety reasons the mass fraction of arsenic and cadmium is constantly monitored in vegetal materials. Additionally, for the labeling purposes, the mass fraction of nutrients as sodium and phosphorus is also measured. Therefore, it is crucial that countries can develop measurement capabilities for these determinations in order to provide reference materials and measurement services, such as proficiency testing schemes. 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 SIM CMWG meeting in November 2019, the SIM.QM-S11 “Supplementary Comparison for elements in Yerba mate” was proposed. In March 2021, SIM authorized the Supplementary Comparison SIM.QM-S11 “Supplementary Comparison for elements in Yerba mate (*Ilex paraguariensis*)”.

The aim of this comparison is to enable NMIs/DIs to demonstrate their competence in the determination of elements at low and high levels in a vegetal material within the high silica content category.

The following sections of this report document the timeline of SIM.QM-S11, the measurands, study material, participants, results, and the measurement capability claims that participation in SIM.QM-S11 can support.

TIMELINE

Table 1 lists the timeline for SIM.QM-S11.

Table 1. Timeline for SIM.QM-S11

Date	Action
November 2019	Proposed to SIM CMWG
March 2021	SIM authorized SIM.QM-S11
April 2021	Call for participation
June 2021 – November 2021	Study samples shipped to participants. The range in shipping times reflects delays from shipping and customs.
February 2022	Deadline for submission of results
June 2024	Draft A report
March 2025	Draft A2 report
May 2025	Draft B report
TBD	Final report

MEASURANDS

The measurands and expected mass fraction (on a dry mass basis) are presented in Table 2.

Table 2. Measurands and expected mass fraction.

Measurand	Expected mass fraction (mg/kg)
Arsenic	0.02 – 1
Cadmium	0.1 – 5
Phosphorus	500 – 5000
Sodium	1 – 100

STUDY MATERIALS

Preparation

Several packs of yerba mate (Ilex paraguariensis) from a batch suspected of contamination were selected. Determinations were performed, confirming that the sample contained quantifiable mass fractions of arsenic and cadmium. The sample was dried in a convection oven at 100 °C for 4 hours. After that, it was firstly grounded using a knife mill. Then, further grounding was done using an ultra-centrifugal mill (resulting in a particle size of approximately 80 μm). Finally, the material was thoroughly mixed using a V-shape mixer. The obtained powder was fractionated into pre-cleaned glass amber bottles containing approximately 25 g of material. A preliminary microbiological study showed undetectable levels (< 10 CFU/g) of aerobic mesophilic bacteria as well as yeast and mold. Nevertheless, the material was γ-irradiated with a dose of 23 kGy to ensure sterilization.

Recommended minimum sample amount

The recommended minimum sample amount for analysis was at least 0.5 g.

Dry mass determination

The determination dry mass correction had to be carried out on a minimum of three separate portions, each weighing 1 g. Samples had to be dried in an air-forced oven at 103 ºC ± 2 ºC for 2 hours. After cooling and weighting, the samples had to be reintroduced into the oven for an additional hour, repeating this step until a constant mass was reached. Constant mass was considered achieved when the difference between weights was less than 0.002 g. In general, constant mass should have been attained in the first 3 hours.

Homogeneity Assessment of Study Material

The homogeneity study was carried out according to ISO GUIDE 35:2017, using one-way ANOVA at 95 % level of confidence. Ten bottles were selected: the first one, the last one and the rest by stratified random sampling.

Determination of Cd was performed by ID-ICP-SFMS, As by SA-ICP-SFMS and Na and P by SA-ICP-OES in three subsamples per bottle. The study material was found to be sufficiently homogeneous. The results of *F*-Test are shown in Table 3.

Table 3. Homogeneity F-Test Results

Element	F	F-critical
Arsenic	2.20	2.39
Cadmium	0.96	2.39
Sodium	1.67	2.39
Phosphorus	1.75	2.39

Results of the homogeneity assessment are presented in Table 4.

Table 4. Homogeneity ANOVA Results

ANOVA Estimate	Arsenic	Cadmium	Sodium	Phosphorus
Within-packet, CV_{wth}:	2.0 %	0.90 %	0.93 %	0.54 %
Between-packet, CV_{btw}:	2.9 %	0.88 %	1.20 %	0.72 %
Total analytical variability, CV:	2.3 %	0.89 %	1.03 %	0.60 %

The results for the homogeneity study are graphically represented in Figure 1 to 4.

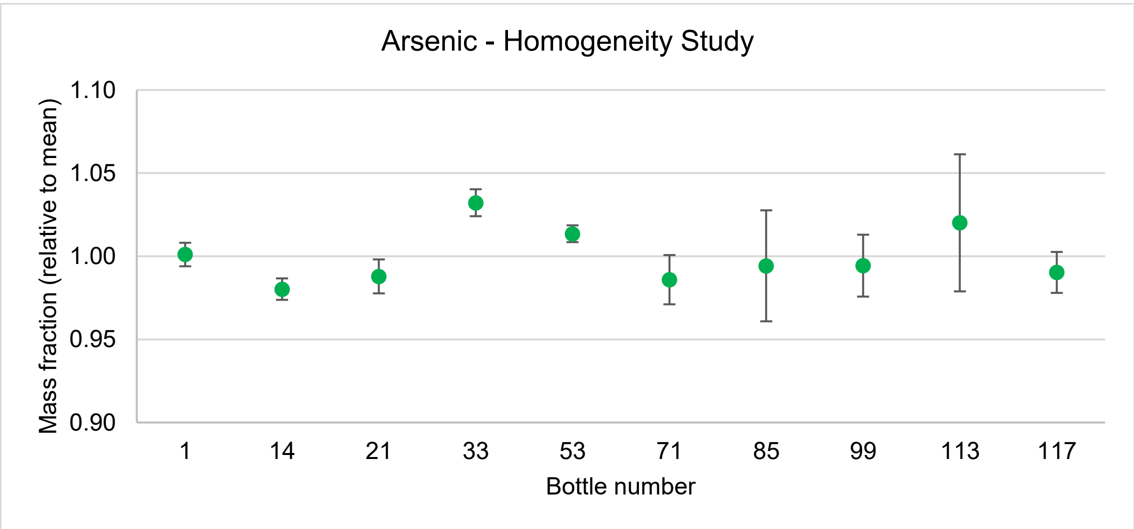

Figure 1. Homogeneity - Arsenic results per bottle.
Error bars represent standard uncertainties between subsamples.

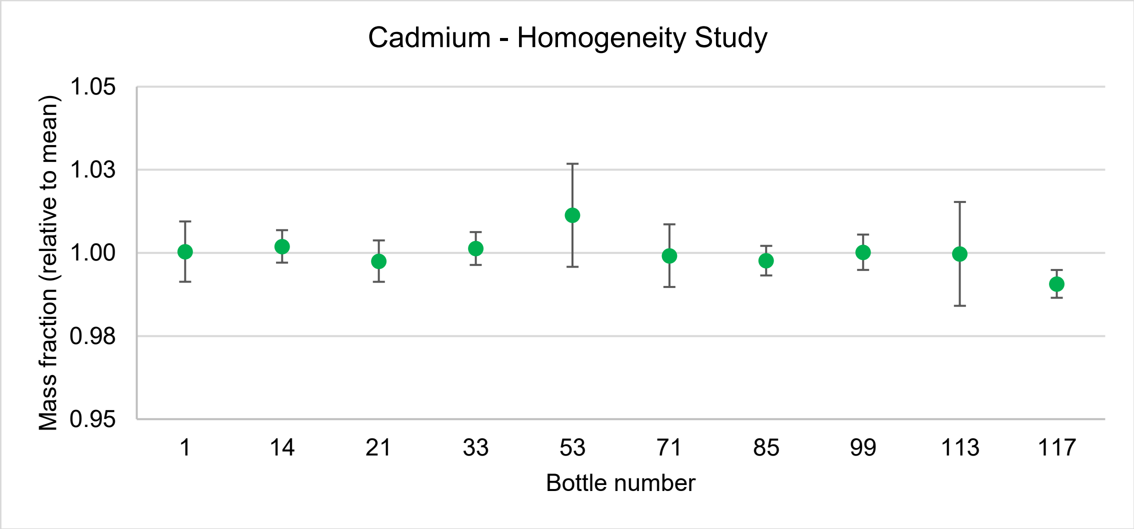

Figure 2. Homogeneity - Cadmium results per bottle.
Error bars represent standard uncertainties between subsamples.

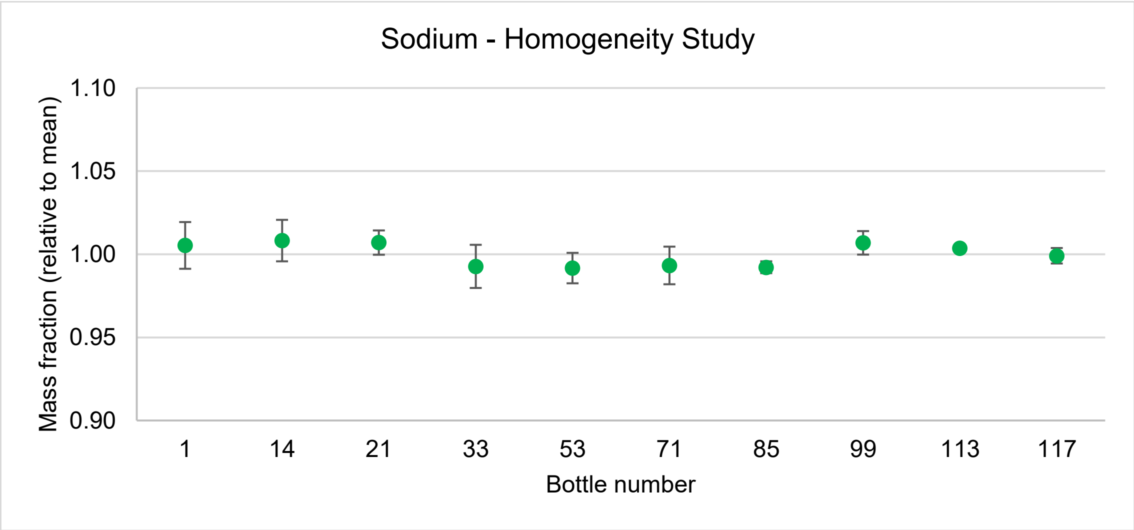

Figure 3. Homogeneity - Sodium results per bottle.
Error bars represent standard uncertainties between subsamples.

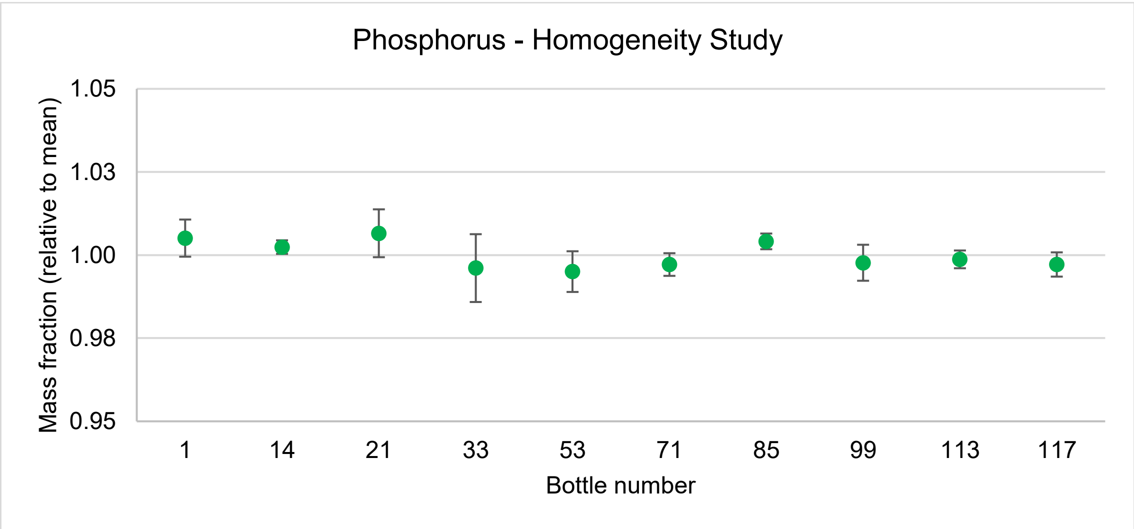

Figure 4. Homogeneity - Phosphorus results per bottle.
Error bars represent standard uncertainties between subsamples.

Stability Assessment of Study Material

Short-term stability

To evaluate a possible sample's instability during transportation due to temperature effect, an isochronous study designed for a period of three weeks at 40 °C was carried out. Each week, two randomly selected bottles were removed from the oven and placed under storage conditions (20 ± 5 °C). Determination of Cd was performed by ID-ICP-SFMS, As by SA-ICP-SFMS and Na and P by SA-ICP-OES on three subsamples per bottle.

The following acceptance criteria was applied:

$|b| < t_{0,95;\, n-2} * s'_b$, where:

• b, slope

• s'_b, slope uncertainty

• n, number of time intervals

It can be concluded that analytes in the sample did not show significant instability after being exposed at 40 °C for 3 weeks. The results are summarized in Table 5 and graphically represented in Figure 5.

Table 5. Results of short-term stability assessment (at 40 ºC for 3 weeks)

Measurand	**Student`s t-test**		**p-value**
	Calculated test statistics	Critical value	
Arsenic	0.676	2.571	0.529
Cadmium	1.196	2.571	0.285
Sodium	0.176	2.571	0.867
Phosphorous	1.038	2.571	0.347

Figure 5. Short-term stabilities of the measurands at 40 ºC for 3 weeks.

Long-term stability

Long term stability was assessed, using the classical approach, for a period that encompassed the sample dispatch and the completion of the supplementary comparison. Three bottles were randomly selected, and three subsamples were taken from each bottle. The results were assessed as for short-term stability.

The results are summarized in Table 6 and graphically represented in Figure 6. The Student's test confirmed that the slope of the lineal regression line was statistically insignificant at 95 % level of confidence.

Table 6. Results of long-term stability assessment

Measurand	Student`s t-test		p-value
	Calculated test statistics	Critical value	
Arsenic	1.415	2.776	0.529
Cadmium	0.138	2.365	0.894
Sodium	1.547	2.776	0.197
Phosphorous	1.925	2.365	0.096

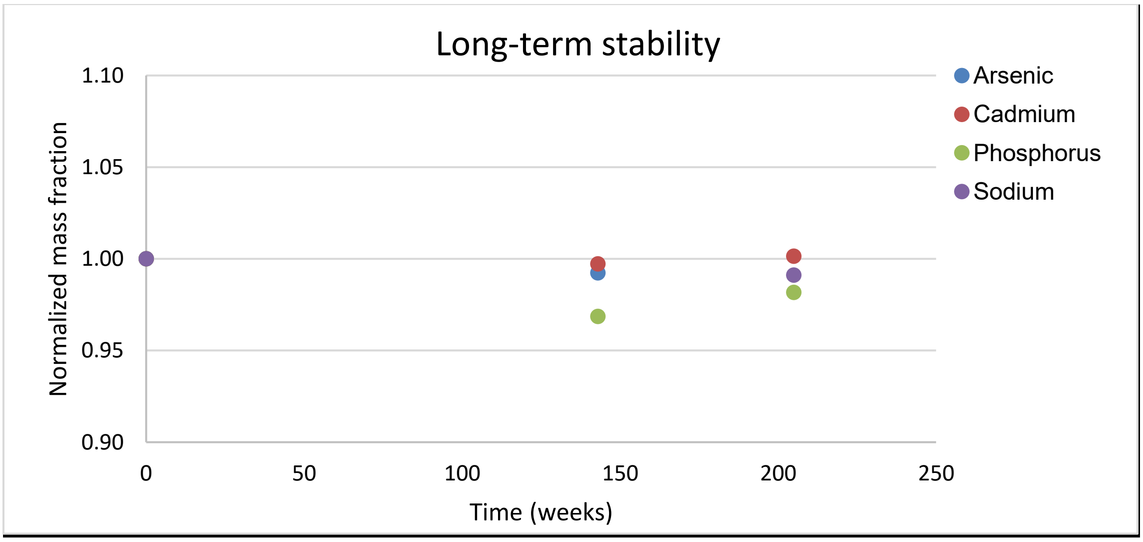

Figure 6. Long-term stability

PARTICIPANTS AND INSTRUCTIONS

The call for participation was distributed in April 2021 and samples were dispatched in June 2021 via DHL express. See Table 1 for a detailed study timeline. Appendix A and B reproduces the Study Protocol and Registration form respectively.

Table 7 lists the institutions that registered for SIM.QM-S11 in alphabetical order.

Table 7. Institutes registered for SIM.QM-S11

NMI or DI	Code	Country	Contact
Instituto Nacional de Tecnología Industrial	INTI	Argentina	Mabel Puelles, Osvaldo Acosta, Hernan Lozano
Instituto Boliviano de Metrología	IBMETRO	Bolivia	Evelyn Mendoza, Paola Avendaño
Instituto Nacional de Metrología, Qualidade e Tecnologia	INMETRO	Brazil	Rodrigo Caciano de Sena, Marcelo Dominguez de Almeida
Instituto de Salud Pública de Chile	ISP	Chile	Soraya Sandoval Riquelme, Javier Vera
Instituto Nacional de Metrología de Colombia	INM	Colombia	Diego A. Garzón Z., Carlos A. España S.
Laboratorio Costarricense de Metrología	LACOMET	Costa Rica	Bryan Calderón Jiménez, Jimmy Venegas Padilla, Katia Rosales Ovares
National Laboratory of Chemical Metrology / General Chemical State Laboratory – Hellenic Institute of Metrology	EXHM	Greece	Elias Kakoulides
Centro Nacional de Metrología	CENAM	Mexico	Maria del Rocio Arvizu Torres
Instituto Nacional de Calidad	INACAL	Peru	Elmer Carrasco Solis, Christian Uribe
Ural Research Institute for Metrology - Affiliated branch of the D.I. Mendeleyev Institute for Metrology	VNIIM-UNIIM	Russia	Egor Sobina, Alena Sobina
Health Sciences Authority	HSA	Singapore	Richard Shin
Jožef Stefan Institute	JSI	Slovenia	Radojko Jaćimović
National Metrology Institute of South Africa	NMISA	South Africa	Maré Linsky
National Institute of Metrology Thailand	NIMT	Thailand	Pranee Phukphatthanachai
Laboratorio Tecnológico del Uruguay	LATU	Uruguay	Ramiro Pérez Zambra, Romina Napoli

Most Institutes received the samples in the period from the end of June to the beginning of July 2021. Due to customs issues, a second sample was sent to INMETRO in September 2021, and INTI received the sample at its laboratory in November 2021. The initial deadline for reporting was October 30, 2021. However, due to shipment delays and the COVID-19 pandemic situation in some institutes, the deadline was rescheduled to February 2022.

To monitor the temperature during transportation and determine whether it exceeded the specified limit of 40 °C, a temperature strip monitor was attached to the samples. No NMI reported that the monitored samples reached temperatures above 40 °C.

In total, 14 of the 15 registered Institutes reported results, because one institute reported issues with the measurement instrument. Besides, LACOMET could only report results for phosphorus due to problems with the sample preparation equipment. INMETRO registered for participation for As, Cd, Na and P but only reported results for Cd.

Participants were instructed to send their results to the coordinator laboratory using the supplied reporting template reproduced in Appendix C. Final results and uncertainty budget were expected to be reported on a dry mass basis from at least five independent replicate measurements in mg/kg for As, Cd and Na, and in mg/g for P.

The participating NMIs/DIs were also asked to include a detailed description of the sample preparation methods, analytical techniques, calibration approach, reference material used for calibration and any correction applied.

RESULTS

Participants were requested to report a single estimate of the mass fraction in mg/kg for As, Cd and Na, and in mg/g for P. In addition to the quantitative results, participants were instructed to describe their analytical methods and approach to uncertainty estimation.

Results were discussed with SIM members, Draft A1 was distributed to all participants in October and presented at the CCQM IAWG meeting held in November 2024.

After discussions with experts, VNIIM-UNIIM's phosphorus results were included in the SCRV calculation, as they used a primary method to assess the purity of the standard employed for their in-house reference material.

Draft A2 was distributed to all participants in March 2025 and presented at the CCQM IAWG meeting held in April 2025.

Methods Used by Participants

Participants were free to use a method of their choice for both sample preparation and measurement method. Table 8 summarizes the sample preparation method, calibration method, analytical instrument as well as the reference material used by the participating NMIs/DIs for SIM.QM-S11.

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

Participant	Measurands	Sample preparation method	Calibration method	Analytical instrument	Reference material used for calibration (traceability)
INTI	As, Cd, Na, P	Microwave assisted digestion: As, P: 0.5 g sample + 4 ml HNO_3 Na, Cd: 0.5 g sample + 4 ml HNO_3+ 0.5 HF	As: Standard addition with Ge as Internal standard Cd: Standard addition with In as Internal standard Na and P: External calibration (calibration curve calculated intercept)	As and Cd: ICP-QMS Na and P: ICP-OES	As: NIST SRM 3103a Cd: NIST SRM 3108 Na: NIST SRM 3152a P: NIST SRM 3139a

EXHM	As, Cd, Na, P	Microwave assisted digestion: 0.5 g sample + 4 ml HNO_3	Standard addition	ICP-SFMS	As: NIST SRM 3103a Cd: NIST SRM 3108 Na: NIST SRM 3152a P: NIST SRM 3139a
JSI	As, Cd, Na	As and Cd: Microwave assisted digestion: 0.15 g sample + 2 ml HNO_3 + 0.02 ml HF Na: 0.46-0.47 g was sealed into a pure polyethylene ampoule.	As and Cd: External calibration with Sc, Y, Rh and Gd as internal standards Na: k0-INAA	As: ICP-QQQMS (O_2) Cd: ICP-QQQMS (He) Na: TRIGA Mark II nuclear reactor (250 kW), HPGe detector	As: NIST SRM 3103a Cd: NIST SRM 3108 Na: ERM-EB530
CENAM	Na	Microwave assisted digestion: 0.5 g sample + 12 ml HNO_3 + 0.5 ml HF	Standard addition with Sr as Internal standard	ICP-OES	Na: NIST SRM 3152a
HSA	As, Cd	Microwave assisted digestion: 0.5-1 g sample + 5 ml HNO_3 + 0.2 ml HF + 2 ml H_2O_2	As: Standard addition with Ga as Internal standard Cd: Exact-matching Isotope Dilution ($^{114}Cd/^{111}Cd$)	As: ICP-SFMS (HR) Cd: ICP-QMS (He)	As: NIST SRM 3103a Cd: NIST SRM 3108
INMC	Cd, Na	Microwave assisted digestion: 0.5 g sample + 4 ml HNO_3 + 2 ml H_2O_2	Cd: Standard addition with In as Internal standard Na: External calibration (Bracketing)	Cd: ICP-QMS Na: F-AAS	Cd: NIST SRM 3108 Na: NIST SRM 919b

INMETRO	Cd	Microwave assisted digestion: 0.5 g sample + 4 ml HNO_3 + 2 ml H_2O_2 + 0.2 ml HF	Standard addition	ICP-QMS	Cd: NIST SRM 3108
ISP	As, Cd	Microwave assisted digestion: 0.5 g sample + 5 ml HNO_3 + 2 ml H_2O_2	As: Standard addition with Ge as Internal standard Cd: Standard addition with Sc as Internal standard	As and Cd: ICP-QMS (He)	As: NIST SRM 3103a Cd: NIST SRM 3108
LATU	As, Cd, Na, P	Microwave assisted digestion: 0.5 g sample + 5 ml HNO_3 + 0.5 ml HF + 2 ml H_2O_2 + 2 ml H_2O	As: Standard addition with Ge as Internal standard Cd: Exact-matching Isotope Dilution ($^{114}Cd/^{111}Cd$) Na and P: Standard addition	As: ICP-SFMS (HR) Cd: ICP-SFMS (LR) Na and P: ICP-OES	As: NIST SRM 3103a Cd: NIST SRM 3108 Na: NIST SRM 3152a P: NIST SRM 3139a
LCM	P	Dry ashing: 2.0 g digested using dry ashing and extracted with 10 ml HCl	External Calibration	UV-visible Spectrophotometry	P: NIST SRM 3139a
INACAL	As, Cd	Microwave assisted digestion: As: 0.5 g sample + 7 ml HNO_3 + 1 ml H_2O_2 Cd: 0.5 g sample + 9 ml HNO_3 + 2 ml H_2O_2	As: Standard addition with In as Internal standard Cd: Standard addition	As: ICP-QMS Cd: GFAAS	As: NIST SRM 3103a Cd: NIST SRM 3108
VNIIM-UNIIM	As, Cd, Na, P	Microwave assisted digestion: 0.5 g sample + 5 ml HNO_3 + 0.1 ml HF + 0.5 ml H_2O_2	Standard addition	ICP-QMS (standard and KED mode)	UNIIM in-house reference material, prepared using high pure substance.

NMISA	As, Cd, Na, P	Microwave assisted digestion: 0.5 g sample + 8 ml HNO_3 + 0.5 ml HF	As and Na: External calibration and Standard addition Cd: Double Isotope Dilution P: Standard addition	As: ICP-QQQMS (O_2) Cd: ICP-SFMS (HR) Na: ICP-QQQMS (He) and ICP-SFMS (HR) P: ICP-SFMS (HR)	As: NIST SRM 3103a Cd: NIST SRM 3108 Na: NIST SRM 3152a P: NIST SRM 3139a
NIMT	As, Cd, Na, P	Microwave assisted digestion: 0.5 g sample + 7.5 ml HNO_3 + 0.1 ml HF + 0.5 ml H_2O_2	As: Standard addition with Rh as Internal standard Cd: Isotope Dilution ($^{112}Cd/^{111}Cd$) Na and P: Standard addition with internal standard	As: ICP-QQQMS (O_2) Cd: ICP-QQQMS Na and P: ICP-OES	As: NIST SRM 3103a Cd: NIST SRM 3108 Na: Inorganic Ventures CGNA1 P: Inorganic Ventures CGP1

JSI was questioned about their decision to use 0.15 g as the sample mass. Their response was "… we used our standard procedure for this type of sample, where we have limitations on the digestion instruments used.…"

All NMIs/DIs participating in SIM.QM-S11, excluding NIMT for Na and P, have ensured the metrological traceability of their outcomes in accordance with CIPM traceability requirements. Most of the participating NMIs/DIs used the following certified reference materials from NIST: SRM 3103a Arsenic, SRM 3108 Cadmium, SRM 3152a Sodium and SRM 3139a Phosphorus.

NIMT utilized commercial standards of sodium and phosphorus. Consequently, in accordance with CIPM traceability requirements, since these calibrants were not provided by a National Metrology Institute, the results will not be used for SCRV calculation.

Dry mass correction factor

Participants were instructed to determinate moisture content on a minimum of three separate portions of 1 g. Table 9 summarizes the dry mass correction factor calculated by each institute.

Table 9. Dry mass correction factor calculated by each institute.

Participant	Number of samples	Moisture content (%) (SD)	Dry mass correction factor
INTI	5	4.54 (0.20)	0.9546
EXHM	5	4.51 (0.024)	0.9549
JSI	4	6.1112 (0.0129)	0.9389
CENAM	8	6.37 (0.86)	0.9363
HSA	6	5.5927 (0.0441) 6.6039 (0.020)	0.9440 0.9340
INMC	3	6.788 (0.031)	0.9321
INMETRO	4	6.91 (0.025)	0.9309
ISP	5	5.735 (0.064)	0.9426
LATU	5	6.78 (0.13)	0.9322
LACOMET	5	7.0838 (0.05)	0.9292
INACAL	3	6.96 (0.096)	0.9304
VNIIM-UNIIM	10	6.10 (0.15)	0.9390
NMISA	5	7.354 (0.026)	0.9265
NIMT	3	6.38 (0.05)	0.9362

HSA was questioned about the two different moisture content results and the participant answer: “The results were corrected for moisture based on the respective bottle used for analysis”.

Participant's results for arsenic, cadmium, sodium and phosphorus

The results for SIM.QM-S11 for the determination of arsenic, cadmium, sodium and phosphorus are detailed in Tables 10 to 13 and presented graphically in Figures 7 to 10.

Participant's results for arsenic

Ten laboratories reported values for mass fraction of arsenic. The results for SIM.QM-S11 for the determination of arsenic are detailed in Table 10 and presented graphically in Figure 7.

Table 10. Reported results for arsenic.

Participant	Reported mass fraction (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)
HSA	0.0528	0.0015	2.57	0.0039
NIMT	0.053	0.001	2	0.002
LATU	0.0565	0.0014	2	0.0029
ISP	0.0575	0.0016	2	0.0033
NMISA	0.0576	0.0029	2	0.0058
JSI	0.0583	0.0022	2	0.0044
INTI	0.0608	0.0031	2	0.0062
EXHM	0.0630	0.0034	2	0.0068
INACAL	0.070	0.002	2	0.004
VNIIM-UNIIM	0.078	0.003	2	0.006

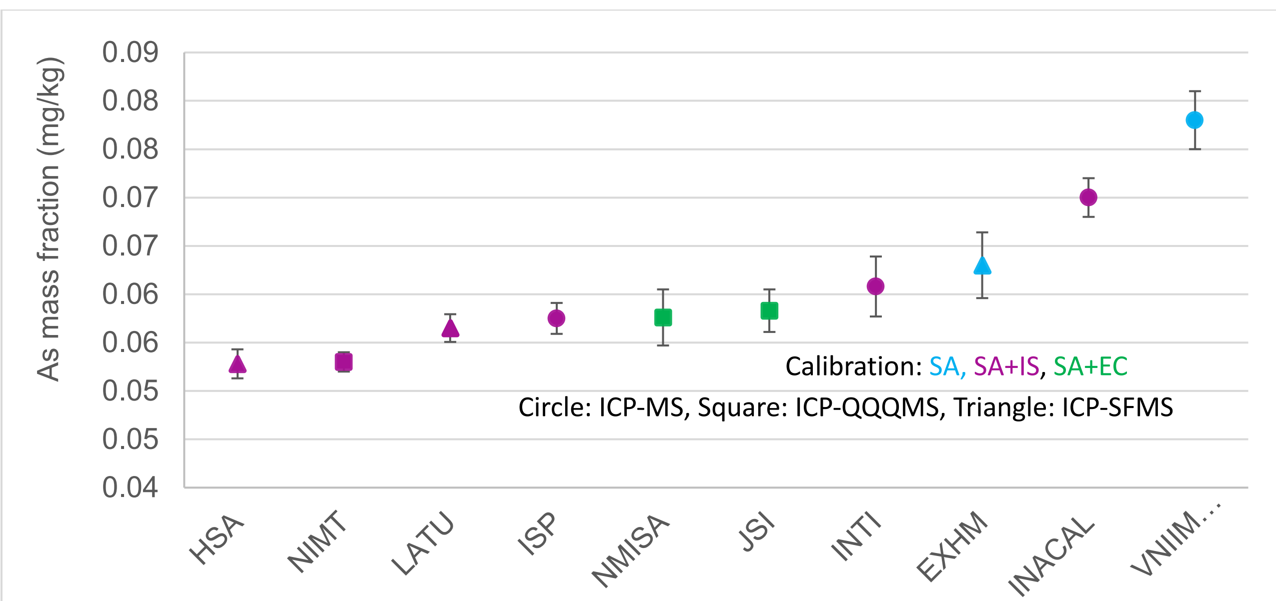

Figure 7. Reported results for arsenic (mg/kg). Error bars represent reported standard uncertainties.

Participant's results for cadmium

Twelve laboratories reported values for mass fraction of cadmium. The results for SIM.QM-S11 for the determination of cadmium are detailed in Table 11 and presented graphically in Figure 8.

Table 11. Reported results for cadmium.

Participant	Reported mass fraction (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)
INMC	0.720	0.0200	1.97	0.039
JSI	0.728	0.023	2	0.046
ISP	0.732	0.011	2	0.023
NIMT	0.750	0.007	2	0.015
HSA	0.7504	0.0074	2.57	0.0190
VNIIM-UNIIM	0.76	0.02	2	0.040
LATU	0.760	0.013	2	0.025
INMETRO	0.766	0.0205	2	0.041
NMISA	0.766	0.023	2	0.046
INACAL	0.795	0.022	2	0.044
INTI	0.800	0.0421	2	0.0842
EXHM	0.810	0.035	2	0.071

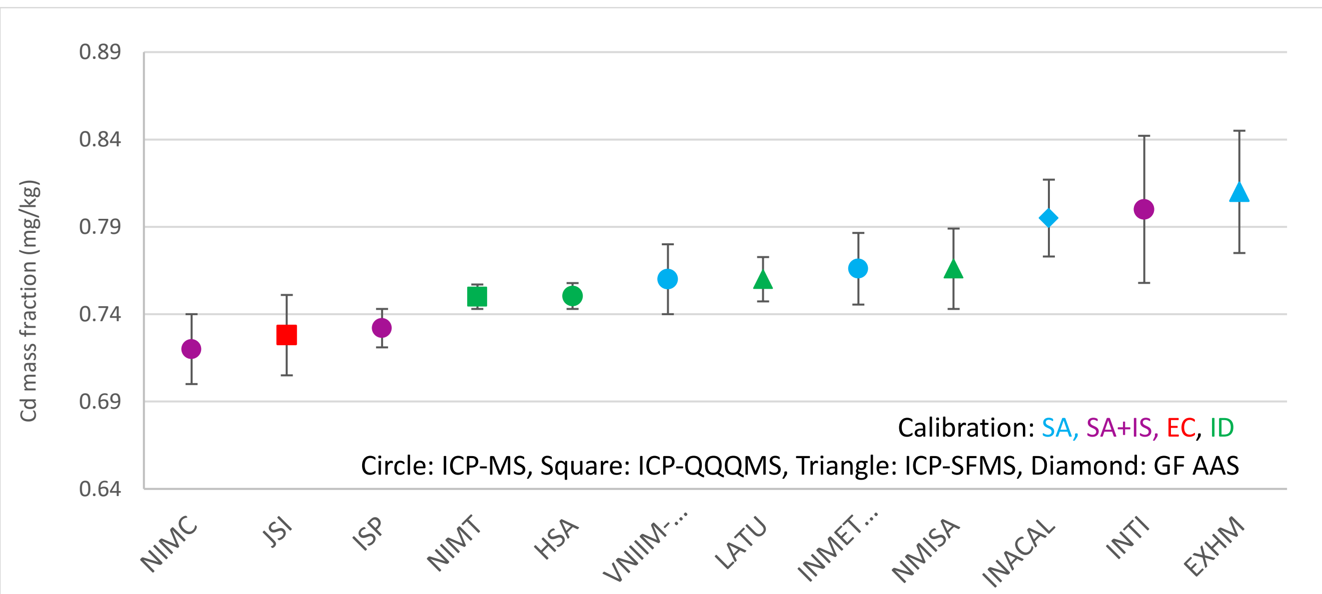

Figure 8. Reported results for cadmium (mg/kg). Error bars represent reported standard uncertainties.

Participant's results for sodium

Nine laboratories reported values for mass fraction of sodium. The results for SIM.QM-S11 for the determination of sodium are detailed in Table 12 and presented graphically in Figure 9.

Table 12. Reported results for sodium.

Participant	Reported mass fraction (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)
INMC	27.1	0.513	1.97	1.0
INTI	32.14	1.85	2	3.69
VNIIM-UNIIM	33.1	1.05	2	2.1
NMISA	33.1	1.9	2	3.8
CENAM	33.8	0.27	2.1	0.57
LATU	34.05	0.55	2	1.10
JSI	34.1	1.2	2	2.4
NIMT	36.7	0.6	2	1.3
EXHM	37.65	2.14	2	4.28

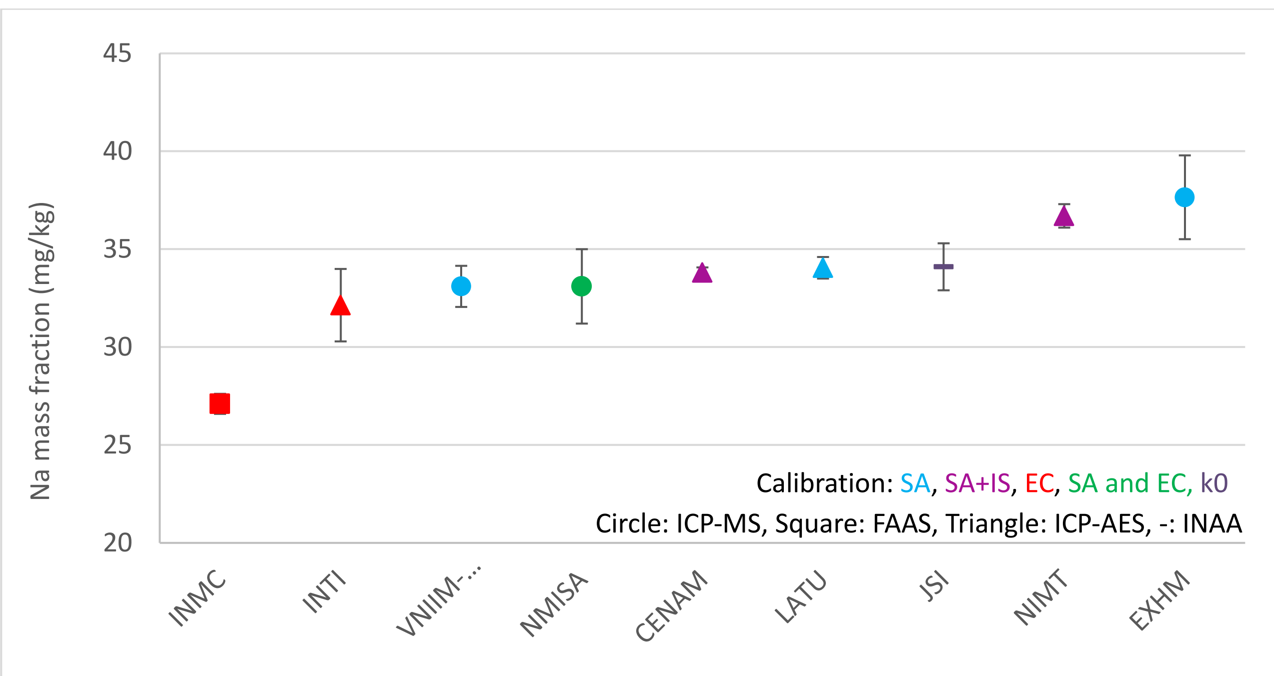

Figure 9. Reported results for sodium (mg/kg). Error bars represent reported standard uncertainties.

Participant's results for phosphorus

Seven laboratories reported values for mass fraction of phosphorus. The results for SIM.QM-S11 for the determination of phosphorus are detailed in Table 13 and presented graphically in Figure 10.

Table 13. Reported results for phosphorus.

Participant	Reported mass fraction (mg/g)	Reported standard uncertainty (mg/g)	Coverage factor, *k*	Expanded uncertainty (mg/g)
NIMT	1.65	0.02	2	0.05
LACOMET	1.667	0.016	2	0.031
NMISA	1.70	0.054	2	0.11
LATU	1.735	0.028	2	0.057
VNIIM-UNIIM	1.736	0.060	2	0.120
EXHM	1.802	0.080	2	0.159
INTI	1.824	0.036	2	0.073

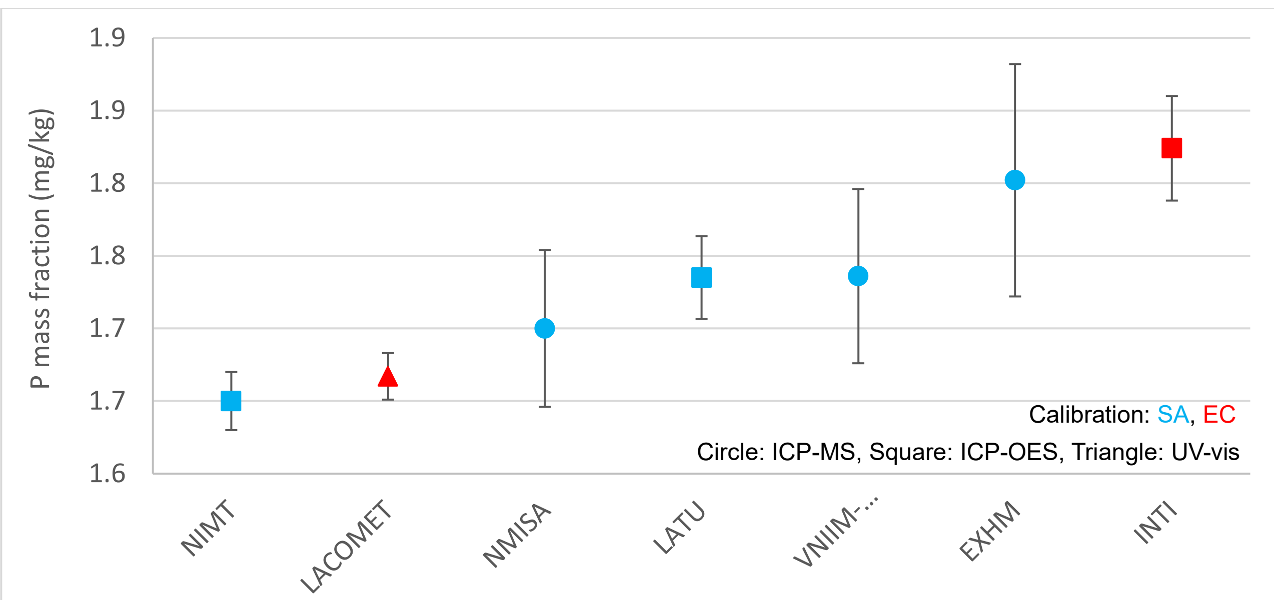

Figure 10. Reported results for phosphorus (mg/g). Error bars represent reported standard uncertainties.

Discussion of results

Nearly all institutes employed microwave-assisted digestion methods for sample preparation. ICP-MS techniques were used for arsenic and cadmium quantification, except for INACAL, which used GF-AAS for cadmium. The most used analytical techniques for the determination of sodium and phosphorus were ICP-OES and ICP-MS. Other techniques used included FAAS, UV-Vis spectrometry, and K0-INAA. Standard addition was used by most institutes for cadmium, arsenic, and phosphorus. Some institutes used isotope dilution for cadmium quantification. For sodium, standard addition and external calibration were the most used calibration techniques.

DETERMINATION OF SUPPLEMENTARY COMPARISON REFERENCE VALUES (SCRV)

DEGREES OF EQUIVALENCE (DoE)

The NIST decision tree (version 1.0.4) was utilized to estimate the SCRV, as well as to determine the degrees of equivalence for each NMI/DI. The selected models for each element were those suggested by the NIST decision tree. The results of the hypothesis tests for homogeneity, symmetry, and normality conducted by the NIST decision tree, as well as the recommended statistical model and the degrees of equivalence for each element, are presented in Appendix D.

The participant's results relative to the SCRV estimation using the NIST decision tree and the degrees of equivalence estimates are presented in Figures 11 to 18.

The NIST decision tree hypothesis test results as well the SCRV and associated uncertainties for each element are presented in Tables 14, 16, 18 and 20.

Degrees of equivalence for each element, along with the reported value (xi) and its standard uncertainty (ui) (adjusted to include the dark uncertainty, if required) are presented in Tables 15, 17, 19 and 21. Adjustment for dark uncertainty was made when the participant's result disagreed with the SCRV without including tau.

Arsenic

Table 14 shows the decision tree hypothesis test results for arsenic in SIM.QM-S11. The NIST decision tree recommends using the Hierarchical Skew Student-Gauss approach.

Table 14. Decision tree hypothesis test results for arsenic.

Decision tree hypothesis	**Results**	**Answers**
Cochran´s test for Homogeneity	$p< 0.001$ Q= 120.1 (Reference distribution: Chi-Square with 9 Degrees of Freedom) Tau est.= 0.006442 Tau/median (x)= 0.1112 Tau/median (u)= 3.068	Assume Homogeneity? No
Miao-Gel-Gastwirth test for Symmetry	p= 0.0288	Assume Symmetry? No
Shapiro-Wilk test for Normality	p= 0.42325	Assume Normality? -

Recommended Approach	**Hierarchical Skew Student-Gauss**
SCRV, mg/kg	0.057506
Standard Uncertainty (u), mg/kg	0.0025487
Dark Uncertainty (σ), mg/kg	0.0034787

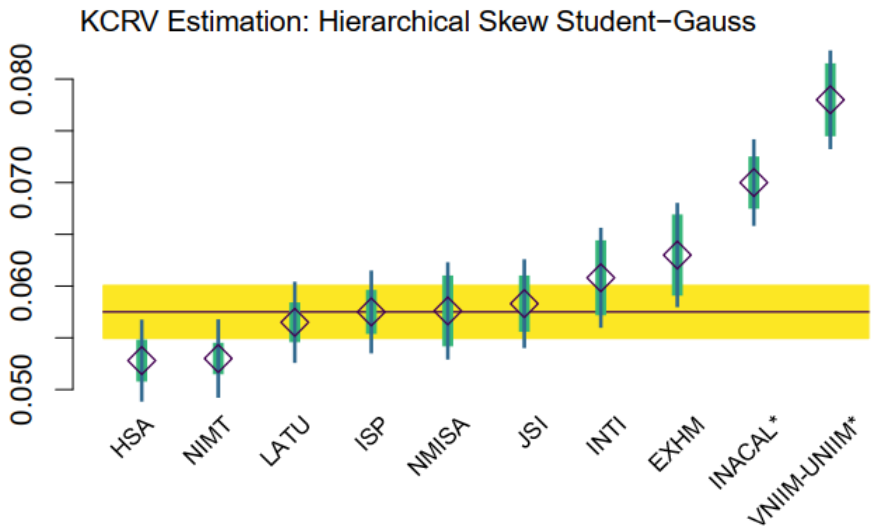

Figure 11. SCRV estimation for arsenic using Hierarchical Skew Student-Gauss model. The black horizontal line represents the SCRV and the yellow shading around the SCRV represents the u(SCRV). For each participant's data point, the heavy vertical bar is their reported uncertainty, and the skinny extension is the contribution of dark uncertainty.

Table 15. Degrees of equivalence for arsenic. In the u_i column, all values are those reported by the participants, unless accompanied by an asterisk (*). Those values accompanied by an asterisk (*) are the reported values and tau summed in quadrature.

Participant	x_i (mg/kg)	u_i (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d/U(d_i)$
HSA	0.0528	0.0015	-0.00471	0.00716	-0.65700
NIMT	0.053	0.001	-0.00451	0.00626	-0.71998
LATU	0.0565	0.0014	-0.00101	0.00663	-0.15173
ISP	0.0575	0.0016	-0.00001	0.00685	-0.00088
NMISA	0.0576	0.0029	0.00009	0.00856	0.01098
JSI	0.0583	0.0022	0.00079	0.00757	0.10485
INTI	0.0608	0.0031	0.00329	0.00888	0.37095
EXHM	0.0630	0.0034	0.00549	0.00926	0.59350
INACAL*	0.070	0.0040*	0.01249	0.01199	1.04238
VNIIM-UNIIM*	0.078	0.0046*	0.02049	0.01282	1.59922

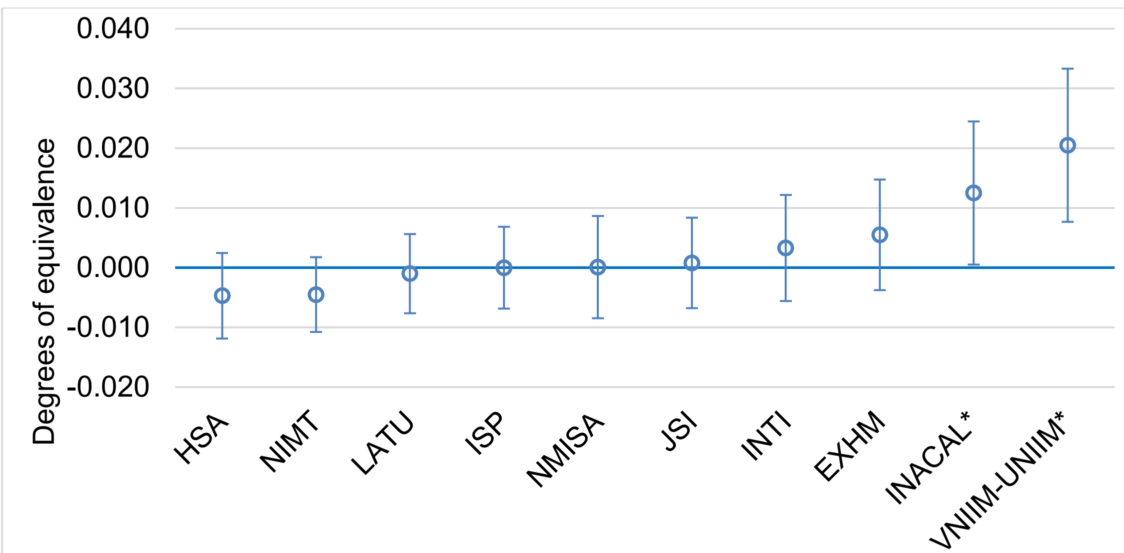

Figure 12. Degrees of equivalence for arsenic (using Hierarchical Skew Student-Gauss model)

Based on the IAWG guidance for making and evaluating CMC claims, the arsenic results from INACAL and VNIIM-UNIIM do not comply with the SCRV value when applying the DoE Recognizing Dark Uncertainty. Therefore, these results should not be used to support CMC claims.

Cadmium

Table 16 shows the decision tree hypothesis test results for cadmium in SIM.QM-S11. The NIST decision tree recommends using the Adaptative Weighted Average approach.

Table 16. Decision tree hypothesis test results for cadmium.

Decision tree hypothesis	Results	Answers
Cochran´s test for Homogeneity	p= 0.13 Q= 16.25 (Reference distribution: Chi-Square with 11 Degrees of Freedom) Tau est.= 0.009829 Tau/median (x)= 0.01293 Tau/median (u)= 0.4854	Assume Homogeneity? Yes
Miao-Gel-Gastwirth test for Symmetry	p= 0.7278	Assume Symmetry? -
Shapiro-Wilk test for Normality	p= 0.5068	Assume Normality? Yes
Recommended Approach	**Adaptative Weighted Average**	
SCRV, mg/kg	0.7526	
Standard Uncertainty (u), mg/kg	0.0054227	
Dark Uncertainty (σ), mg/kg	0.0098293	

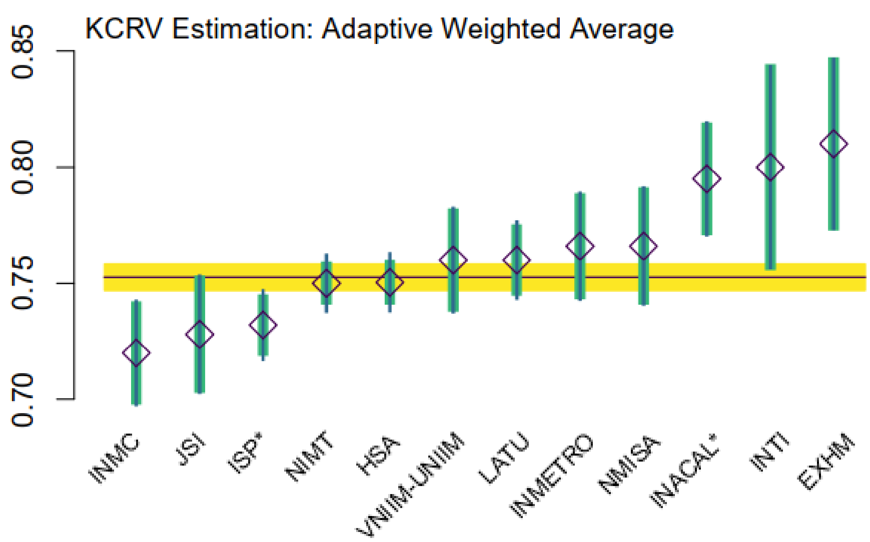

Figure 13. SCRV estimation for cadmium using Adaptive Weighted Average model. The black horizontal line represents the SCRV and the yellow shading around the SCRV represents the u(SCRV). For each participant's data point, the heavy vertical bar is their reported uncertainty, and the skinny extension is the contribution of dark uncertainty.

Table 17. Degrees of equivalence for cadmium. In the u_i column, all values are those reported by the participants, unless accompanied by an asterisk (*). Those values accompanied by an asterisk (*) are the reported values and tau summed in quadrature.

Participant	x_i (mg/kg)	u_i (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d/U(d_i)$
INMC	0.720	0.0200	-0.03260	0.03781	-0.86216
JSI	0.728	0.023	-0.02460	0.04415	-0.55717
ISP*	0.732	0.015*	-0.02060	0.02825	-0.72928
NIMT	0.750	0.007	-0.00260	0.01284	-0.20252
HSA	0.7504	0.0074	-0.00220	0.01423	-0.15462
VNIIM-UNIIM	0.76	0.02	0.00740	0.03787	0.19540
LATU	0.760	0.013	0.00740	0.02429	0.30464
INMETRO	0.766	0.0205	0.01340	0.03939	0.34020
NMISA	0.766	0.023	0.01340	0.04361	0.30725
INACAL*	0.795	0.024*	0.04240	0.04709	0.90040
INTI	0.800	0.0421	0.04740	0.08142	0.58219
EXHM	0.810	0.035	0.05740	0.06876	0.83480

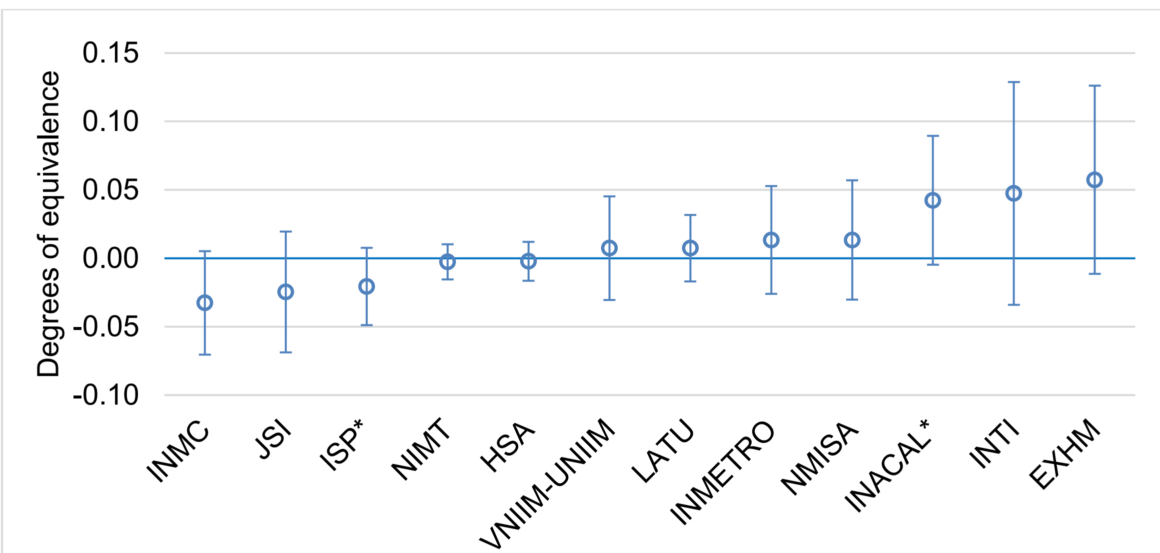

Figure 14. Degrees of equivalence for cadmium

Sodium

Table 18 shows the decision tree hypothesis test results for sodium in SIM.QM-S11. The NIST decision tree recommends using the Hierarchical Laplace-Gauss approach.

Table 18. Decision tree hypothesis test results for sodium.

Decision tree hypothesis	Results	Answers
Cochran´s test for Homogeneity	p< 0.001 Q= 148.8 (Reference distribution: Chi-Square with 7 Degrees of Freedom) Tau est.= 3.188 Tau/median (x)= 0.09531 Tau/median (u)= 2.834	Assume Homogeneity? No
Miao-Gel-Gastwirth test for Symmetry	p= 0.6412	Assume Symmetry? Yes
Shapiro-Wilk test for Normality	p= 0.0002022	Assume Normality? No
Recommended Approach	**Hierarchical Laplace-Gauss**	
SCRV, mg/kg	33.46	
Standard Uncertainty (u), mg/kg	0.6635	
Dark Uncertainty (σ), mg/kg	2.179	

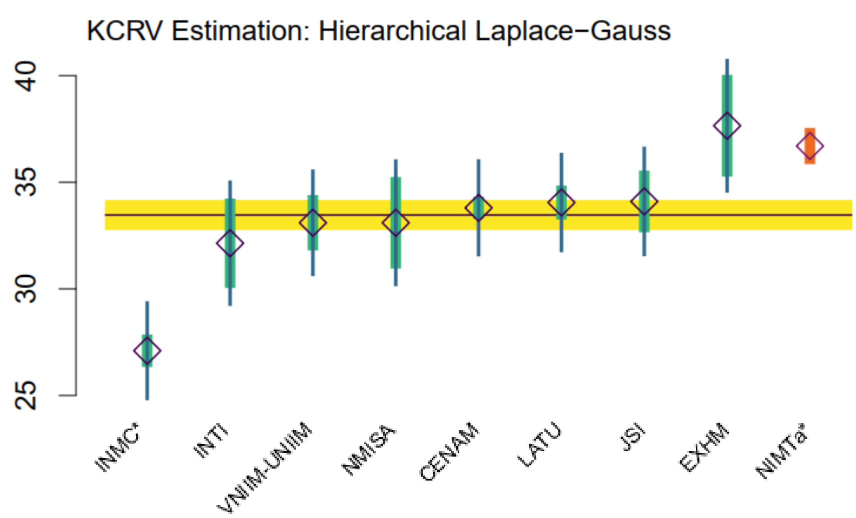

Figure 15. SCRV estimation for sodium using Hierarchical Laplace-Gauss model. The black horizontal line represents the SCRV and the yellow shading around the SCRV represents the u(SCRV). For each participant's data point, the heavy vertical bar is their reported uncertainty, and the skinny extension is the contribution of dark uncertainty. Results in red are the ones not used for SCRV calculations.

Table 19. Degrees of equivalence for sodium. In the u_i column, all values are those reported by the participants, unless accompanied by an asterisk (*). Those values accompanied by an asterisk (*) are the reported values and tau summed in quadrature.

Participant	x_i (mg/kg)	u_i (mg/kg)	d_i (mg/kg)	$U(d_i)$ (mg/kg)	$d/U(d_i)$
INMC*	27.1	2.24*	-6.4	5.550	-1.146
INTI	32.14	1.85	-1.32	3.903	-0.338
VNIIM-UNIIM	33.1	1.05	-0.4	2.473	-0.146
NMISA	33.1	1.90	-0.4	3.999	-0.090
CENAM	33.8	0.27	0.3	1.445	0.235
LATU	34.05	0.55	0.59	1.726	0.342
JSI	34.1	1.20	0.6	2.729	0.235
EXHM	37.65	2.14	4.19	4.505	0.930
NIMT[a]*	*36.7*	*2.26**	*3.2*	*5.543*	*0.585*

[a] not used in the SCRV calculations.

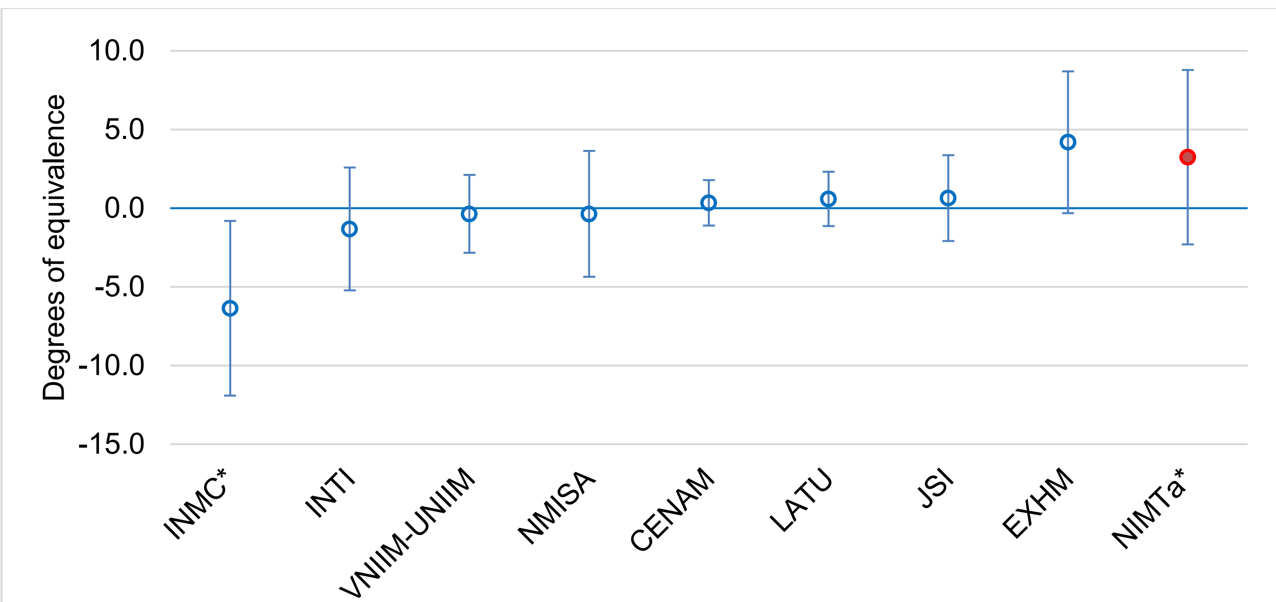

Figure 16. Degrees of equivalence for sodium

Based on the IAWG guidance for making and evaluating CMC claims, the sodium result from INMC do not comply with the SCRV value when applying the DoE Recognizing Dark Uncertainty. Therefore, this result should not be used to support CMC claims.

Phosphorus

Table 20 shows the decision tree hypothesis test results for phosphorus in SIM.QM-S11. The NIST decision tree recommends using the Hierarchical Gauss-Gauss approach.

Table 20. Decision tree hypothesis test results for phosphorus.

Decision tree hypothesis	**Results**	**Answers**
Cochran´s test for Homogeneity	p= 0.0016 Q= 19.46 (Reference distribution: Chi-Square with 5 Degrees of Freedom) Tau est.= 0.05938 Tau/median (x)= 0.03422 Tau/median (u)= 1.32	Assume Homogeneity? No
Miao-Gel-Gastwirth test for Symmetry	p= 0.3098	Assume Symmetry? Yes
Shapiro-Wilk test for Normality	p= 0.3889	Assume Normality? Yes

Recommended Approach	**Hierarchical Gauss-Gauss**
SCRV, mg/g	1.738
Standard Uncertainty (u), mg/g	0.02325
Dark Uncertainty (σ), mg/g	0.05381

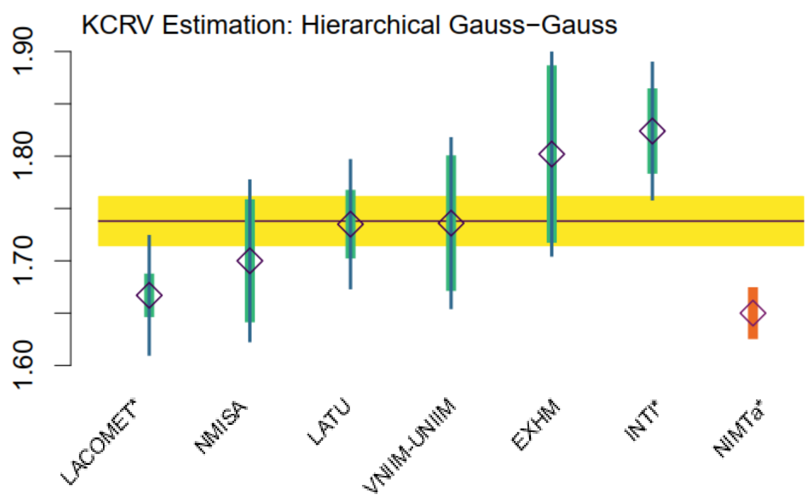

Figure 17. SCRV estimation for phosphorus using Hierarchical Gauss-Gauss model. The black horizontal line represents the SCRV and the yellow shading around the SCRV represents the u(SCRV). For each participant's data point, the heavy vertical bar is their reported uncertainty, and the skinny extension is the contribution of dark uncertainty. Results in red are the ones not used for SCRV calculations.

Table 21. Degrees of equivalence for phosphorus. In the u_i column, all values are those reported by the participants, unless accompanied by an asterisk (*). Those values accompanied by an asterisk (*) are the reported values and tau summed in quadrature.

Participant	x_i (mg/g)	u_i (mg/g)	di (mg/g)	U(di) (mg/g)	d/U(di)
LACOMET*	1.667	0.056*	-0.0710	0.1437	-0.4941
NMISA	1.70	0.054	-0.0380	0.1164	-0.3265
LATU	1.735	0.028	-0.0030	0.0724	-0.0415
VNIIM-UNIIM	1.736	0.060	-0.0020	0.1279	-0.0156
EXHM	1.802	0.080	0.0640	0.1635	0.3914
INTI*	1.824	0.065*	0.0860	0.1548	0.5556
NIMT[a]*	*1.65*	*0.057**	*-0.0880*	*0.1453*	*-0.6056*

[a] not used in the SCRV calculations.

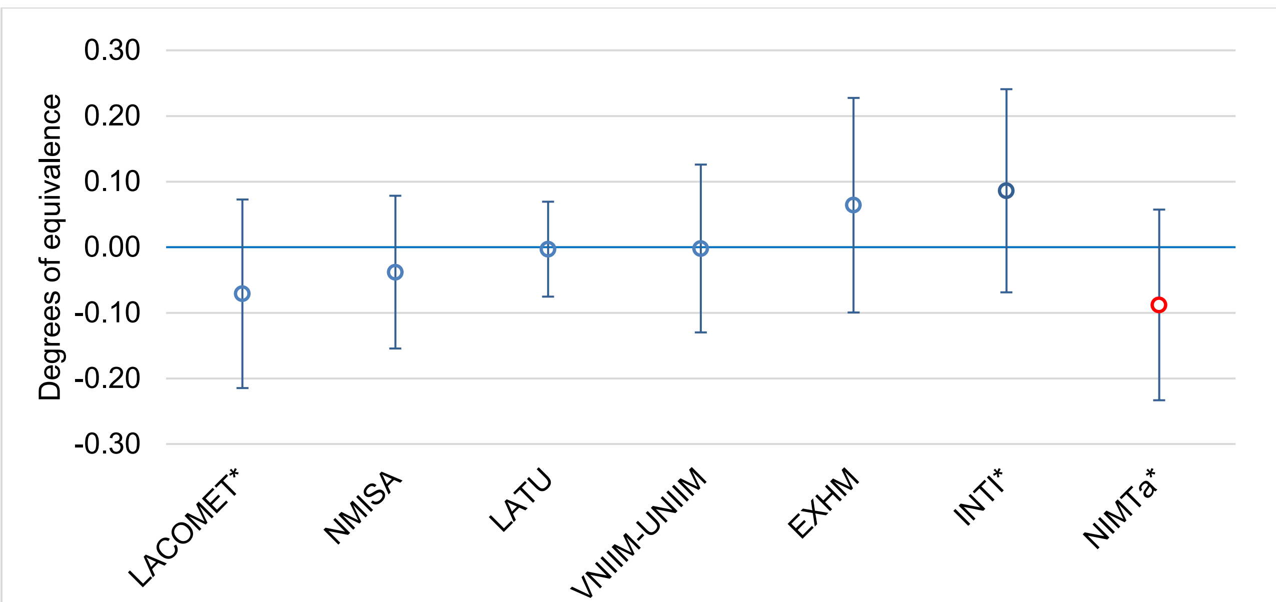

Figure 18. Degrees of equivalence for phosphorus

USE OF SIM.QM-S11 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

How far the light shines, Core Capability Statements and CMC support

Successful participation in **SIM.QM-S11** demonstrates the following measurement capabilities in plants and other high silica content related materials:

- Arsenic: Metalloids and semi-metals at mass fraction levels above 20 µg/kg.
- Cadmium: Transition elements at mass fraction levels above 50 µg/kg (except Hg).
- Phosphorus: Non-metals (except: H, C, O, N) at mass fraction levels above 50 µg/kg.
- Sodium: Alkali and alkaline earth elements at mass fraction levels above 50 µg/kg.

Table 18 shows the Core Capability table with the measurement space covered by the study.

Table 22. Core Capability table

Analyte groups	Matrix challenges						Calibration materials and solutions
	Water/aqueous	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)							
		Na					
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					
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)							
		P					
Halogens (F, Cl, Br, I)							
Rare Earth Elements (Lanthanides, Actinides)							
Inorganic species (elemental, anions, cations)							
Small organo-metallics							
Proteins							
Nanoparticles							

Low level (e.g. below 50 µg/kg)

High level (e.g. above 50 µg/kg)

CONCLUSION

For all measurands, most participating NMIs/DI`s results were in agreement with the SCRV without considering dark uncertainty.

For some participants who obtained values of d/U(di) greater than one, agreement with the Standard Reference Value (SCRV) was attained by expanding their uncertainty assessment to include dark uncertainty.

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Appendix A. Study protocol

LABORATORIO TECNOLÓGICO DEL URUGUAY

SIM.QM-S11

Supplementary Comparison of elements in Yerba mate (*Ilex paraguariensis*)

Study Protocol

December 2020

Ramiro Pérez Zambra, Romina Napoli, Elizabeth Ferreira

Montevideo-Uruguay

1. INTRODUCTION

Yerba mate (*Ilex paraguariensis*, Aquilfoliaceae) is a native plant which grows in the subtropical regions of South America: Paraguay, Brazil, Argentina and Uruguay. It is consumed as an infusion called "mate" in the before mentioned countries as well as all around the world as tea. Due to safety reasons the mass fraction of arsenic and cadmium is constantly monitored. Besides, the mass fraction of nutrients as sodium and phosphorus is also measured for labeling purposes.

The aim of this comparison is to enable NMIs/DIs to demonstrate their competence in the determination of elements at low and high levels in vegetal material within the high silica content category.

2. TIMELINE

Sample preparation:	October, 2019
Homogeneity Testing:	April, 2020
Stability Testing:	October, 2020
Distribution of protocol and questionnaire:	December, 2020
Call for participation:	March, 2021
Registration deadline:	April, 2021
Distribution of samples:	July, 2021
Deadline for submission of results:	November, 2021
Preliminary discussion of results:	February, 2022

Table1: Timeline

3. MEASURANDS

Analyte and expected mass fraction (on a dry mass basis).

As: (0.02 – 1) mg/kg

Cd: (0.1 – 5) mg/kg

Na: (1 – 100) mg/kg

P: (500 – 5000) mg/kg

4. STUDY MATERIAL

4.1 Preparation

Several packs of yerba mate (*Ilex paraguariensis*) from a batch with suspected contamination were purchased from the local market. Determinations were performed and it was confirmed that the sample contains arsenic and cadmium in quantifiable mass fractions. The sample was dried in a convection oven at 100 ºC for 4 hours. After that, it was firstly grinded using a knife mill, in a second step using an ultra-centrifugal mill (particle size approx. 80 μm) and thoroughly mixed with a V-mixer. The obtained powder was bottled into pre-cleaned amber glass bottles. Each bottle contains approx. 25 g of material. Preliminary microbiological testing showed undetectable (< 10 UFM/g) quantities of aerobic mesophilic microbes, as well as yeast and mold. Nevertheless, the material was γ-irradiated with a dose of 23 kGy to guarantee sterilization.

4.2 Recommended Minimum sample amount

The recommended minimum sample amount for analysis is at least 0.5 g.

4.3 Dry mass determination

The dry mass correction determination must be performed on a minimum of three separate portions of 1 g each. Samples must be dried in an air-forced oven at (103 ± 2) ºC for 2 hours. After cooling and weighing, introduce the samples again in the oven for one hour. Leave until the samples are cooled and weigh them again. Constant mass is achieved when the difference between successive weights is less than 0.002 g. If necessary, introduce the sample in the oven for one more hour. In general, constant mass is attained in the first 3 hours.

4.4 Homogeneity Assessment of Study Material

The homogeneity study was carried out according to ISO GUIDE 35:2017, using one-way ANOVA. Ten bottles were selected: the first one and the last one of the lot. The rest were chosen by stratified random sampling.

Determination of Cd was performed by ID-

-SFMS, As by SA-ICP-SFMS and Na and P by SA-ICP-OES on three subsamples per bottle and per parameter.

Results of *F*-Test are shown in the following table:

Element	F	F-critical
Arsenic	2.20	2.39
Cadmium	0.96	2.39
Sodium	1.67	2.39
Phosphorus	1.75	2.39

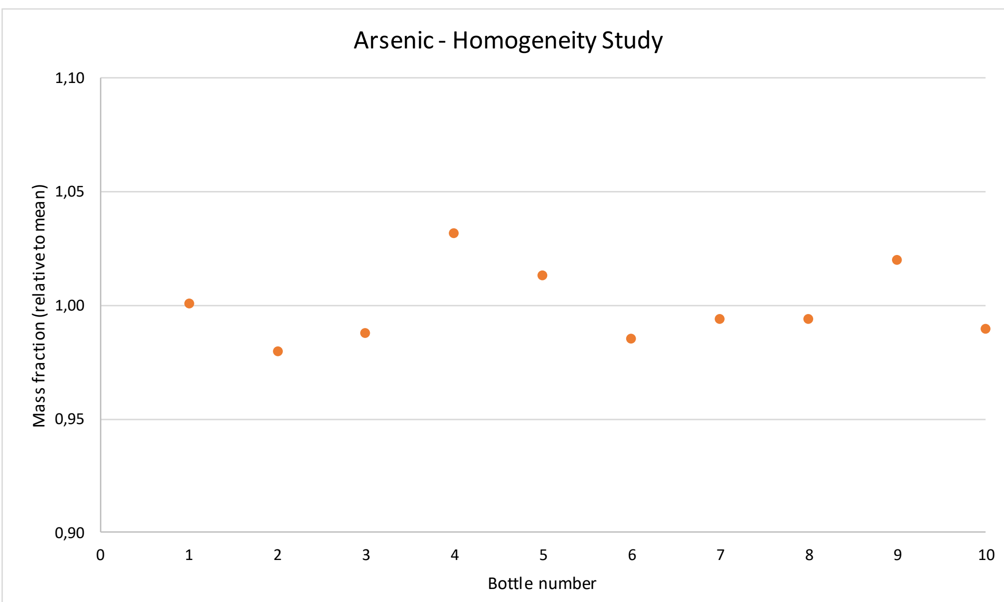
Table 2: Homogeneity *F*-Test Results

It can be concluded that analytes in the samples did not show significant inhomogeneity.

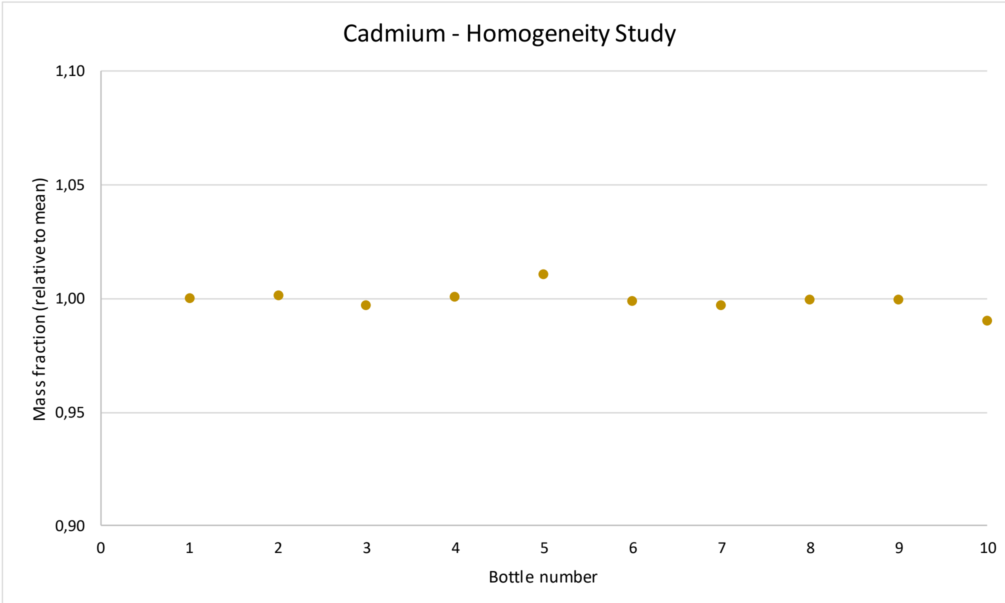
In the next table, variability figures are shown:

ANOVA Estimate	Arsenic	Cadmium	Sodium	Phosphorus
Within-packet, CV_{wth}:	2.9%	0.88%	0.46%	0.54%
Between-packet, CV_{btw}:	2.0%	0.90%	0.28%	0.72%
Total analytical variability, CV:	2.3%	0.89%	0.33%	0.60%

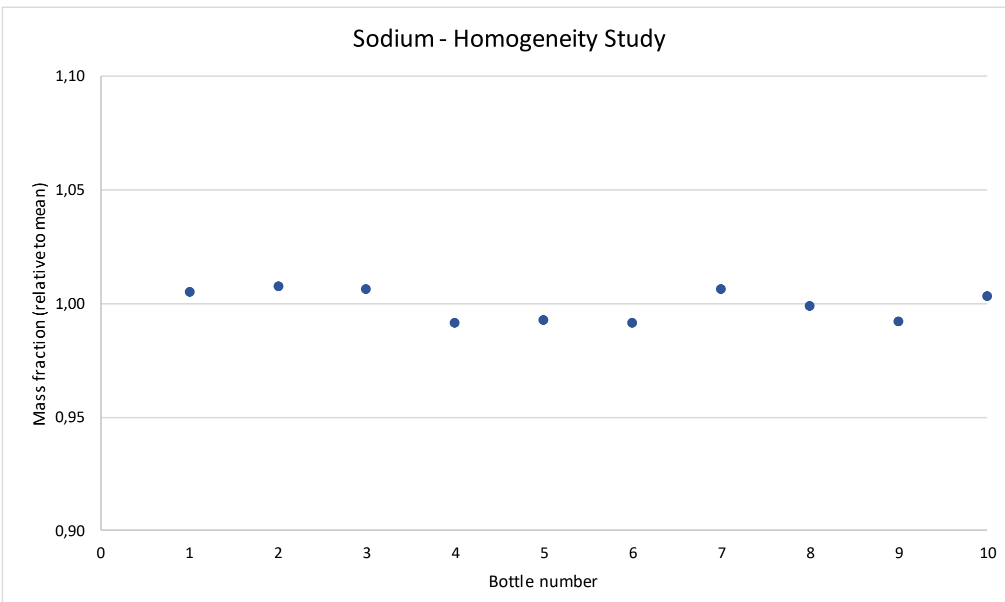
Table 3: Homogeneity ANOVA Results



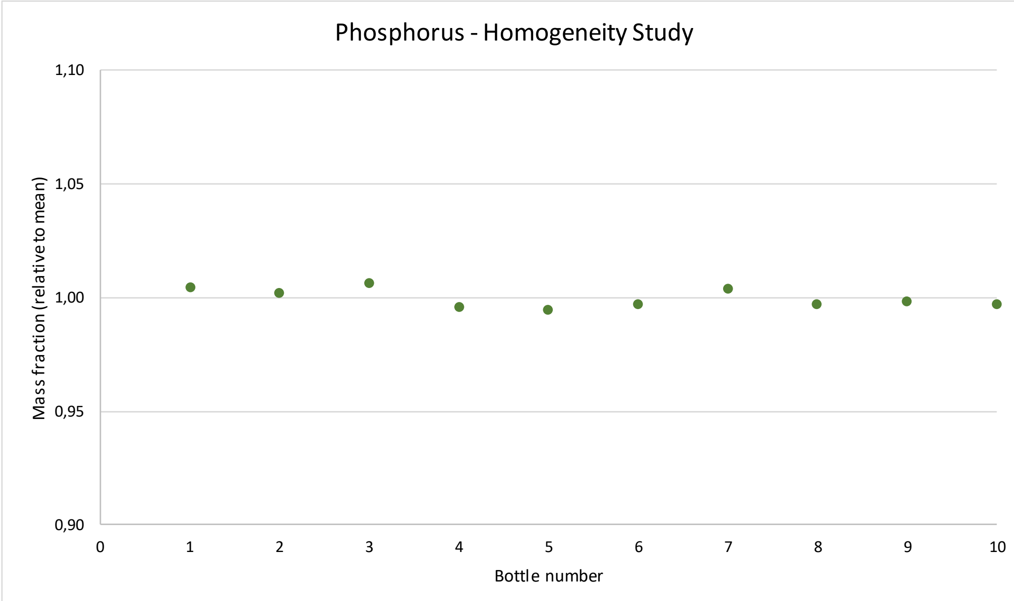
Graph 1: Homogeneity - Arsenic results per bottle



Graph 2: Homogeneity - Cadmium results per bottle



Graph 3: Homogeneity - Sodium results per bottle



Graph 4: Homogeneity - Phosphorus results per bottle

4.5 Stability Assessment of Study Material

To evaluate a possible sample's instability during transportation due to temperature, an isochronous study was designed and carried out for a period of three weeks at 40 °C. Two bottles were removed from the oven each week. Determination of Cd was performed by ID-ICP-SFMS, As by SA-ICP-SFMS and Na and P by SA-ICP-OES on three subsamples per bottle and per parameter.

The following acceptance criteria was applied:

$|b| < t_{0,95};n\text{-}2 * s'b$, where

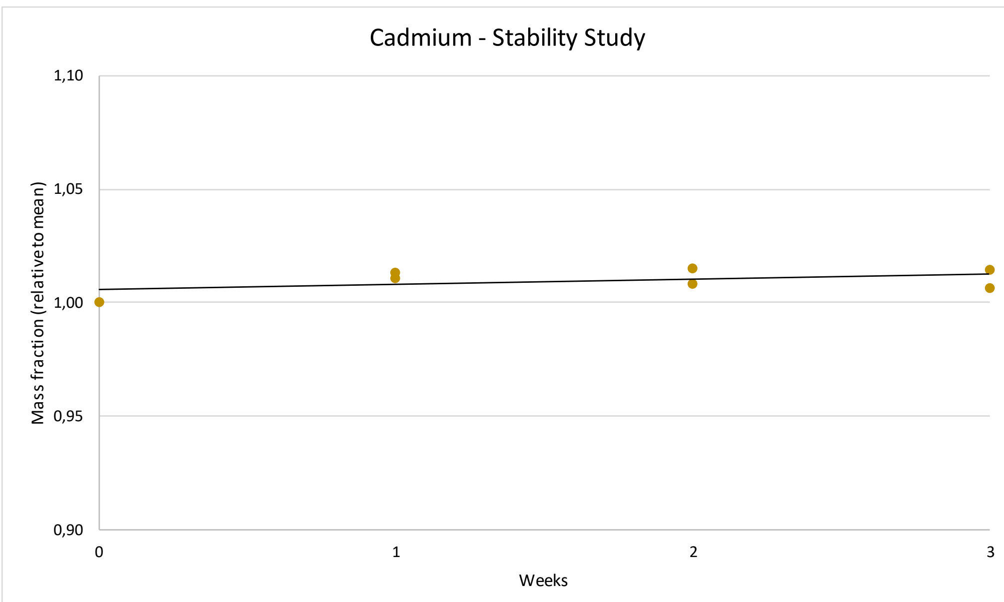
• b, slope

• s'b, slope uncertainty

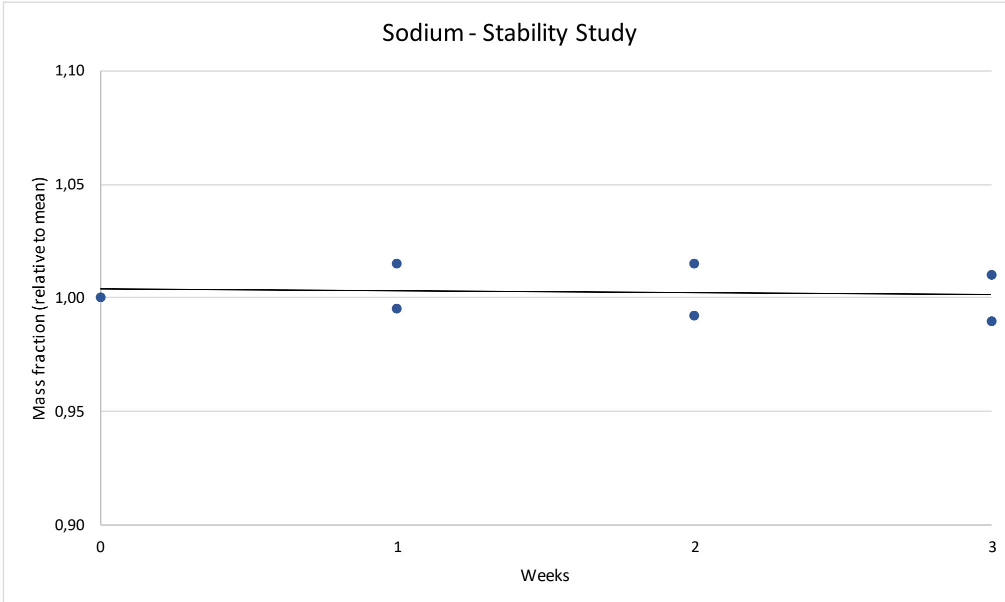
• n, number of time intervals

It can be concluded that analytes in the samples did not show significant instability after being exposed at 40°C for 3 weeks.

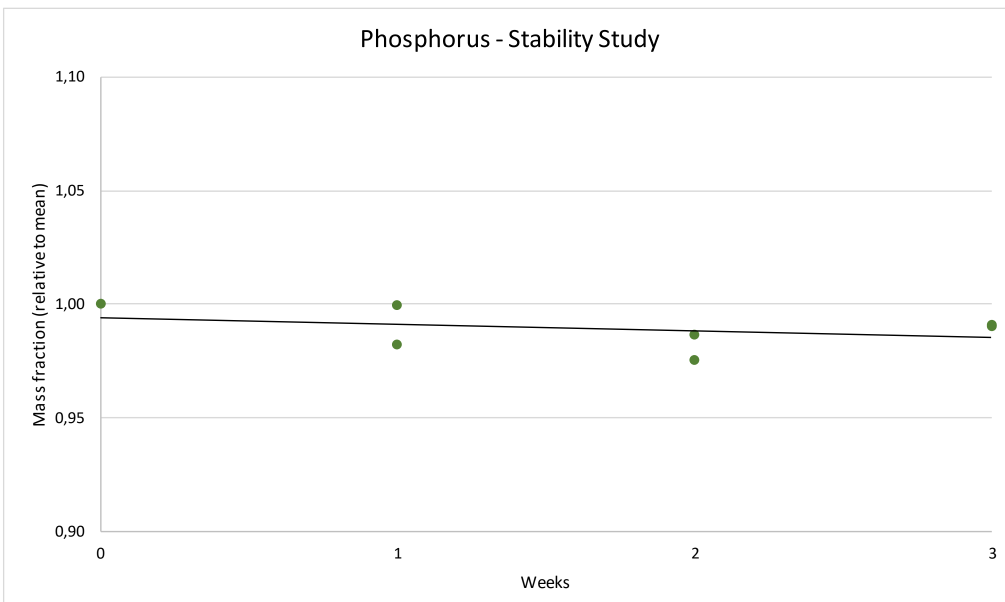
Graph 5: Stability study – Arsenic



Graph 6: Stability study - Cadmium



Graph 7: Stability study – Sodium



Graph 8: Stability study - Phosphorus

Long term stability studies will be carried out during the comparison schedule. Bottles which are stored at room temperature will be selected. Determination will be performed, and data will be evaluated as for short-term stability studies.

5. Instructions and sample distribution

A bottle containing 25 g of material will be sent to participants. A temperature label indicator will be attached to the bottle to establish whether maximum temperature has been reached during transportation. The material must be stored at room temperature, between 15 °C and 27 °C. Participants will be asked to return the sample receipt form in due time.

If the results of this comparison are to be used to support CMC claims, then the calibrations should be carried out by using standards with metrological traceability to the SI, in accordance with section 3 in CIPM MRA-G-13 (https://www.bipm.org/utils/common/documents/CIPM-MRA/CIPM-MRA-G-13.pdf). Commercially available calibration materials usually should not be employed.

6. Report of results

Final results should be returned to the coordinator laboratory using the supplied reporting template.

All participants must include:

- Final results and uncertainty budget, reported as mg/kg on dry mass basis, from at least 5 independent replicate measurements.
- A detailed description of sample preparation methods, analytical techniques, calibration approach, calibration standards, and any correction applied.

7. Use of SIM.QM-S11 in support of calibration and measurement capability (CMC) claims

7.1 How far the light shines

Successful participation in this supplementary comparison will help demonstrate capabilities for the determination of elements in plants and other high silica content related materials.

It will support CMCs in the groups:

- Arsenic: Metalloids and semi-metals at mass fraction levels above 20 µg/kg.
- Cadmium: Transition elements at mass fraction levels above 50 µg/kg.
- Phosphorus: Non-metals (except: C, O, N) at mass fraction levels above 50 µg/kg.
- Sodium: Alkali and alkaline earth elements at mass fraction levels above 50 µg/kg.

7.2 Core Capability table

Analyte groups	Matrix challenges						Calibration materials and solutions
	Water/aqueous	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)							
		Na					
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					
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)							
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)		Above 20 µg/kg					
Non-metals (P, S, C, N, O)							
		P					
Halogens (F, Cl, Br, I)							
Rare Earth Elements (Lanthanides, Actinides)							
Inorganic species (elemental, anions, cations)							
Small organo-metallics							
Proteins							
Nanoparticles							

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

8. References

International Organization for Standardization. (2017). Reference materials – Guidance for characterization and assessment of homogeneity and stability (ISO/GUIDE 35).

Appendix B. Registration form

LABORATORIO TECNOLÓGICO DEL URUGUAY

SIM.QM-S11 / SIM.QM-P25

Supplementary Comparison of elements in

Yerba mate (*Ilex paraguariensis*)

Registration Form

April, 2021

Ramiro Pérez Zambra, Romina Napoli, Elizabeth Ferreira

Montevideo-Uruguay

1. Contact Information

Date	
Name of Institute	
Acronym	
Department/Laboratory	
NMI or DI	
Country	
Contact person/s	
e-mail	
Telephone number	
Address	
Zip Code	
Special custom requirements/documentation	

Import taxes or extra charges that could be arise during sample transportation are responsibility of the participant Institute.

2. Interest of participation

Measurand	Mass fraction range (mg/kg)	Supplementary comparison SIM.QM-S11 (Yes/No)	Pilot study SIM.QM-P25 (Yes/No)
Arsenic	0.02-1		
Cadmium	0.1-5		
Sodium	1-100		
Phosphorus	500-5000		

Please complete the questionnaire electronically and return it by email to rperez@latu.org.uy by May 31, 2021.

Appendix C. Reporting form

SIM.QM-S11&P25

General Information

Date (YYYY/MM/DD)	
Institute Name	
Acronym	
Country	
Contact person/s	
e-mail	
Analyst/s	

Results

	As (mg/kg)	Cd (mg/kg)	Na (mg/kg)	P (mg/g)
Mass fraction reported				
Combined standard uncertainty (u_c)				
Coverage factor (k)				
Expanded uncertainty (U)				
Relative Expanded uncertainty (%)				

SIM.QM-S11&P25 (element)

Results

Date of analysis (YYYY/MM/DD)	

Replicate	As (mg/kg)	Bottle Number
1		
2		
3		
4		
5		

Mean	
Standard deviation	
Relative standard deviation (%)	

Determination of moisture

Date of analysis	

Replicate	Moisture (%)	Bottle Number
1		
2		
3		
4		
5		

Mean	
Standard deviation	
Relative standard deviation (%)	

Analytical Approach

Technique	
Quantification method	
MRC Calibrant	
Source of traceability	
Sample preparation	
Instrument configuration	
Mesurment conditions	
Equation	

Quality control

MRC/MR/Spike/other	
Name and Producer	
Assigned value and uncertainty	

Results	
Acceptance Criteria	
Has the acceptance criteria been met?	

Uncertainty Budget

Parameter	Source of uncertainty	Typical value	Standard Uncertainty	Unit	Type

Combined standard uncertainty (u_c)	
Coverage factor (k)	
Expanded uncertainty (U)	
Relative Expanded uncertainty (%)	

Appendix D. NIST decision tree report –

D1 - Arsenic

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	5	0.0528	0.0015	5
TRUE	14	0.0530	0.0010	60
TRUE	9	0.0565	0.0014	60
TRUE	8	0.0575	0.0016	60
TRUE	13	0.0576	0.0029	60
TRUE	3	0.0583	0.0022	60
TRUE	1	0.0608	0.0031	60
TRUE	2	0.0630	0.0034	60
TRUE	11	0.0700	0.0020	60
TRUE	12	0.0780	0.0030	60

Date: 2024-02-20
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 592
Selected Procedure: Hierarchical Skew Student-Gauss
Consensus estimate: 0.057506
Standard uncertainty: 0.0025487
95% coverage interval: (0.052474, 0.062538)
Dark uncertainty (tau): 0.0034787
Tau posterior 0.025 and 0.975 quantiles: (0.00069635,0.0094048)

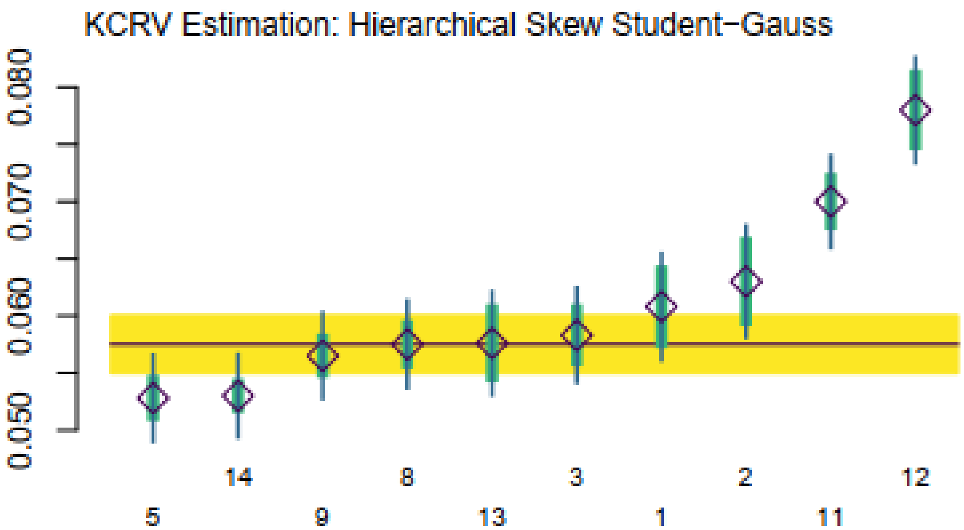
Decision Tree Hypothesis test results

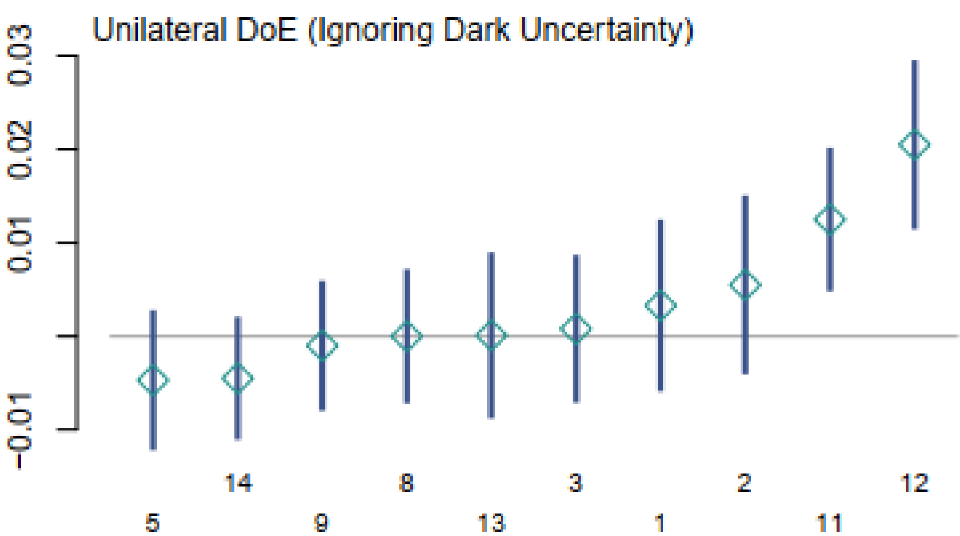
Cochran's test for Homogeneity:
p-value: $p < 0.001$
Q = 120.1 (Reference Distribution: Chi-Square with 9 Degrees of Freedom)
tau est. = 0.006442
tau/median(x) = 0.1112
tau/median(u) = 3.068

Shapiro-Wilk test for Normality: p = 0.42325

Miao-Gel-Gastwirth test of Symmetry: p = 0.0288

Plots


KCRV Estimation: Hierarchical Skew Student−Gauss
0.050
0.060
0.070
0.080
5
14
9
8
13
3
1
2
11
12


Unilateral DoE (Ignoring Dark Uncertainty)
−0.01
0.01
0.02
0.03
5
14
9
8
13
3
1
2
11
12

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
5	5	-0.0047061	0.0071629	-0.0118690	0.0024569
14	14	-0.0045061	0.0062585	-0.0107650	0.0017525
9	9	-0.0010061	0.0066301	-0.0076362	0.0056241
8	8	-0.0000061	0.0068543	-0.0068603	0.0068482
13	13	0.0000939	0.0085574	-0.0084634	0.0086513
3	3	0.0007939	0.0075729	-0.0067789	0.0083668
1	1	0.0032939	0.0088799	-0.0055859	0.0121740
2	2	0.0054939	0.0092570	-0.0037630	0.0147510
11	11	0.0124940	0.0073626	0.0051313	0.0198570
12	12	0.0204940	0.0087381	0.0117560	0.0292320

Lab Uncertainties Table

lab	x	u	nu	ut
5	0.0528	0.0015	5	0.0037883
14	0.0530	0.0010	60	0.0036195
9	0.0565	0.0014	60	0.0037498
8	0.0575	0.0016	60	0.0038290
13	0.0576	0.0029	60	0.0045289
3	0.0583	0.0022	60	0.0041159
1	0.0608	0.0031	60	0.0046595
2	0.0630	0.0034	60	0.0048643
11	0.0700	0.0020	60	0.0040126
12	0.0780	0.0030	60	0.0045936

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
5	-0.0047061	0.0055275	0.011999	-0.0167050	0.0072925	0.0032370	0.0071629	-0.0118690	0.0024569
14	-0.0045061	0.0052891	0.011608	-0.0161140	0.0071020	0.0027574	0.0062585	-0.0107650	0.0017525
9	-0.0010061	0.0053674	0.011630	-0.0126360	0.0106240	0.0029176	0.0066301	-0.0076362	0.0056241
8	-0.0000061	0.0054401	0.011837	-0.0118430	0.0118310	0.0030209	0.0068543	-0.0068603	0.0068482
13	0.0000939	0.0059385	0.012652	-0.0125580	0.0127460	0.0038860	0.0085574	-0.0084634	0.0086513
3	0.0007939	0.0056904	0.012177	-0.0113830	0.0129710	0.0033859	0.0075729	-0.0067789	0.0083668
1	0.0032939	0.0060718	0.012860	-0.0095666	0.0161540	0.0040563	0.0088799	-0.0055859	0.0121740
2	0.0054939	0.0062889	0.013248	-0.0077536	0.0187410	0.0042692	0.0092570	-0.0037630	0.0147510
11	0.0124940	0.0055459	0.011986	0.0005082	0.0244800	0.0032629	0.0073626	0.0051313	0.0198570
12	0.0204940	0.0060822	0.012815	0.0076792	0.0333090	0.0039723	0.0087381	0.0117560	0.0292320

MCMC Sampler Diagnostics Table (if applicable)

If one of the Bayesian models is run (Hierarchical Gauss-Gauss, Hierarchical Laplace-Gauss, or Hierarchical Skew-Student-t), then diagnostics for the MCMC sampler will be given below. As a general recommendation, if any of the R-hat values are greater than 1.05, then the sampler may not have reached equilibrium, and the "Total Number of MCMC Steps" should be increased, and the run repeated. The "Number of MCMC Warm-Up Steps" should be about half of the "Total Number of MCMC Steps." The "Effective Sample Size" (n.eff) is approximately the size of the MCMC sample that the results are based on.

	Rhat	n.eff
delta	1.003	1200
deviance	1.001	34000
lambda[1]	1.001	50000
lambda[2]	1.001	50000
lambda[3]	1.001	50000
lambda[4]	1.001	26000
lambda[5]	1.001	50000
lambda[6]	1.001	50000
lambda[7]	1.001	32000
lambda[8]	1.001	16000
lambda[9]	1.001	29000
lambda[10]	1.001	39000
mu	1.003	1600
nu	1.001	6200
sigma[1]	1.001	26000
sigma[2]	1.001	41000
sigma[3]	1.001	43000
sigma[4]	1.001	30000
sigma[5]	1.001	29000
sigma[6]	1.001	45000
sigma[7]	1.001	50000
sigma[8]	1.001	50000
sigma[9]	1.001	39000
sigma[10]	1.001	50000
tau	1.002	1800

D2 – Cadmium

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	6	0.7200	0.0200	238
TRUE	3	0.7280	0.0230	60
TRUE	8	0.7320	0.0110	60
TRUE	14	0.7500	0.0070	60
TRUE	5	0.7504	0.0074	5
TRUE	12	0.7600	0.0200	60
TRUE	9	0.7600	0.0130	60
TRUE	7	0.7660	0.0205	60
TRUE	13	0.7660	0.0230	60
TRUE	11	0.7950	0.0220	60
TRUE	1	0.8000	0.0421	60
TRUE	2	0.8100	0.0350	60

Date: 2024-02-20
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 223
Selected Procedure: Adaptive Weighted Average
Consensus estimate: 0.7526
Standard uncertainty: 0.0054227
Standard uncertainty (using parametric bootstrap): 0.0056467
95% coverage interval: (0.74197, 0.76323)
95% coverage interval (using parametric bootstrap): (0.7414, 0.76379)
Dark uncertainty (tau): 0.0098293

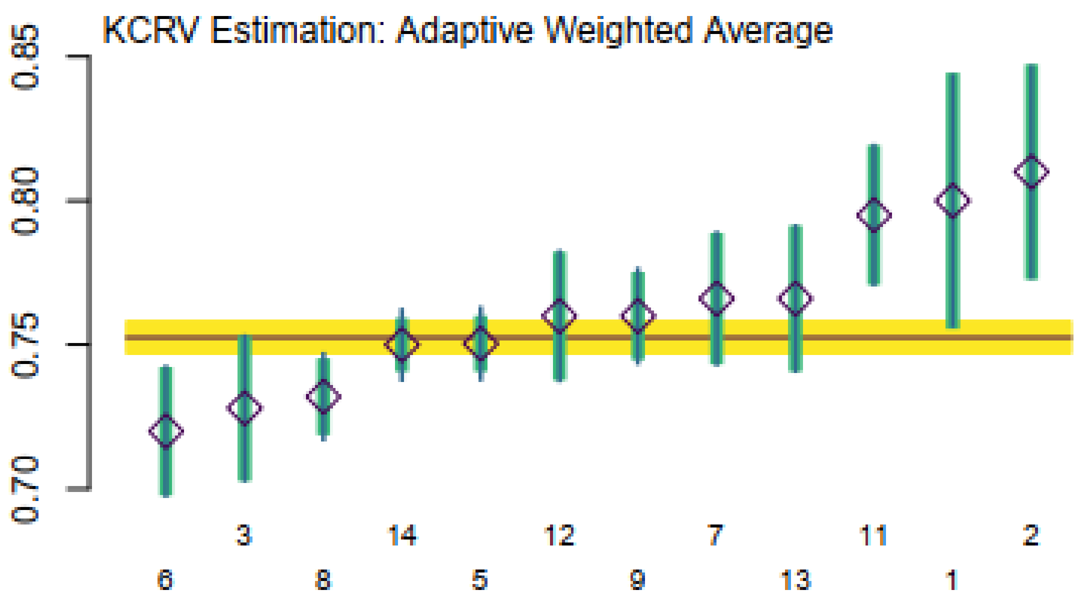
Decision Tree Hypothesis test results

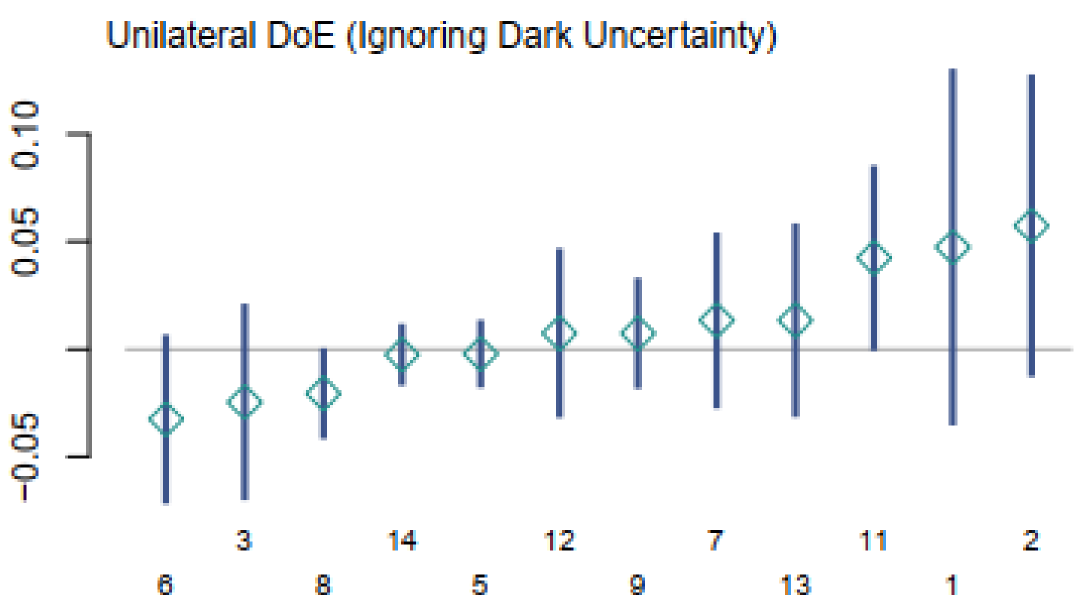
Cochran's test for Homogeneity:
p-value: 0.13
Q = 16.25 (Reference Distribution: Chi-Square with 11 Degrees of Freedom)
tau est. = 0.009829
tau/median(x) = 0.01293
tau/median(u) = 0.4854

Shapiro-Wilk test for Normality: p = 0.5068

Miao-Gel-Gastwirth test of Symmetry: p = 0.7278

Plots


KCRV Estimation: Adaptive Weighted Average
0.70
0.75
0.80
0.85
3
14
12
7
11
2
6
8
5
9
13
1


Unilateral DoE (Ignoring Dark Uncertainty)
−0.05
0.05
0.10
3
14
12
7
11
2
6
8
5
9
13
1

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
6	6	-0.0325970	0.037812	-0.070409	0.0052147
3	3	-0.0245970	0.044152	-0.068749	0.0195550
8	8	-0.0205970	0.019633	-0.040230	-0.0009641
14	14	-0.0025973	0.012838	-0.015435	0.0102400
5	5	-0.0021973	0.014228	-0.016425	0.0120300
12	12	0.0074027	0.037871	-0.030468	0.0452730
9	9	0.0074027	0.024291	-0.016888	0.0316940
7	7	0.0134030	0.039389	-0.025986	0.0527920
13	13	0.0134030	0.043613	-0.030210	0.0570160
11	11	0.0424030	0.041536	0.000867	0.0839380
1	1	0.0474030	0.081417	-0.034015	0.1288200
2	2	0.0574030	0.068759	-0.011357	0.1261600

Lab Uncertainties Table

lab	x	u	nu	ut
6	0.7200	0.0200	238	0.022285
3	0.7280	0.0230	60	0.025012
8	0.7320	0.0110	60	0.014752
14	0.7500	0.0070	60	0.012067
5	0.7504	0.0074	5	0.012303
12	0.7600	0.0200	60	0.022285
9	0.7600	0.0130	60	0.016298
7	0.7660	0.0205	60	0.022735
13	0.7660	0.0230	60	0.025012
11	0.7950	0.0220	60	0.024096
1	0.8000	0.0421	60	0.043232
2	0.8100	0.0350	60	0.036354

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
6	-0.0325970	0.021874	0.042966	-0.0755640	0.010369	0.0192960	0.037812	-0.070409	0.0052147
3	-0.0245970	0.024504	0.047811	-0.0724080	0.023214	0.0225050	0.044152	-0.068749	0.0195550
8	-0.0205970	0.014109	0.028247	-0.0488450	0.007650	0.0101290	0.019633	-0.040230	-0.0009641
14	-0.0025973	0.011664	0.024392	-0.0269890	0.021795	0.0064856	0.012838	-0.015435	0.0102400
5	-0.0021973	0.011838	0.024555	-0.0267520	0.022357	0.0070396	0.014228	-0.016425	0.0120300
12	0.0074027	0.021707	0.043030	-0.0356270	0.050432	0.0191930	0.037871	-0.030468	0.0452730
9	0.0074027	0.015784	0.031755	-0.0243520	0.039157	0.0124240	0.024291	-0.016888	0.0316940
7	0.0134030	0.022345	0.043273	-0.0298700	0.056676	0.0199230	0.039389	-0.025986	0.0527920

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
13	0.0134030	0.024663	0.049088	-0.0356850	0.062491	0.0223530	0.043613	-0.030210	0.0570160
11	0.0424030	0.023791	0.047090	-0.0046869	0.089492	0.0216480	0.041536	0.000867	0.0839380
1	0.0474030	0.043321	0.084112	-0.0367090	0.131510	0.0419130	0.081417	-0.034015	0.1288200
2	0.0574030	0.035835	0.071916	-0.0145130	0.129320	0.0345140	0.068759	-0.011357	0.1261600

MCMC Sampler Diagnostics Table (if applicable)

If one of the Bayesian models is run (Hierarchical Gauss-Gauss, Hierarchical Laplace-Gauss, or Hierarchical Skew-Student-t), then diagnostics for the MCMC sampler will be given below. As a general recommendation, if any of the R-hat values are greater than 1.05, then the sampler may not have reached equilibrium, and the "Total Number of MCMC Steps" should be increased, and the run repeated. The "Number of MCMC Warm-Up Steps" should be about half of the "Total Number of MCMC Steps." The "Effective Sample Size" (n.eff) is approximately the size of the MCMC sample that the results are based on.

D3 – Sodium

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	6	27.10	0.513	238
TRUE	1	32.14	1.850	60
TRUE	12	33.10	1.050	60
TRUE	13	33.10	1.900	60
TRUE	4	33.80	0.270	18
TRUE	9	34.05	0.550	60
TRUE	3	34.10	1.200	60
FALSE	14	36.70	0.600	60
TRUE	2	37.65	2.140	60

Date: 2024-05-27
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 662
Selected Procedure: Hierarchical Laplace-Gauss
Consensus estimate: 33.46
Standard uncertainty: 0.6635
95% coverage interval: (32.13, 34.8)
Dark uncertainty (tau): 2.179
Tau posterior 0.025 and 0.975 quantiles: (1.065,4.981)

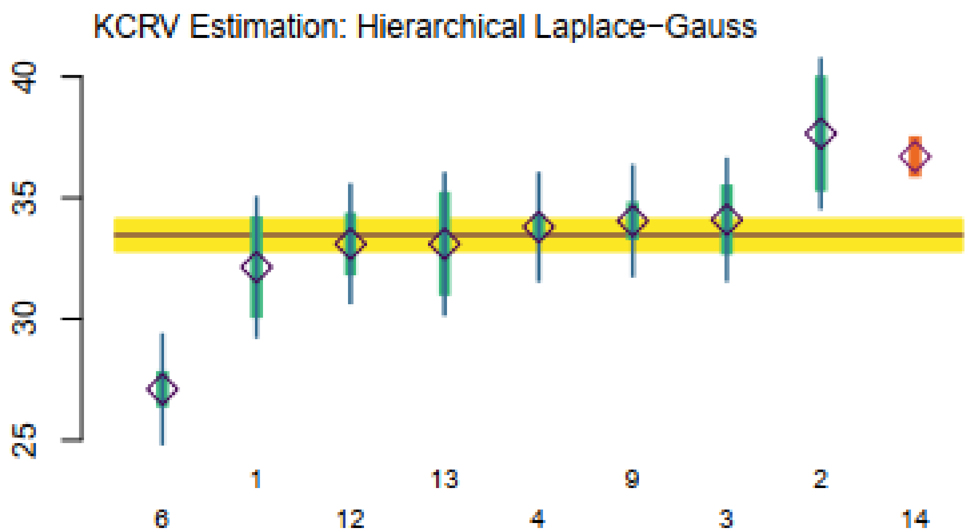
Decision Tree Hypothesis test results

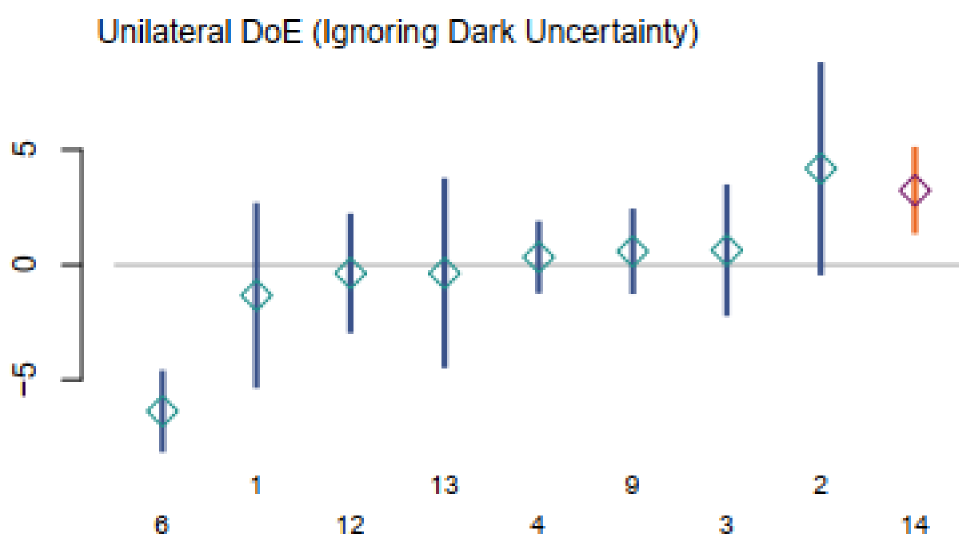
Cochran's test for Homogeneity:
p-value: $p < 0.001$
Q = 148.8 (Reference Distribution: Chi-Square with 7 Degrees of Freedom)
tau est. = 3.188
tau/median(x) = 0.09531
tau/median(u) = 2.834

Shapiro-Wilk test for Normality: p = 0.0002022

Miao-Gel-Gastwirth test of Symmetry: p = 0.6412

Plots


KCRV Estimation: Hierarchical Laplace−Gauss
40
35
30
25
1
13
9
2
6
12
4
3
14


Unilateral DoE (Ignoring Dark Uncertainty)
5
0
−5
1
13
9
2
6
12
4
3
14

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
6	6	-6.3650	1.652	-8.0170	-4.712
1	1	-1.3250	3.903	-5.2270	2.578
12	12	-0.3646	2.473	-2.8370	2.108
13	13	-0.3646	3.999	-4.3630	3.634
4	4	0.3354	1.445	-1.1100	1.781
9	9	0.5854	1.726	-1.1410	2.312
3	3	0.6354	2.729	-2.0930	3.364
14	14	3.2350	1.762	1.4740	4.997
2	2	4.1850	4.505	-0.3193	8.690

Lab Uncertainties Table

lab	x	u	nu	ut
6	27.10	0.513	238	2.239
1	32.14	1.850	60	2.859
12	33.10	1.050	60	2.419
13	33.10	1.900	60	2.891
4	33.80	0.270	18	2.196
9	34.05	0.550	60	2.248
3	34.10	1.200	60	2.488
14	36.70	0.600	60	2.260
2	37.65	2.140	60	3.054

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
6	-6.3650	2.746	5.550	-11.910	-0.8148	0.8409	1.652	-8.0170	-4.712
1	-1.3250	3.275	6.504	-7.829	5.1800	1.9840	3.903	-5.2270	2.578
12	-0.3646	2.890	5.783	-6.148	5.4190	1.2520	2.473	-2.8370	2.108
13	-0.3646	3.312	6.556	-6.920	6.1910	2.0230	3.999	-4.3630	3.634
4	0.3354	2.698	5.455	-5.119	5.7900	0.7250	1.445	-1.1100	1.781
9	0.5854	2.727	5.522	-4.937	6.1080	0.8703	1.726	-1.1410	2.312
3	0.6354	2.943	5.848	-5.213	6.4830	1.3880	2.729	-2.0930	3.364
14	3.2350	2.747	5.543	-2.307	8.7780	0.8911	1.762	1.4740	4.997
2	4.1850	3.447	6.810	-2.625	11.0000	2.2880	4.505	-0.3193	8.690

MCMC Sampler Diagnostics Table (if applicable)

If one of the Bayesian models is run (Hierarchical Gauss-Gauss, Hierarchical Laplace-Gauss, or Hierarchical Skew-Student-t), then diagnostics for the MCMC sampler will be given below. As a general recommendation, if any of the R-hat values are greater than 1.05, then the sampler may not have reached equilibrium, and the "Total Number of MCMC Steps" should be increased, and the run repeated. The "Number of MCMC Warm-Up Steps" should be about half of the "Total Number of MCMC Steps." The "Effective Sample Size" (n.eff) is approximately the size of the MCMC sample that the results are based on.

	Rhat	n.eff
deviance	1.001	50000
lambda[1]	1.001	39000

3

	Rhat	n.eff
lambda[2]	1.001	18000
lambda[3]	1.001	50000
lambda[4]	1.001	50000
lambda[5]	1.001	50000
lambda[6]	1.001	50000
lambda[7]	1.001	50000
lambda[8]	1.001	44000
mu	1.001	42000
sigma[1]	1.001	50000
sigma[2]	1.001	50000
sigma[3]	1.001	50000
sigma[4]	1.001	50000
sigma[5]	1.001	38000
sigma[6]	1.001	50000
sigma[7]	1.001	50000
sigma[8]	1.001	50000
tau	1.001	50000

D4 - Phosphorus

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	14	1.650	0.020	60
TRUE	10	1.667	0.016	60
TRUE	13	1.700	0.054	60
TRUE	9	1.735	0.028	60
TRUE	12	1.736	0.060	60
TRUE	2	1.802	0.080	60
TRUE	1	1.824	0.036	60

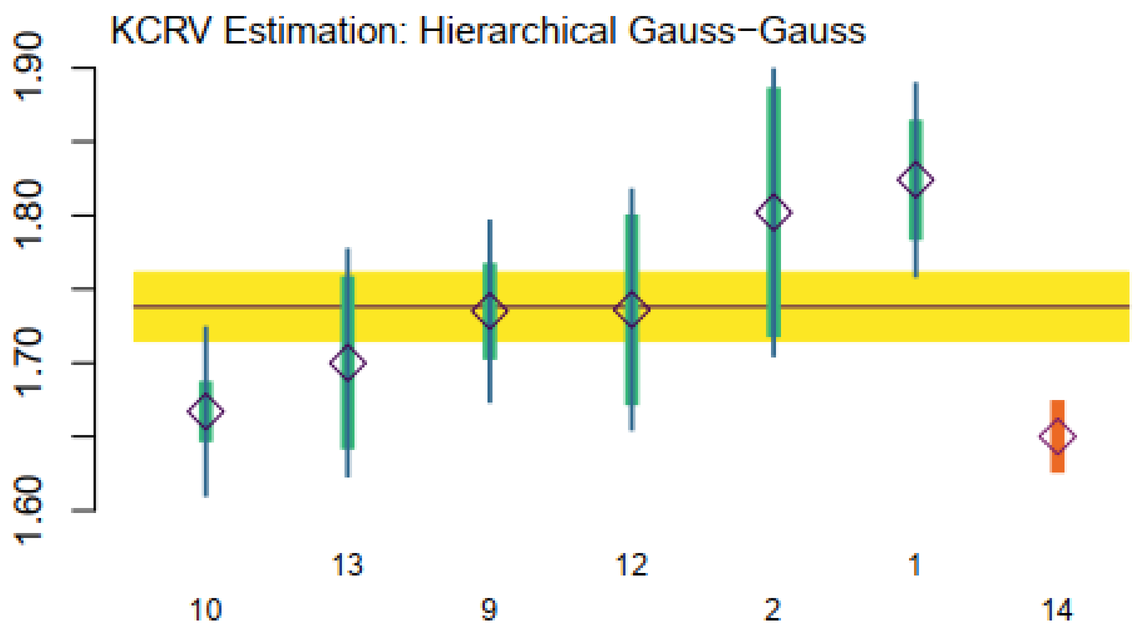
Date: 2025-03-21
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 728
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 1.738
Standard uncertainty: 0.02325
95% coverage interval: (1.692, 1.784)
Dark uncertainty (tau): 0.05381
Tau posterior 0.025 and 0.975 quantiles: (0.02108,0.1271)

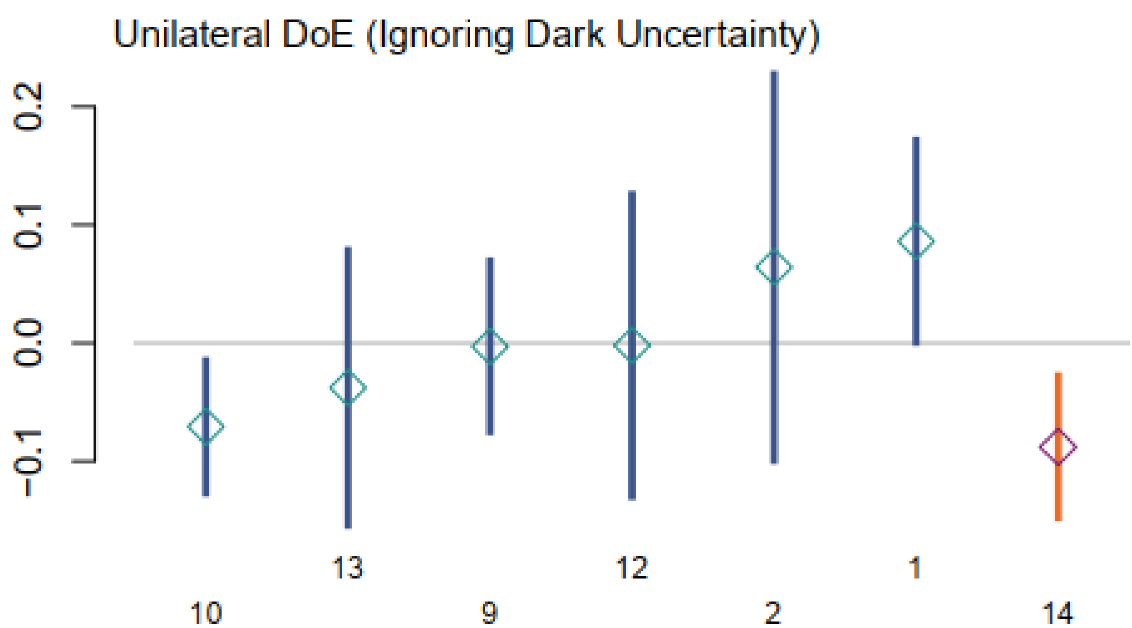
Decision Tree Hypothesis test results

Cochran's test for Homogeneity:
p-value: 0.0016
Q = 19.46 (Reference Distribution: Chi-Square with 5 Degrees of Freedom)
tau est. = 0.05938
tau/median(x) = 0.03422
tau/median(u) = 1.32

Shapiro-Wilk test for Normality: p = 0.3889

Miao-Gel-Gastwirth test of Symmetry: p = 0.3098


KCRV Estimation: Hierarchical Gauss−Gauss
1.60
1.70
1.80
1.90
13
12
1
10
9
2
14


Unilateral DoE (Ignoring Dark Uncertainty)
−0.1
0.0
0.1
0.2
13
12
1
10
9
2
14

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
14	14	-0.087960	0.06016	-0.1481000	-0.02780
10	10	-0.070960	0.05614	-0.1271000	-0.01482
13	13	-0.037960	0.11640	-0.1544000	0.07846
9	9	-0.002964	0.07235	-0.0753100	0.06939
12	12	-0.001964	0.12790	-0.1299000	0.12590
2	2	0.064040	0.16350	-0.0994200	0.22750
1	1	0.086040	0.08546	0.0005809	0.17150

Lab Uncertainties Table

lab	x	u	nu	ut
14	1.650	0.020	60	0.05741
10	1.667	0.016	60	0.05614
13	1.700	0.054	60	0.07623
9	1.735	0.028	60	0.06066
12	1.736	0.060	60	0.08060
2	1.802	0.080	60	0.09641
1	1.824	0.036	60	0.06474

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
14	-0.087960	0.07224	0.1453	-0.23330	0.05736	0.03061	0.06016	-0.1481000	-0.02780
10	-0.070960	0.07128	0.1437	-0.21470	0.07276	0.02850	0.05614	-0.1271000	-0.01482
13	-0.037960	0.08772	0.1730	-0.21100	0.13510	0.05930	0.11640	-0.1544000	0.07846
9	-0.002964	0.07482	0.1491	-0.15210	0.14620	0.03674	0.07235	-0.0753100	0.06939
12	-0.001964	0.09143	0.1811	-0.18310	0.17910	0.06498	0.12790	-0.1299000	0.12590
2	0.064040	0.10570	0.2076	-0.14360	0.27170	0.08367	0.16350	-0.0994200	0.22750
1	0.086040	0.07774	0.1548	-0.06872	0.24080	0.04339	0.08546	0.0005809	0.17150

MCMC Sampler Diagnostics Table (if applicable)

If one of the Bayesian models is run (Hierarchical Gauss-Gauss, Hierarchical Laplace-Gauss, or Hierarchical Skew-Student-t), then diagnostics for the MCMC sampler will be given below. As a general recommendation, if any of the R-hat values are greater than 1.05, then the sampler may not have reached equilibrium, and the "Total Number of MCMC Steps" should be increased, and the run repeated. The "Number of MCMC Warm-Up Steps" should be about half of the "Total Number of MCMC Steps." The "Effective Sample Size" (n.eff) is approximately the size of the MCMC sample that the results are based on.