CCQM-K158
Elements and inorganic arsenic in rice flour

Key Comparison Final Report

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SUMMARY

KRISS and NMIJ jointly coordinated the CCQM-K158 comparison on elements and inorganic As in polished rice flour. The study comprised two parts, Part A and Part B. Successful participation in formal international comparisons is essential for documenting calibration and measurement capability claims (CMCs) by national metrology institutes (NMIs) and designated institutes (DIs). CCQM-K158 specifically supports CMCs within the food category, corresponding to the sample matrix labeled "High organic content" in the new CC table for broad claims. Simultaneously, the CCQM-P200 comparison ran in parallel with the key comparison CCQM-K158.

In Part A, sixteen NMIs/DIs participated. Participants were requested to measure the mass fractions of Cu, Hg, K, Na, Pb, and Sb in rice flour, expressed in $\mathrm{mg \cdot kg^{-1}}$, on a dry mass basis. Most NMIs/DIs adopted microwave-assisted acid digestion in a closed vessel for sample pretreatment, except for NIS, which used open vessel acid digestion with heating. Majority of the participants used isotope dilution (ID) ICP-MS, except for K and Na. ICP-MS or ICP-OES with standard addition calibration and k_0 INAA were also applied specially for elements of which ID is impossible or difficult to access. ICP-MS, ICP-OES, AAS methods were also used with external calibration.

In Part B, fifteen NMIs/DIs participated. Participants were requested to evaluate the mass fractions, expressed in $\mathrm{mg \cdot kg^{-1}}$, of total arsenic and inorganic arsenic (the sum of As (III) and As (V)) in polished rice flour. For total As, thirteen NMIs/DIs reported their analytical results, where all the NMIs/DIs, except for JSI, adopted ICP-MS with a microwave acid digestion. JSI adopted k_0-INAA after pelletizing the sample. For inorganic As, seven NMIs/DIs reported their analytical results, where all the NMIs/DIs adopted liquid chromatography-ICP-MS with a thermostatically controlled extraction using diluted acids.

The results of all the participating NMIs/DIs were evaluated against the key comparison reference value (KCRV). The KCRV and associated uncertainty were estimated from reported results, excluding outliers, using NIST decision tree (NDT) as an estimator of the KCRVs.

Successful participation in CCQM-K158 Part A demonstrates measurement capabilities for determining mass fractions of alkali and alkaline earth (K, Na), transition (Cu, Hg, Pb), and metalloid/semi-metal (Sb) elements in mass fraction range above 0.05 $\mathrm{mg \cdot kg^{-1}}$, in high organic content matrices such as grains, beans, and related samples. Similarly, successful participation in CCQM-K158 Part B demonstrates measurement capabilities to determine mass fractions of total arsenic and water-soluble arsenic species such as inorganic arsenic (the sum of As (III) and As (V)), mono-, di-, tri-, and tetra-methyl arsenic compounds (MAA, DMAA, TMAO, TeMA), arsenocholine (AsC), and arsenobetaine (AsB), in mass fraction range above 0.05 $\mathrm{mg \cdot kg^{-1}}$ in grains, beans, and related samples.

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ACRONYMS

ANOVA: Analysis of variance
CCQM: Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology
CMC: Calibration and Measurement Capability
CRM: Certified Reference Material
CV-AAS: Cold Vapor generation Atomic Absorption Spectroscopy
DI: Designated Institute
DoE: Degrees of Equivalence
ET-AAS: ElectroThermal Atomic Absorption Spectroscopy
FAAS: Flame Atomization Atomic Absorption Spectroscopy
GSA: Gravimetric Standard Addition
HG-AAS: Hydride Generation Atomic Absorption Spectroscopy
IAWG: Inorganic Analysis Working Group
ICP-MS: Inductively Coupled Plasma Mass Spectrometry
ICP-MS/MS: Triple Quadrupole Inductively Coupled Plasma Mass Spectrometry
ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry
ICP-SFMS: Sector Field type Inductively Coupled Plasma Mass Spectrometry
ID: Isotope Dilution
INAA: Instrumental Neutron Activation Analysis
KCRV: Key Comparison Reference Value
LC: Liquid Chromatography
MC ICP-MS: Multi-Collector Inductively Coupled Plasma Mass Spectrometry
MW: Microwave
NDT: NIST Decision Tree
NMI: National Metrology Institute
SA: Standard Addition
SRM: Standard Reference Material (brand name of NIST CRMs)

INTRODUCTION

Rice is a staple food for approximately half of the world’s population, playing a crucial role in global nutrition. Ensuring accurate and precise measurement of nutrient and hazardous elements in rice is essential for reliable assessments of nutritional quality and potential health hazards. Food authenticity and traceability is another important issue related to food safety. Therefore, the Inorganic Analysis Working Group (IAWG) within the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) periodically conducts key comparisons (KCs) and pilot studies (PS) for the analysis of elements in foods to establish measurement equivalence and provide evidence supporting calibration and measurement capability (CMC) claims made by National Metrology Institutes (NMIs) and Designated Institutes (DIs).

In April 2019, the CCQM approved the Key Comparison (KC), CCQM-K158 “Elements and inorganic As in polished rice flour”. This comparison was designed to assess participant’s capabilities for the analysis of essential and hazardous elements and arsenic compounds in cereals, beans, and their products. The study aligned with the 5-year plan of the CCQM-IAWG.

CCQM-K158 is a successive comparison for CCQM-K24 (Cadmium amount content in rice, finalized in 2003), CCQM-K108 (Cd, As, inorganic arsenic, and DMAA in brown rice flour, finalized in 2015) and CCQM-K108.2014 (arsenic species and total arsenic in brown rice flour, finalized in 2017). Therefore, it supports CMCs within category of Food, which corresponds to the sample matrix of “High organics content” in the new CC table for broad claims.

CCQM-K158 was jointly coordinated by the Korea Research Institute of Standards and Science (KRISS) and the National Metrology Institute of Japan (NMIJ). This comparison was divided into two parts (Part A and Part B). The Part A was organized by KRISS and the mass fractions of Cu, Hg, K, Na, Pb, and Sb were the measurands. The Part B was organized by NMIJ, and the mass fractions of total and inorganic arsenic were the measurands. It should be noted that the test samples used for Part A and Part B are from different batches.

This report provides detailed information on the timeline, measurands, study materials, participating laboratories, results, and the measurement capability claims supported by participation in CCQM-K158 Part A and Part B. The appendices include official communication materials and information related to the NIST decision tree report for each measurand.

CCQM-K158 Part A

TIMELINE

The timeline for CCQM-K158 Part A is shown in Table A1.

Table A1: Timeline for CCQM-K158 Part A

Date	Action
Oct. 2018	Proposed to CCQM
Apr. 2019	IAWG authorized CCQM-K158 Part A & Part B
Feb. 2021	Call for participation to IAWG members
Apr. to Jun. 2021[a]	Study samples shipped to participants. The range in shipping times reflects delays from shipping and customs.
Mar. 2022[b]	Results due to coordinating laboratory.
Apr. 2022	First discussion in IAWG (online)
Sep. to Nov. 2022	Second discussion in IAWG (online), especially for estimating key comparison reference value (KCRV) using NIST decision tree.
Apr. and Nov. 2023	Additional discussions on using NIST decision tree in IAWG
Apr. 2024	Draft A report for Part A distributed to participants
Sep. 2024	Draft A report (Part A & B merged) distributed to participants
Nov. 2024	Draft B report (Part A & B merged) distributed to IAWG
Dec. 2024	Final report approved by IAWG

[a] NIS received the sample in June 2021, due to custom clearance delay.

[b] The reporting deadline had been set at the end of September 2021, but it was extended several times under the COVID-19 pandemic situation. The deadline was finally extended to the end of March 2022.

MEASURANDS

The measurands of CCQM-K158 Part A are the mass fractions of copper, mercury, potassium, sodium, lead, and antimony in rice flour on a dry mass basis as shown in Table A2. The mass fraction range of Hg was modified from (0.5-5) mg/kg in the original protocol to (0.1-5) mg/kg during the study to reflect potential loss of spiked Hg during the production of the test material.

Table A2: Measurands of CCQM-K158 Part A

Measurand	Approximate Mass fraction (mg/kg)	Natural /Spiked	Description
Cu	0.5-5	Natural	Transition element
Hg	0.1-5 (Modified from 0.5-5)	Spiked	Toxic element, strong memory effect in ICPMS
K	100-1000	Natural	Severe isobaric interferences in ICPMS, Instrumental blank control
Na	2-10	Natural	Monoisotopic element, instrumental blank control
Sb	0.5-5	Spiked	Metalloid
Pb	0.1-1	Spiked	Toxic element, Hg interference

STUDY MATERIALS

The comparison material was polished rice flour prepared by freeze-drying, pulverization, sieving to obtain particles with sizes between 50 μm to 250 μm. Then, hazardous elements, As, Cd, Hg, Ni, Sb, and Pb, were spiked in the rice flour and mixed thoroughly in a paste form. Freeze-drying and pulverization of the paste followed by sieving and V-mixing resulted in homogenized rice powder. The homogenized powder was placed into amber glass bottles (20 g each) and sterilized with γ-ray irradiation (^{60}Co, 25 kGy). The bottles were individually vacuum-sealed into aluminum coated plastic bags. The bottles were stored at room temperature.

Each participant received two bottles containing approximately 20 g of rice flour each. The recommended minimum sample amount for analysis was 0.2 g. Measurement results were to be reported on a dry-mass basis. The recommended sample amount for moisture content determination was at least 0.5 g.

Dry Mass Determination

It was instructed to measure moisture content of the rice flour sample by taking subsamples before and after the subsampling for analyses. The recommended procedure was to dry the sample to constant mass in a desiccator with fresh P_2O_5 at room temperature for 7 days. Participant might check if constant mass was reached by extending the drying one more week. A sample size of 0.5 g or more was recommended for the determination of moisture content. The elemental contents determined should be reported on the dry mass basis.

Homogeneity Assessment of Study Material

The homogeneity of the test sample was carried out using 12 bottles selected by systematic sampling from the batch. Single subsample of about 0.2 g was taken from each bottle for the homogeneity assessment. The result of the homogeneity assessment is in Table A3 and graphically presented in Figure A1. It was found that the test sample was sufficiently homogeneous for the elements of interest in this study.

Table A3: Result of the homogeneity assessment

Measurand	Analytical Method	Relative standard deviation due to between-bottle inhomogeneity (%)
Cu	ID ICP-MS	0.95
Hg	ID ICP-MS	0.85
K	ID ICP-MS	0.59
Na	ICP-OES	0.41
Pb	ID ICP-MS	0.67
Sb	ID ICP-MS	0.32

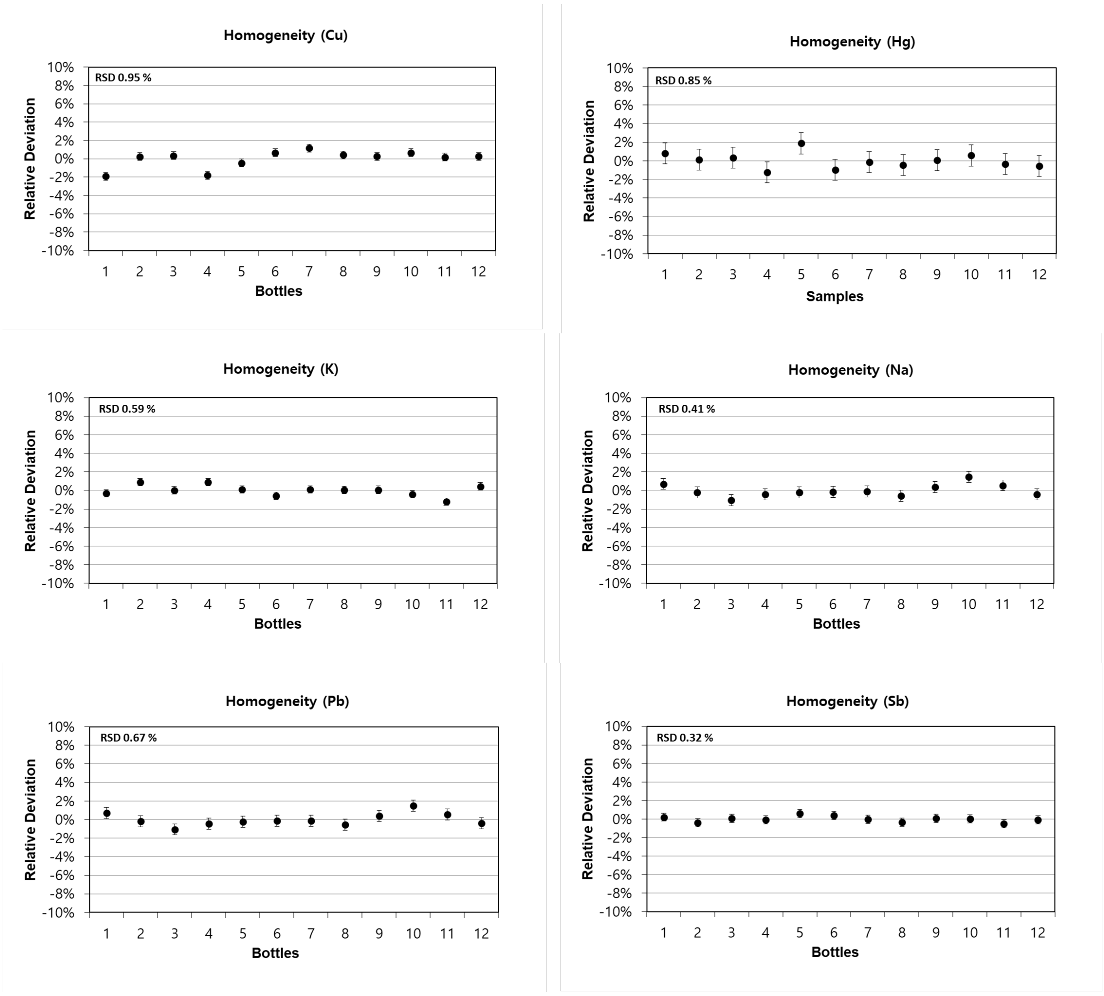


Figure A1: Homogeneity assessment

error bar: standard uncertainty for individual sample measurement

Stability Assessment of Study Material

Although the study material was presumed to be stable more than 5 years for the elements chosen as measurands in this study, both the long-term and short-term transport stability analysis were carried out. For the short-term stability (STS) assessment, five bottles were kept at 50 °C for 7 days to test the stability during transportation at an extreme condition. The long-term stability (LTS) for more than 5 months was investigated using five bottles stored at ambient temperature (15 °C to 25 °C). Table A4 summarizes the results of the long-term and short-term stability assessments for sample used for CCQM-K158 Part A. The stability data are also shown graphically in Figure A2. The LTS and STS assessments didn't show any instability of the study material during the duration of the comparison at the storage and transport conditions. In the table A4, the difference between the mass fractions determined for characterization (i.e., at the beginning of the stability study) and stability assessment, $\left|w_{\text{char}} - w_{\text{stability}}\right|$, for each measurand was less than associated combined expanded uncertainty, $k\sqrt{u_{\text{char}}^2 + u_{\text{stability}}^2}$.

Table A4: Results of the long-term and short-term stability assessments

Measurand	Stability Type	Stability Condition	Analytical Method	$\lvert w_{\text{char}}-w_{\text{stability}}\rvert$	$k\cdot(u_{\text{char}}^2+u_{\text{stability}}^2)^{1/2}$ $k = 2$
Cu	LTS	26 months, RT	ID ICP-MS	0.0256	0.0327
	STS	7 days, 50 °C	ID ICP-MS	0.0198	0.0336
Hg	LTS	10 months, RT	ID ICP-MS	0.0045	0.0207
	STS	7 days, 50 °C	ID ICP-MS	0.0000	0.0223
K	LTS	5 months, RT	ICP-OES	1.23	4.89
	STS	7 days, 50 °C	ICP-OES	0.83	4.66
Na	LTS	5 months, RT	ICP-OES	0.052	0.062
	STS	7 days, 50 °C	ICP-OES	0.045	0.047
Sb	LTS	10 months, RT	ID ICP-MS	0.0092	0.0142
	STS	7 days, 50 °C	ID ICP-MS	0.0011	0.0173
Pb	LTS	26 months, RT	ID ICP-MS	0.0038	0.0076
	STS	7 days, 50 °C	ID ICP-MS	0.0012	0.0088

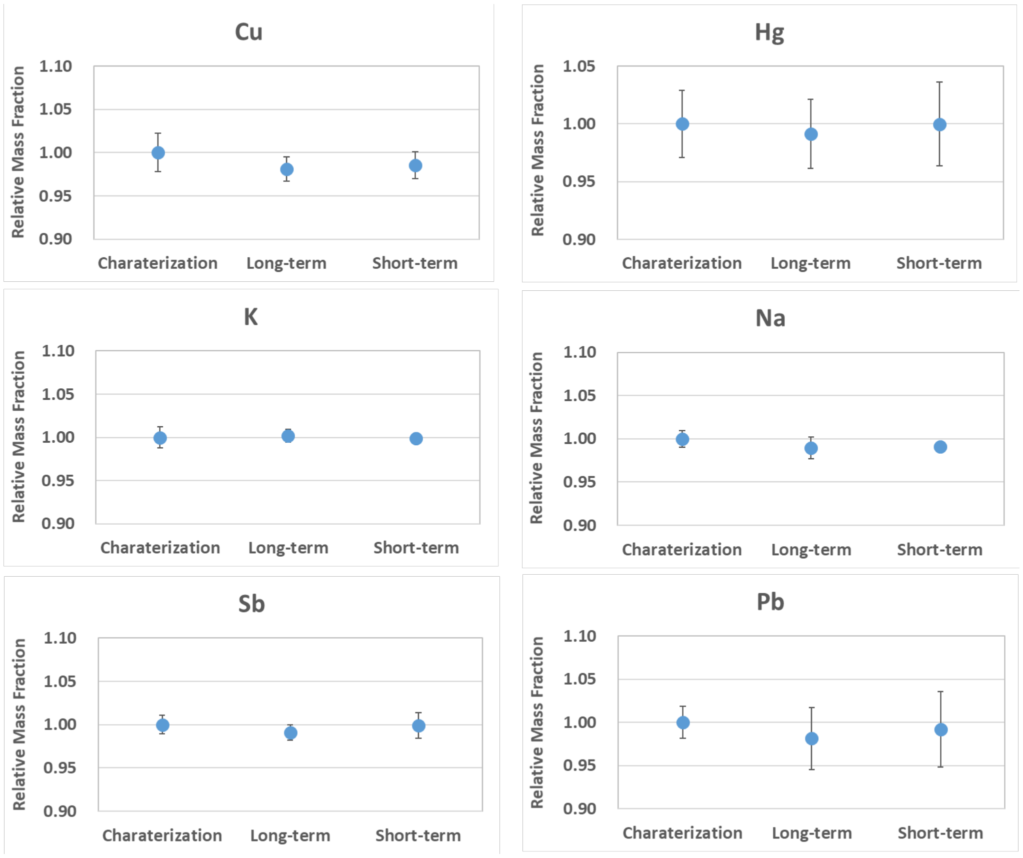


Figure A2: Long-term and short-term stability assessment

error bar: expanded uncertainty

PARTICIPANTS, INSTRUCTIONS AND SAMPLE DISTRIBUTION

The call for participation was distributed in Feb. 2021. Table A5 lists the 17 institutions that registered for CCQM-K158 Part A. The samples were distributed from April 2021. Most of participants received samples successfully within a few days, while several participants experienced customs clearance delay. Appendix A reproduces the Call for Participation and the study Protocol.

The participants were asked to report the mass fraction of each measurand on the dry mass basis, accompanied by a full uncertainty budget. For each measurand, only one result was accepted as KC result. In the case when multiple results from different methods were reported, one should either report one composite result (e.g., an average value from different methods) or submit only one result for KC while reporting the other results for PS. Reporting the details of the procedure (including details of sample treatment/digestion), the calibration standard and the traceability link, and the instrument(s) used was required using the reporting form distributed to participants as in the Appendix B.

The reporting deadline had been set at the end of September 2021, but it had to be extended three times under the COVID-19 pandemic situation. First extension was to the end of October 2021, due to a hard lockdown of some institutes for several months. Second extension was to the end of February 2022, due to the significant delay in the sample receipt of NIS. The final extension was to the end of March 2022, due to delay a supplement of consumable instrumental to NIS under the COVID-19 pandemic situation.

All the results, except for VNIIFTRI were reported by the end of Feb. 2022. VNIIFTRI could not report their results due to instrument problem, which had not been resolved before the extended reporting deadline. Among 17 registered NMIs/DIs, 16 participants reported their measurement results.

The result of comparison was first discussed at the online IAWG meeting in April 2022. The discussion regarding the estimation of the key comparison reference value (KCRV) including the adaptation of the NIST decision tree (NDT) continued via additional online meeting among participants in Sep. 2022 followed by online fall IAWG meeting in Nov. 2022 and on-site spring IAWG meeting in April 2023. See Table A1 for study timeline.

Table A5: Institutions registered for CCQM-K158 Part A

NMI or DI	Code	Country	Contact	Additional Contributors
Government Laboratory	GLHK	Hong Kong, China	Wai-hong Fung Siu-kuen Tong	Chun-wai Tse
Health Sciences Authority	HSA	Singapore	Richard Shin	Fransiska Dewi Sim Lay Peng Wesley Yu Zongrong Leung Ho Wah

NMI or DI	Code	Country	Contact	Additional Contributors
Instituto Nacional de Metrología de Colombia	INMC	Colombia	Carlos Andrés España Sánchez	Johanna Paola Abella Fabián Niño Quintero
Instituto Nacional de Tecnología Industrial	INTI	Argentina	Osvaldo Acosta Mabel Puelles	
Jožef Stefan Institute	JSI	Slovenia	Radojko Jaćimović Marta Jagodic Hudobivnik	Darja Mazej Ermira Begu Milena Horvat
Korea Research Institute of Standards and Science	KRISS	Korea	Yong-Hyeon Yim Kyoung-Seok Lee	Youngran Lim Jong Wha Lee Hana Cho Myung Chul Lim Jinil Kim Sook Heun Kim
Laboratorio Tecnológico del Uruguay	LATU	Uruguay	Ramiro Pérez Zambra Romina Napoli	
Federal Institute of Metrology	METAS	Switzerland	Silvia Mallia	Simon Lobsiger
National Institute of Standards	NIS	Egypt	Randa N. Yamani	Moustafa M. Elmasry
National Metrology Institute of Japan	NMIJ/AIST	Japan	Yanbei Zhu	
National Metrology Institute of South Africa	NMISA	South Africa	Angelique Botha	
National Institute of Metrology of Thailand	NIMT	Thailand	Nattikarn Ornthai	Usana Thiengmanee Suttinun Taebunpakul Nunnapus Laitip
Physikalisch-Technische Bundesanstalt	PTB	Germany	Olaf Rienitz	Axel Pramann, Volker Goerlitz, Anita Roethke, Ursula Schulz, Jessica Towara, Carola Pape, Samuel Henjes
National Institute of Metrology, China	NIM	China	Xiao Li Qian Ma	
National Measurement Institute, Australia	NMIA	Australia	Jeffrey Merrick	Ian White Elizabeth Tully
Instituto Nacional de Metrologia	INMETRO	Brazil	Marcia Silva da Rocha Thiago de Oliveira Araujo	Marcelo Domingues de Almeida Vânia Silva de Oliveira
Russian Metrological Institute of Technical Physics and Radio Engineering	VNIIFTRI	Russia	Aleksey Stakheev	

RESULTS

Participants were requested to report a single estimate of the mass fraction [mg/kg] for copper, mercury, potassium, sodium, lead, and antimony in rice flour on a dry mass basis. In addition to the quantitative results, participants were instructed to describe their analytical methods and approach to uncertainty estimation. Appendix C reproduces the reporting form for part A.

CCQM-K158 Part A results were received from 16 of the 17 institutions that received samples.

Methods Used by Participants

Specific analytical method was not recommended or preferred for the measurements. Participants were allowed to select any method(s) of their choices. The analytical techniques adopted by the participants were summarized in Table A6.

For sample preparation for ICP-MS, ICP-OES, and AAS, all the participants except for NIS used closed microwave assisted digestion with different acid combinations. NIS carried out acid digestion with heating in an open vessel. JSI adopted non-destructive sample preparation method without acid digestion for k_0-INAA.

Most of the participants employed robust calibration approaches including isotope dilution and standard addition for elimination of non-spectral interferences. External calibration and bracketing calibration were also used with or without internal standard elements. For elimination of spectral interferences in ICP-MS measurements, participants applied either medium- or high-resolution mode using a sector field ICP-MS or collision mode with helium gas using a quadrupole ICP-MS.

Table A6: Summary of measurement methods used for CCQM-K158 Part A

Participating NMI/DI	Measurand	Sample preparation method	Calibration method	Analytical instrument	Reference material used for calibration (traceability)
GLHK	Hg, Pb, Sb	Closed MW digestion with HNO_3, $AuCl_3$	Double ID (Hg, Sb), Standard addition with internal standard (Pb)	ICP-MS with He mode	NIST SRM 3133 (Hg) NIST SRM 3128 (Pb) NIST SRM 3102a (Sb) ERM-AE640 ^{202}Hg Eurisotop ^{123}Sb
HSA	Cu, Hg, Pb, Sb	Closed MW digestion with HNO_3, HF, H_2O_2	Double ID	ICP-MS with He mode (Cu, Hg, Pb) ICP-SFMS with high resolution (Sb)	NIST SRM 3114 (Cu) NIST SRM 3133 (Hg) NIST SRM 3128 (Pb) NIST SRM 3102a (Sb) ORNL ^{65}Cu ORNL ^{201}Hg NIST SRM 981, ORNL ^{206}Pb ISOFLEX ^{123}Sb

Participating NMI/DI	Measurand	Sample preparation method	Calibration method	Analytical instrument	Reference material used for calibration (traceability)
INMC	K, Pb	Closed MW digestion with HNO_3, H_2O_2	Bracketing calibration (K), Standard addition with internal standard (Pb)	FAAS (K) ICP-MS (Pb)	NIST SRM 999c (KCl) NIST SRM 3128 (Pb)
INMETRO	Pb	Closed MW digestion with HNO_3, H_2O_2	External calibration	ICP-MS	NIST SRM 3128 (Pb)
INTI	Cu, Hg, Pb, Sb	Closed MW digestion with HNO_3	External calibration (Cu, Pb, Sb), Standard addition (Hg)	ICP-MS (Cu, Pb, Sb), CV-AAS (Hg)	NIST SRM 3114 (Cu) NIST SRM 3133 (Hg) NIST SRM 3128 (Pb) NIST SRM 3102a (Sb)
JSI	Cu, Hg, K, Na, Pb, Sb	Closed MW digestion with HNO_3 (Cu, Hg, Pb), No digestion (K, Na, Sb)	External calibration with internal standard (Cu, Hg, Pb), k_0 method with Al-0.1%Au alloy (K, Na, Sb)	ICP-MS (Cu, Hg, Pb), k_0-INAA (K, Na, Sb)	NIST SRM 3114 (Cu) NIST SRM 3133 (Hg) NIST SRM 3128 (Pb) Al-0.1%Au alloy (ERM-EB530A) was validated by NIST SRM 3121 Au standard solution
KRISS	Cu, Hg, K, Na, Pb, Sb	Closed MW digestion with HNO_3 (Cu, K, Na, Pb, Sb) Closed MW digestion with HNO_3, then diluted with HCl (Hg)	Double ID (Cu, Hg, K, Pb, Sb), Standard addition with internal standard (Na)	ICP-SFMS with low (Hg, Pb), medium (Cu, Sb), and high (K) resolution, ICP-MS/MS with NH3 mode (Pb), ICP-OES (Na)	KRISS primary standard for each element ORNL ^{65}Cu JRC AE 640 ^{202}Hg ORNL ^{41}K NIST SRM 981 NIST SRM 991 ^{206}Pb ORNL ^{123}Sb
LATU	Cu, Hg, K, Pb	Closed MW digestion with HNO_3, HF, H_2O_2 (Cu, K, Pb), Closed MW digestion with HNO_3, H_2O_2 then diluted with BrCl (Hg)	Double ID (Cu, Hg, Pb) Standard addition (K)	ICP-SFMS with low (Hg, Pb), and medium (Cu) resolution, ICP-OES (K)	SMU B12 (Cu) NIST SRM 3133 (Hg) NIST SRM 3141a (K) NIST SRM 3128 (Pb) ^{65}Cu ^{199}Hg ^{206}Pb NIST SRM 981
METAS	Pb	Closed MW digestion with HNO_3, H_2O_2	Double ID	ICP-SFMS	NIST SRM 3128 (Pb) ISC Sci. ^{207}Pb

Participating NMI/DI	Measurand	Sample preparation method	Calibration method	Analytical instrument	Reference material used for calibration (traceability)
NIM	Hg, Pb	Closed MW digestion with HNO_3, HCl (Hg), Closed MW digestion with HNO_3 (Pb)	Double ID	ICP-MS/MS	NIM GBW08617 (Hg) NIM GBW08619 (Pb) NIM GBW04443 ^{202}Hg NIM GBW04442 ^{207}Pb
NIMT	Cu, Hg, K, Na, Pb, Sb	Closed MW digestion with HNO_3, H_2O_2	Double ID (Cu, Hg, Pb) Standard addition with internal standard (K, Na, Sb)	ICP-MS/MS (Cu, Hg, Pb, Na, Sb) ICP-OES (K)	NIST SRM 3114 (Cu) NIST SRM 3133 (Hg) NIST SRM 3141a (K) Inorganic Ventures CGNA1 (Na) NIST SRM 3128 (Pb) NIST SRM 3102a (Sb) ORNL ^{65}Cu ORNL ^{201}Hg ORNL ^{206}Pb
NIS	Cu, Hg, K, Na, Pb	Open digestion with HNO_3, H_2O_2	External calibration	ET-AAS (Cu, Pb) HG-AAS (Hg) FAAS (K, Na)	NIS CRM 010 (from NIST SRM C1251 for Cu) NIST SRM 3133 (Hg) NIS CRM 018 (K) NIS CRM 020 (Na) NIST SRM 3128 (Pb)
NMIA	Hg, Pb, Sb	Closed MW digestion with HNO_3, HCl	Double ID	ICP-SFMS with low resolution	NIST SRM 3133 (Hg) NIST SRM 3128 (Pb) NIST SRM 3102a (Sb) ORNL ^{201}Hg NIST SRM 981 NIST SRM 991 ^{206}Pb ISOFLEX ^{123}Sb
NMIJ/AIST	Cu, K, Na, Pb, Sb	Closed MW digestion with HNO_3	Standard addition with internal standard	ICP-MS/MS with He mode	JCSS elemental standard for each element
NMISA	Cu, Hg, K, Na, Pb	Closed MW digestion with HNO_3, H_2O_2	Double ID (Cu, Hg, Pb) External calibration with internal standard (K, Na)	ICP-SFMS with low (Hg, Pb), medium (Cu, Na), and high (K) resolution	NIST SRM 3114 (Cu) NIST SRM 3133 (Hg) NIST SRM 3141a (K) NIST SRM 3152a (Na) NIST SRM 3128 (Pb) Spectrascan ^{65}Cu CIL ^{198}Hg Inorganic Venture ^{206}Pb
PTB	K, Pb	Closed MW digestion with HNO_3, H_2O_2	Bracketing calibration with internal standard (K) Double ID (Pb)	ICP-OES (K) MC-ICP-MS (Pb)	BAM-Y010: BAM-A-primary-KCl-1 (K) BAM-Y004: BAM-A-primary-Pb-1 (Pb) NIST SRM 981 NIST SRM 991 ^{206}Pb

Calibration Materials Used by Participants

Participants were allowed to establish the metrological traceability of their results to the SI using a direct realization via a primary method, certified reference materials (CRMs) from an NMI/DI having the required CMC claims, or by preparing their own calibration standards using commercially available high purity materials for which they determined the purity themselves. All participants claimed the traceability of the calibrants used in the comparison. NIMT, however, used a commercial standard solution for the calibration of Na measurement. Due to lack of metrological traceability, their Na result was not included in the KCRV calculation.

Moisture Content

Participants were asked to determine the moisture content in the sample to report the mass fractions of elements on a dry mass basis. The reported mass fractions of dried sample are summarized in Table A7. Due to misunderstanding of the protocol, several results were obtained using different drying methods. To evaluate the equivalence of different drying methods used by participants, the coordinating laboratory carried out sample drying experiment. It showed that it didn't have noticeable influences in the final results. For example, the dried mass fractions determined by using $CaSO_4$ (Drierite) and P_2O_5 as a desiccant were almost equivalent with relative difference less than 0.12 %. Oven drying at 90 °C resulted in slight decrease of dry mass, while slight increases of dry mass were observed for 130 °C oven drying, However, their influence on the final mass fraction value was less than 0.6 %, relatively.

Table A7: Reported mass fractions of dried sample

NMI/DI	Dry mass fraction, f_{drymass} (g/g)	Standard deviation of f_{drymass} (g/g)	Subsample mass (g)	No. of subsamples	Drying method
GLHK	0.9877	0.0038	0.5	6	$CaSO_4$ desiccant, at least 7 days to achieve constant mass
	0.9849	0.0025	0.5	6	
	0.9858	0.0021	0.5	6	
HSA	0.9816	0.0025	0.5	3	P_2O_5 desiccant, 7 days
	0.9757	0.0019	0.5	3	
INMC	0.8915	0.0000	1.0	2	130 °C oven, 2 hours
INMETRO	0.9867	0.0015	0.5	6	90 °C oven, constant mass
INTI	0.9807	0.0024	0.5	4	P_2O_5 desiccant, 7 days
JSI	0.9823	0.0011	1.0	4	P_2O_5 desiccant, 7 days
KRISS	0.9833	0.0013	0.5	3	P_2O_5 desiccant, 7 days
	0.9825	0.0006	0.5	4	
LATU	0.9576	0.0028	0.5	3	P_2O_5 desiccant, 7 days
	0.9834	0.0024	0.5	3	

NMI/DI	Dry mass fraction, f_{drymass} (g/g)	Standard deviation of f_{drymass} (g/g)	Subsample mass (g)	No. of subsamples	Drying method
METAS	0.9776	0.0001	5.0	2	133 °C oven, 90 min
NIM	0.9817	0.0013	0.5	4	P_2O_5 desiccant, 7 days
NIMT	0.9741	0.0014	0.5	3	P_2O_5 desiccant, 7 days
NIS	0.9333	0.0013	1.0	3	P_2O_5 desiccant, 7 days
NMIA	0.9836	0.0015	0.5	6	P_2O_5 desiccant, 7 days
NMIJ	0.9815	0.0005	0.5	4	P_2O_5 desiccant, 7 days
NMISA	0.98539	0.00030	0.8	3	P_2O_5 desiccant, 7 days
PTB	0.9822	0.0034	0.8	8	P_2O_5 desiccant, at least 7 days to achieve constant mass

Participant Results

The results for CCQM-K158 Part A for the determination of copper, mercury, potassium, sodium, antimony, and lead are detailed in Tables A8-A13 and presented graphically in Figures A3-A8. In Table A8-A13, participant's result includes the degrees of freedom. The degrees of freedom were regarded as 60 for participants reporting the coverage factor of 2, when they were not specified by the participants.

Table A8: Reported results for Cu

Participating NMI/DI	Reported mass fraction (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)	Degrees of freedom
NIS	0.939	0.035	2	0.070	60
INTI	1.054	0.055	2	0.110	60
NIMT	1.322	0.020	2	0.040	60
HSA	1.352	0.015	2.36	0.036	8
KRISS	1.3640	0.0062	2.03	0.013	34
NMIJ	1.374	0.018	1.96	0.036	3084
LATU	1.381	0.020	2	0.040	60
NMISA	1.385	0.033	2	0.066	60
JSI	1.490	0.060	2	0.120	5

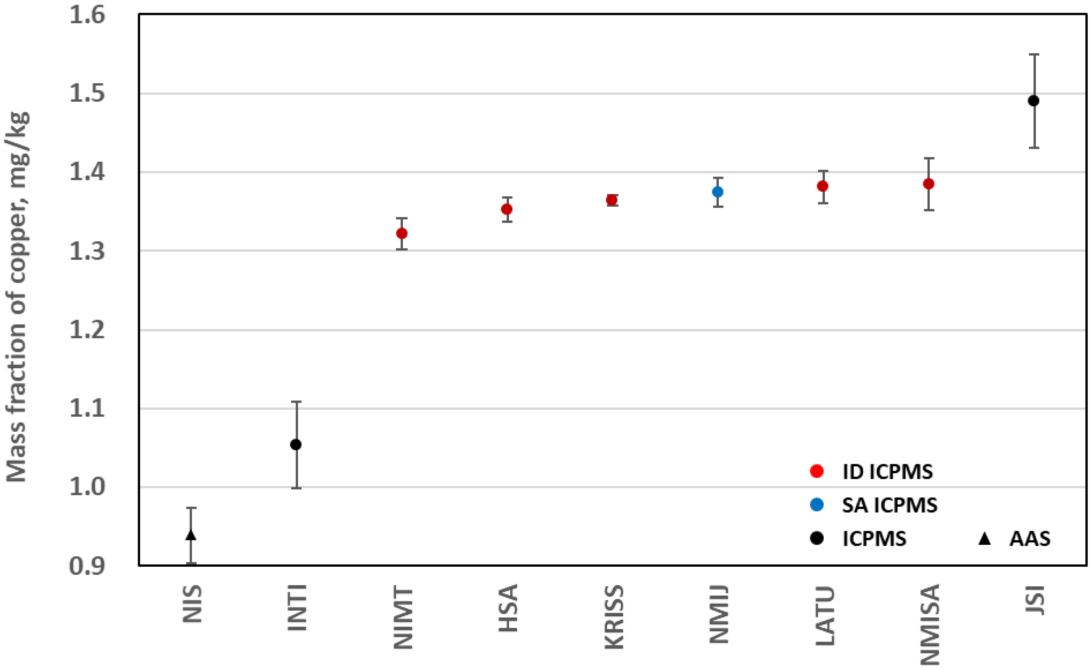


Figure A3: Reported results for Cu, mg/kg
error bar: reported standard uncertainty

Table A9: Reported results for Hg

Participating NMI/DI	Reported mass fraction (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)	Degrees of freedom
INTI	0.439	0.040	2	0.079	60
JSI	0.441	0.015	2	0.030	5
NMISA	0.456	0.006	2	0.012	60
GLHK	0.474	0.013	2	0.027	60
NMIA	0.478	0.010	2.18	0.022	12.4
NIM	0.483	0.006	2	0.013	60
HSA	0.4838	0.0032	2	0.0064	12
LATU	0.491	0.008	2	0.017	60
NIMT	0.497	0.005	2	0.010	60
KRISS	0.5016	0.0043	1.96	0.0084	717
NIS	1.116	0.038	2	0.075	60

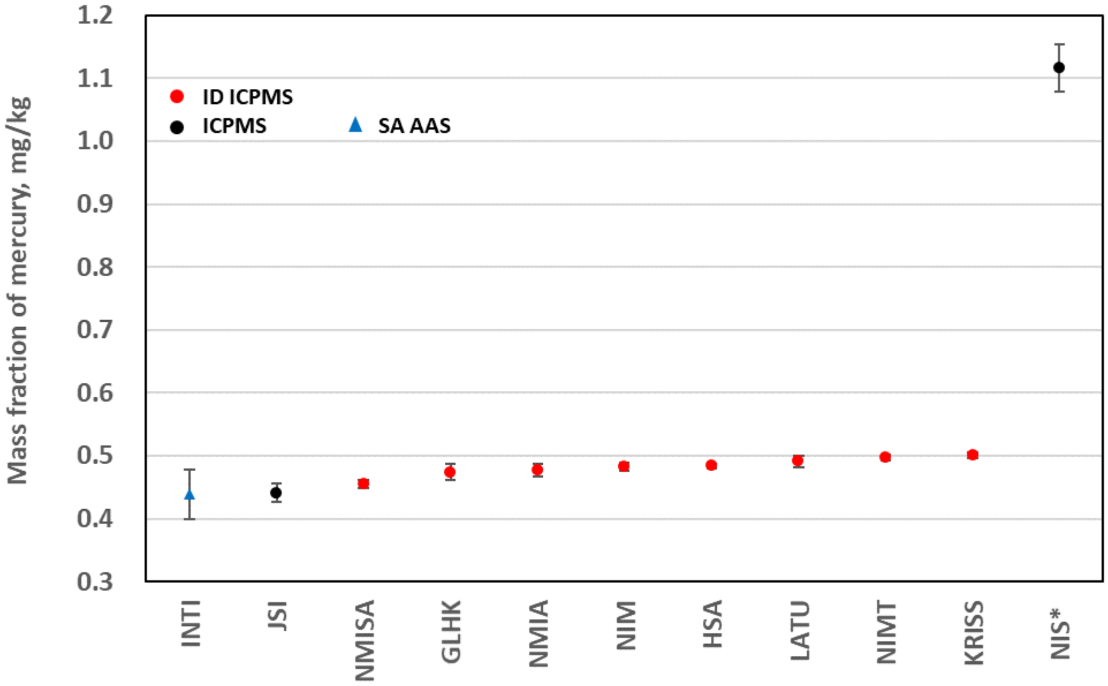


Figure A4: Reported results for Hg, mg/kg
error bar: reported standard uncertainty

Table A10: Reported results for K

Participating NMI/DI	Reported mass fraction (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)	Degrees of freedom
NIMT	539	21	2	43	60
NIS	541	40	2	79	60
NMISA	583	12	2	24	60
JSI	591	18	2.31	42	8
PTB	609.3	3.9	1.97	7.7	180
KRISS	613.6	1.9	1.97	3.7	230
INMC	617	12	1.97	24	238
NMIJ	617.2	8.2	1.96	16.1	77770000
LATU	622.0	7.8	2	15.6	60

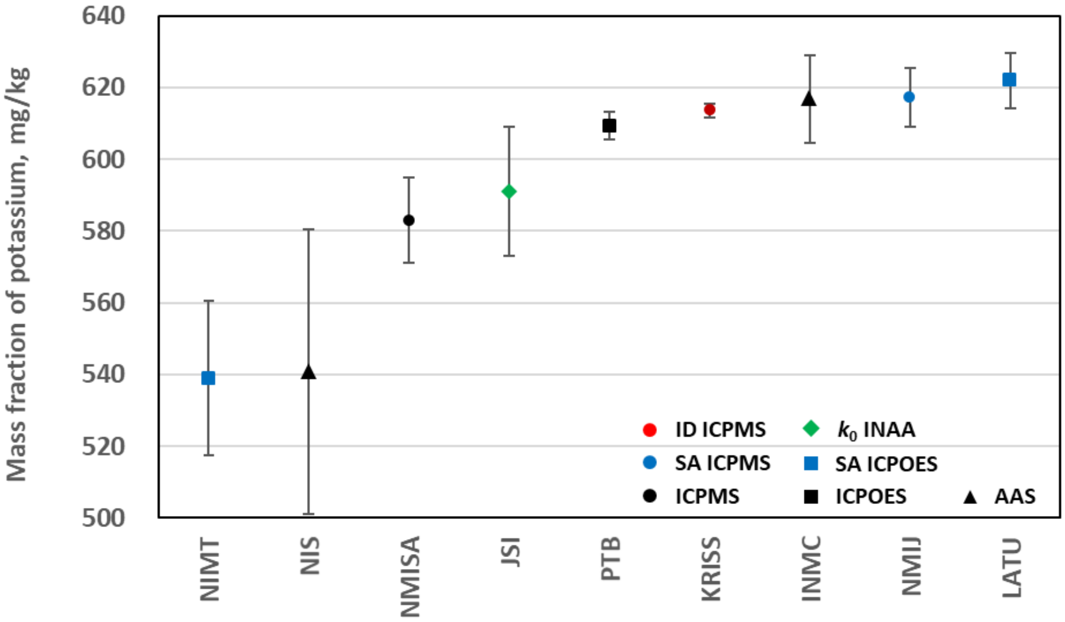


Figure A5: Reported results for K, mg/kg
error bar: reported standard uncertainty

Table A11: Reported results for Na

Participating NMI/DI	Reported mass fraction (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)	Degrees of freedom
NIS	3.66	0.12	2	0.24	60
JSI	5.25	0.16	2.31	0.37	8
KRISS	5.38	0.18	2.78	0.50	4
NMIJ	5.431	0.090	1.96	0.177	1905
NMISA	5.45	0.14	2	0.28	60
NIMT	8.75	0.44	2	0.88	60

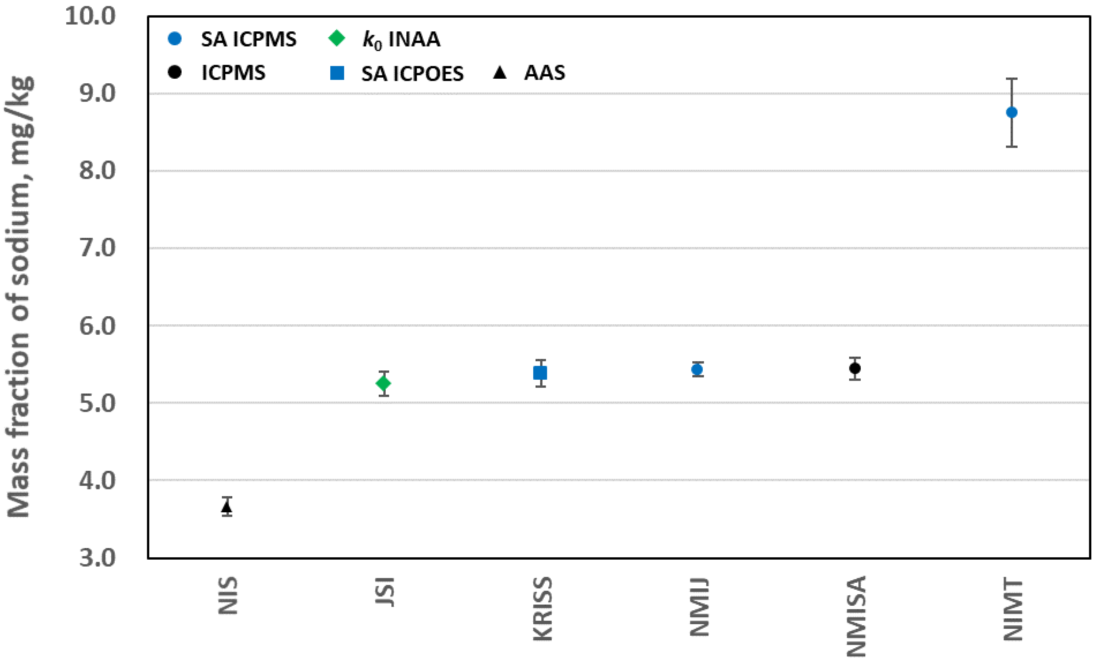


Figure A6: Reported results for Na, mg/kg

error bar: reported standard uncertainty

Table A12: Reported results for Pb

Participating NMI/DI	Reported mass fraction (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)	Degrees of freedom
NMISA	0.1570	0.0034	2	0.0068	60
INMC	0.183	0.014	1.97	0.028	238
METAS	0.198	0.005	2	0.010	60
JSI	0.204	0.006	2.57	0.015	5
GLHK	0.2146	0.0045	2	0.0090	60
NMIJ	0.2146	0.0028	2.01	0.0056	46
NIMT	0.215	0.003	2	0.006	60
HSA	0.2168	0.0043	2.00	0.0094	12
LATU	0.2181	0.0033	2	0.0066	60
KRISS	0.2186	0.0033	2.36	0.0078	7
PTB	0.2189	0.0022	2.05	0.0045	29
NIS	0.220	0.019	2	0.038	60
NIM	0.221	0.002	2	0.004	60
NMIA	0.2305	0.0036	2.36	0.0085	7.68
INTI	0.2415	0.0086	2	0.0172	60
INMETRO	0.2448	0.0047	2	0.0094	60

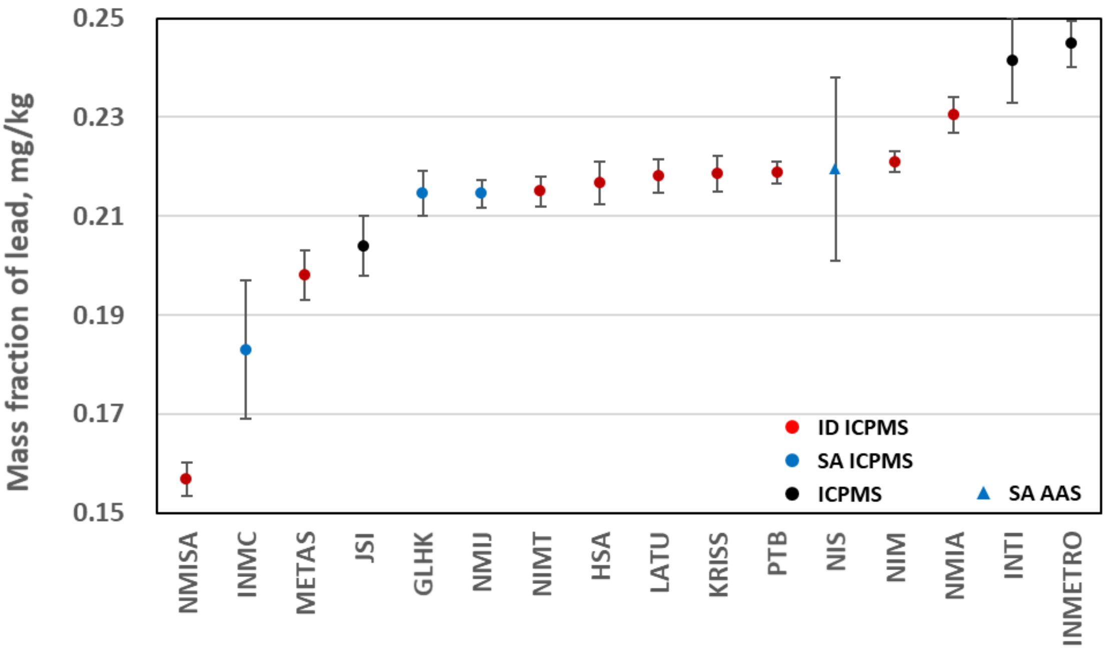


Figure A7: Reported results for Pb, mg/kg

error bar: reported standard uncertainty

Table A13: Reported results for Sb

Participating NMI/DI	Reported mass fraction (mg/kg)	Reported standard uncertainty (mg/kg)	Coverage factor, *k*	Expanded uncertainty (mg/kg)	Degrees of freedom
NIMT	0.939	0.021	2	0.042	60
JSI	0.946	0.033	2.31	0.076	8
INTI	0.999	0.038	2	0.076	60
GLHK	1.007	0.019	2	0.039	60
NMIA	1.011	0.018	2.07	0.037	23.6
KRISS	1.0115	0.0038	1.96	0.0074	1003
HSA	1.017	0.018	2.36	0.042	7
NMIJ	1.0217	0.0066	1.96	0.013	869

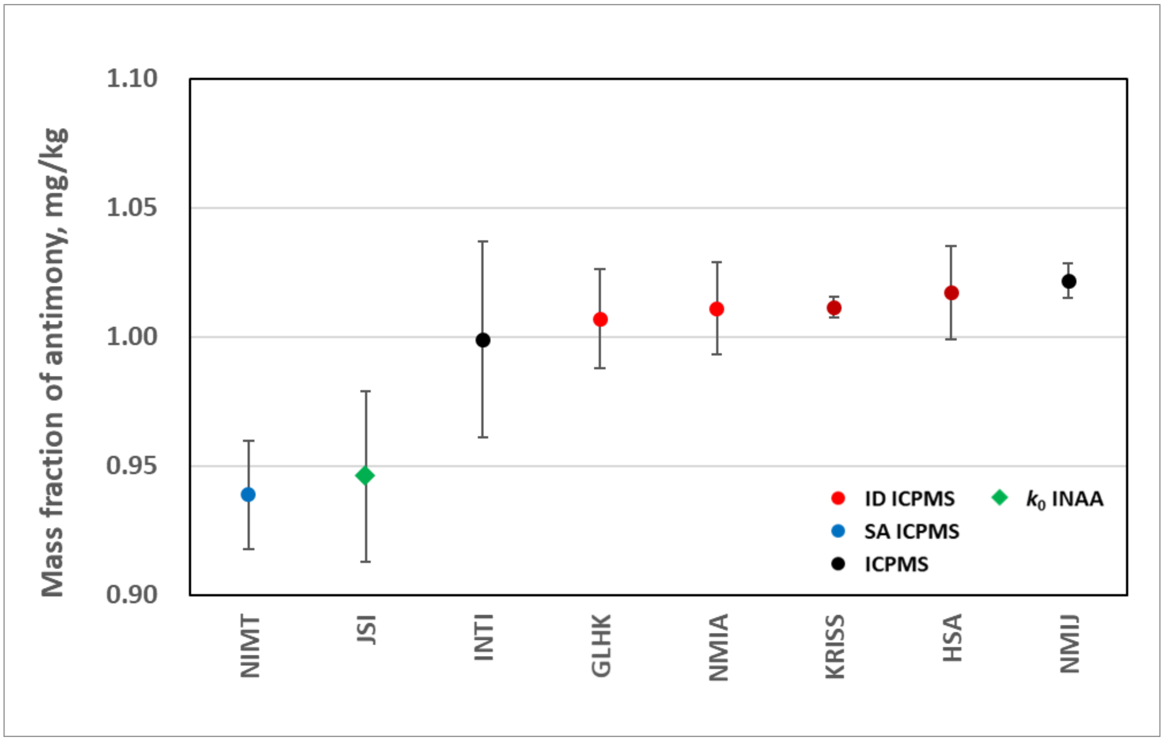


Figure A8: Illustrated reported results for Sb, mg/kg

error bar: reported standard uncertainty

Discussion of Results

Copper (Cu)

For copper, results obtained by ID ICP-MS and SA ICP-MS were narrowly distributed within ±3 %. NIS and INTI reported lower values and asked to review potential calculation errors or technical issues. NIS used electrothermal (ET) vaporization AAS with external calibration, while INTI used ICPMS with external calibration. Additionally, NIS carried out remeasurement and found that their originally reported result was biased. The new result of NIS was 1.389 mg/kg with standard uncertainty of 0.075 mg/kg. INTI couldn't find any technical issues that may cause bias in their result. Therefore, only the result from NIS was excluded for the calculation of key comparison reference value (KCRV).

Mercury (Hg)

Most of the participants used ID ICP-MS for mercury measurement and their results were distributed within ±5 %. NIS used hydride generation (HG) AAS with external calibration and reported about twice higher value than the median of participants' results. They were asked to investigate potential technical issues. They found calculation error and recalculated result was 0.513 mg/kg with standard uncertainty of 0.038 mg/kg, which is closer to the median value, and it was decided that their original result treated as the outlier after the IAWG discussions.

Potassium (K)

For potassium measurement, various analytical methods were used including ID ICP-MS, k_0-INAA, SA ICP-MS, SA ICP-OES, ICP-MS, ICP-OES, and AAS. Except for the results from NIMT and NIS, participants results were distributed within ±4 %. NIMT found that the quality control results were not consistent and agreed to exclude their result for the KCRV calculation. NIS found calculation error in the original result. It was agreed to treat it as the outlier. The recalculated result was 611 mg/kg with standard uncertainty of 40 mg/kg.

Sodium (Na)

Various analytical methods were used for sodium measurement including k_0-INAA, SA ICP-MS, SA ICP-OES, ICP-MS, and AAS. Four results were well-agreed within ±2 %, but those from NIS and NIMT were deviated more than 30 % from the median of the participants' results. NIS found that the original result was over-corrected the blank and reported revised value of 5.42 mg/kg with standard uncertainty of 0.16 mg/kg. NIMT found that the quality control results were not consistent and used commercial standard for the calibration. Both NIS and NIMT agreed to exclude their result for the KCRV calculation of sodium.

Lead (Pb)

ID ICPMS was the major analytical method used for lead measurement. Six ID ICP-MS results were well-matched within ±1.5 % from the median of ID ICP-MS results, but not all the ID ICP-MS results showed good agreements within stated uncertainties. The other analytical techniques used were SA ICP-MS, SA ICP-OES, ICP-MS methods. The overall participants' results were distributed in the range of ±20 %. No technical issues were found and all results were used for the KCRV calculation of lead.

Antimony (Sb)

The four ID ICP-MS results for antimony measurement were matched very well each other. The result obtained by k_0-INAA (JSI) and the NIMT's result using SA ICP-MS were slightly lower than the others. From the follow-up investigation, NIMT found a problem in the quality control experiment and agreed to exclude their result for the KCRV calculation. In October 2022, JSI re-investigated Sb content applying the k_0-INAA but using the new bottle No. 354 (during the study, bottle No. 341 was used). In the re-investigated study, three replicates were used, and an average mass fraction with a standard uncertainty of 1.006 mg/kg ± 0.036 mg/kg was obtained. This additional investigation of Sb content shows no significant differences with the reported value during the CCQM-K158 study.

KEY COMPARISON REFERENCE VALUE (KCRV)

The implementation of NIST decision tree (NDT) [1] for systematic choice of estimators of the KCRV and degrees of equivalence (DoEs) has been discussed in the IAWG. Using the NDT, version 1.0.4, the KCRV and associated uncertainty for each measurand was calculated. The NDT uses a series of statistical tests of hypotheses on the homogeneity, symmetry, and Gaussian distribution of a dataset to recommend the best statistical model for fitting the dataset. Then, the KCRV and its associated uncertainty, dark uncertainty (where applicable), and DoEs were estimated from the fitting based on the recommended statistical model. The detailed NDT reports including the statistical tests are in the appendix D.

The KCRVs proposed using the NDT are listed in Table A14 and graphically presented with participants' data in Figures A9-A14. The NDT recommended the Hierarchical Gauss + Gauss model for Cu, Hg, while the Adaptive Weighted Average model was chosen for K, Na, and Sb. For Pb, the Hierarchical Laplace + Gauss model was recommended. Dark uncertainties were relatively small or negligible for K, Na, and Sb compared with those for Hg, Cu, and Pb (appendix D).

Table A14: Key Comparison Reference Values proposed by using the NIST decision tree

Measurand	Estimator	*KCRV* (mg/kg)	$u(KCRV)$ (mg/kg)	$U_{95}(KCRV)$ (mg/kg)
Cu	Hierarchical Gauss + Gauss	1.345	0.030	0.061
Hg	Hierarchical Gauss + Gauss	0.4788	0.0059	0.0117
K	Adaptive Weighted Average	611.6	3.3	6.3
Na	Adaptive Weighted Average	5.399	0.064	0.125
Pb	Hierarchical Laplace + Gauss	0.2166	0.0030	0.0061
Sb	Adaptive Weighted Average	1.0130	0.0050	0.0100

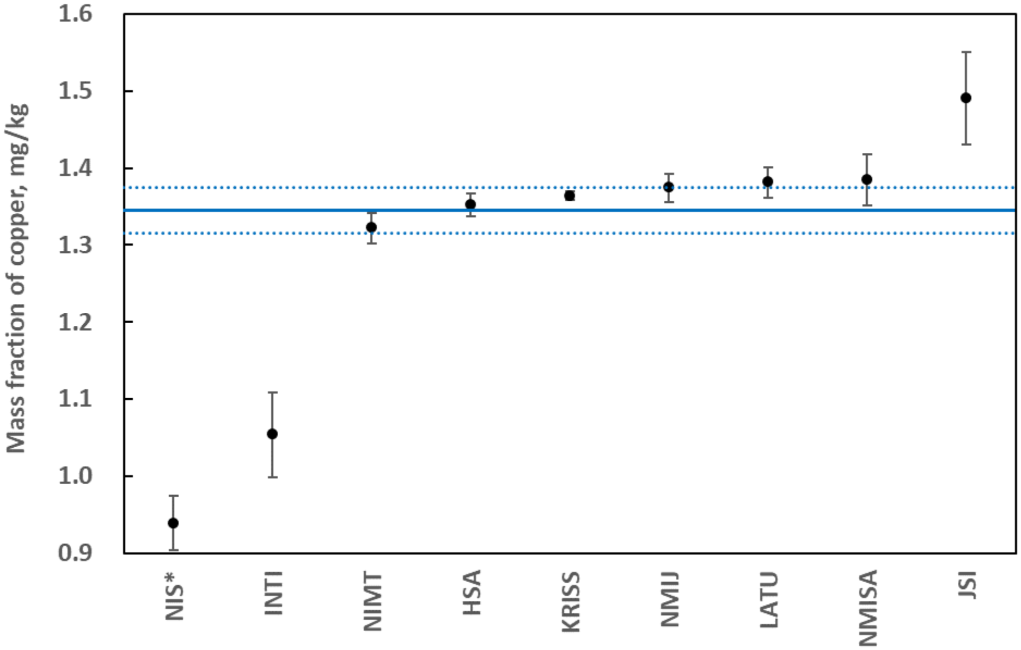


Figure A9: Reported results with KCRV for Cu, mg/kg
error bar: reported standard uncertainty, solid line: KCRV, dash lines: standard uncertainty of KCRV, symbol *: indicates reported result excluded from the KCRV calculation

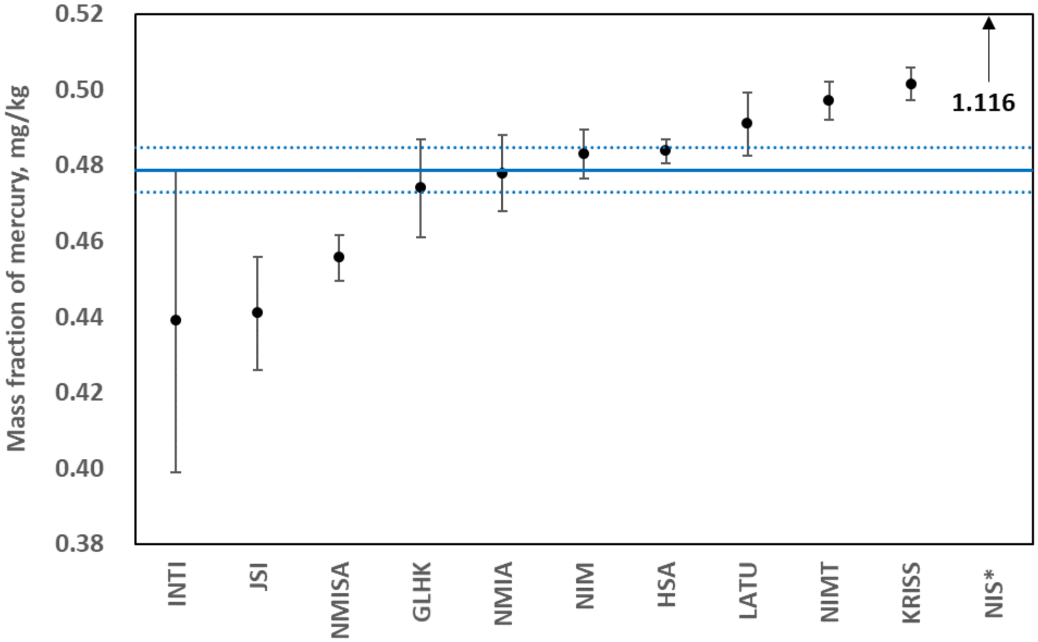


Figure A10: Reported results with KCRV for Hg, mg/kg
error bar: reported standard uncertainty, solid line: KCRV, dash lines: standard uncertainty of KCRV, symbol *: indicates reported result excluded from the KCRV calculation

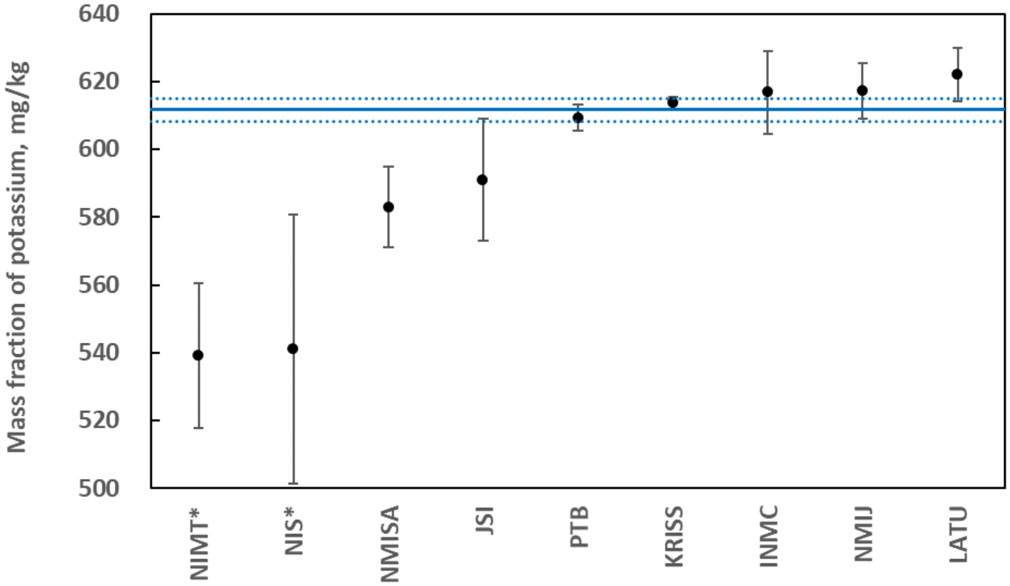


Figure A11: Reported results with KCRV for K, mg/kg
error bar: reported standard uncertainty, solid line: KCRV, dash lines: standard uncertainty of KCRV, symbol *: indicates reported result excluded from the KCRV calculation

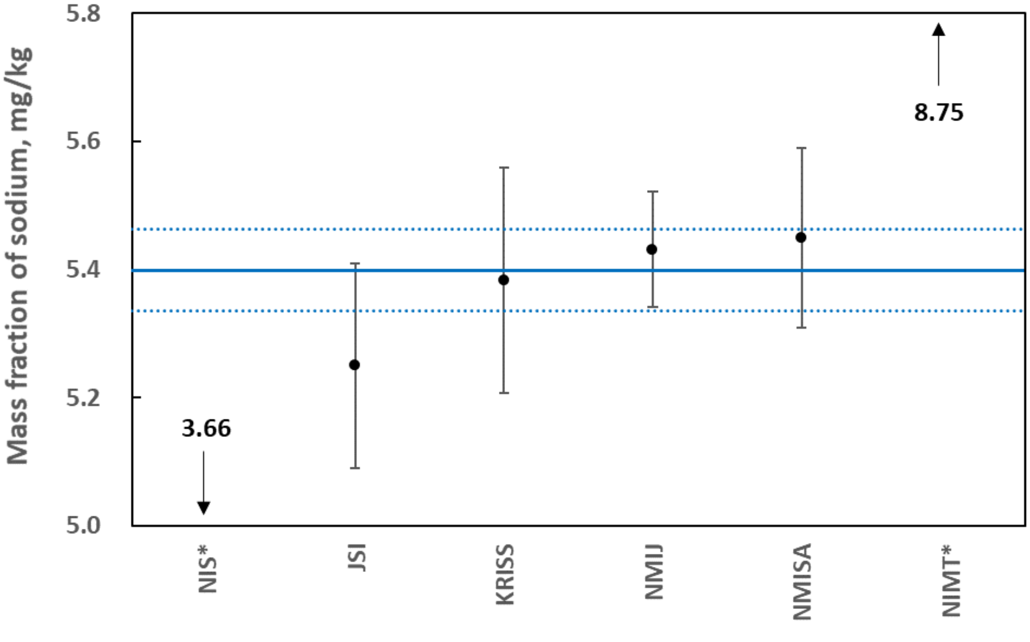


Figure A12: Reported results with KCRV for Na, mg/kg
error bar: reported standard uncertainty, solid line: KCRV, dash lines: standard uncertainty of KCRV, symbol *: indicates reported result excluded from the KCRV calculation

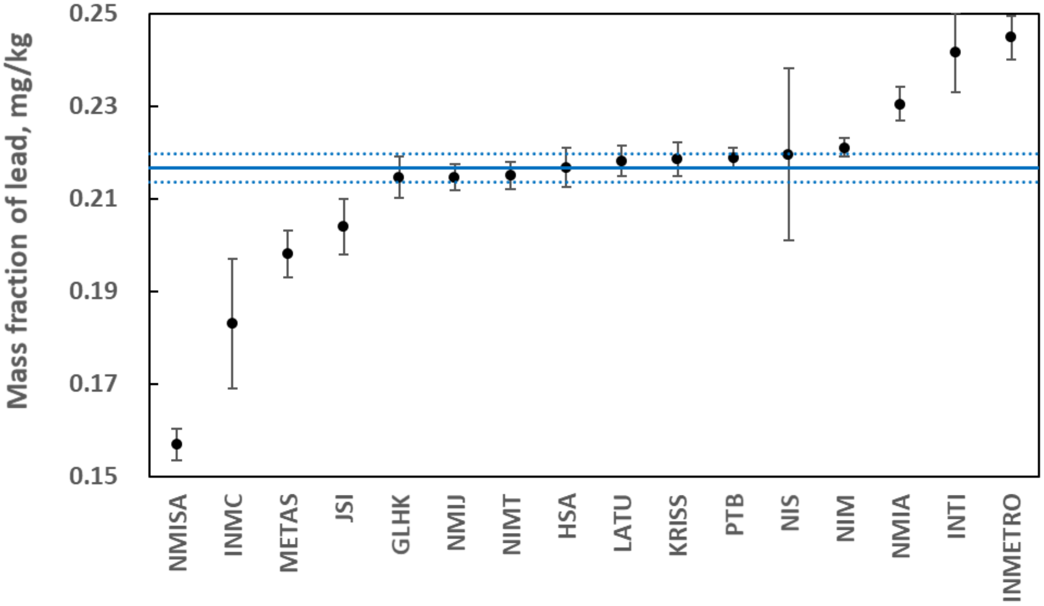


Figure A13: Reported results with KCRV for Pb, mg/kg
error bar: reported standard uncertainty, solid line: KCRV,
dash lines: standard uncertainty of KCRV

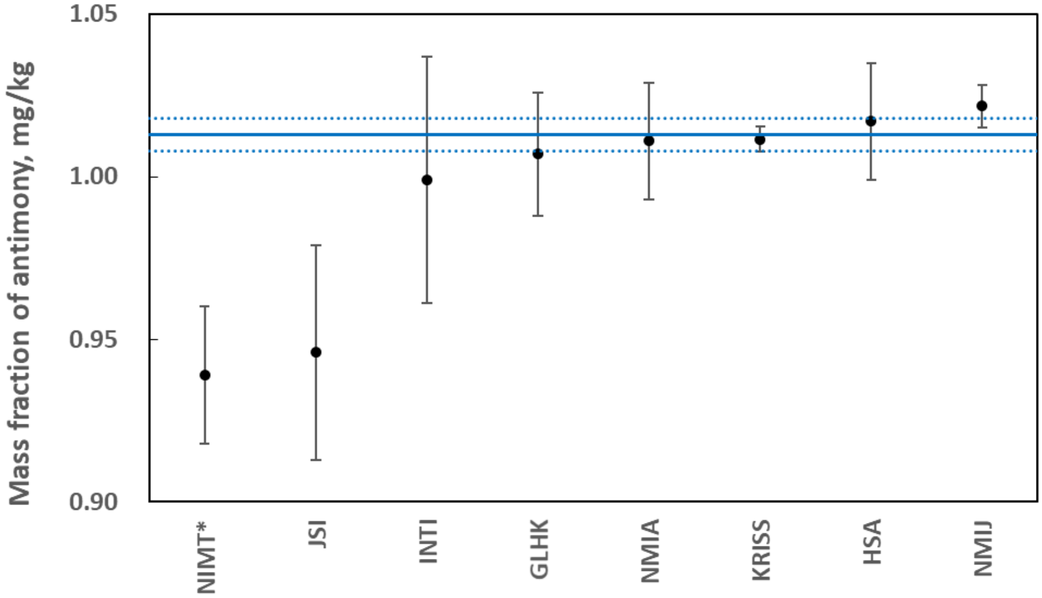


Figure A14: Reported results with KCRV for Sb, mg/kg
error bar: reported standard uncertainty, solid line: KCRV, dash lines: standard uncertainty of KCRV, symbol *: indicates reported result excluded from the KCRV calculation

DEGREES OF EQUIVALENCE (DoE)

The absolute DoEs for the participants in CCQM-K158 Part A are estimated as the signed difference between the participant's result (x_i) and the KCRV: $D_i = x_i - \text{KCRV}$. They are listed in Tables A15-A20 and graphically shown in Figures A15-A20. For the NDT procedures used to estimate the KCRVs, the expanded uncertainty of D_i, $U(D_i)$, is half the shortest interval centered on D_i that is believed to encompass the true value with 95 % probability, where the endpoints of the interval are derived directly from a large sample drawn from the corresponding probability distribution. Therefore, the error bars in the plots represent the expanded uncertainties of D_i at 95 % confidence level, $U(D_i)$. In these figures, the horizontal line denotes perfect agreement with the KCRV, the black dot represents the D_i value, and the uncertainty bars represent $U(D_i)$.

Table A15: Degrees of Equivalence for Cu

NMI/DI	Reported mass fraction, x_i (mg/kg)	Standard uncertainty, u_i (mg/kg)	Difference from KCRV, D_i (mg/kg)	Expanded uncertainty of the difference, $U(D_i)$ (mg/kg)	$D_i/U(D_i)$
NIS*	0.939	$0.088^{\#}$	-0.406	0.213	-1.90
INTI	1.054	$0.097^{\#}$	-0.291	0.229	-1.27
NIMT	1.322	0.020	-0.023	0.072	-0.32
HSA	1.352	0.015	0.007	0.070	0.10
KRISS	1.3640	0.0062	0.0188	0.0625	0.30
NMIJ	1.374	0.018	0.029	0.070	0.41
LATU	1.381	0.020	0.036	0.072	0.50
NMISA	1.385	0.033	0.040	0.089	0.45
JSI	1.490	0.060	0.145	0.156	0.93

The symbol * indicates reported result excluded from the KCRV calculation.

The values with symbol # are the participant's reported uncertainty and the dark uncertainty, τ, summed in quadrature.

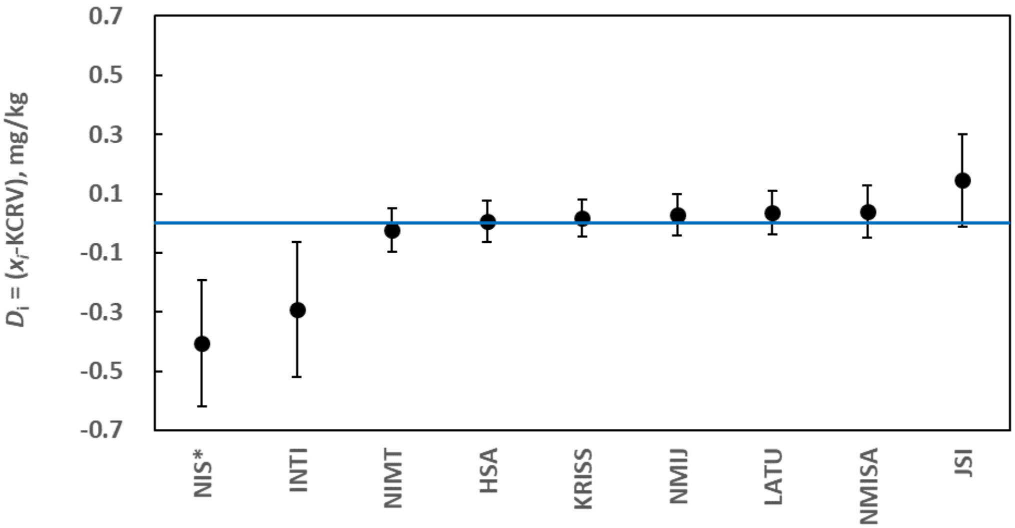


Figure A15: Degrees of Equivalence for Cu associated with the KCRV

Dots represent the D_i, error bars their approximate 95 % expanded uncertainties, $U(D_i)$. The blue horizontal line denotes perfect agreement with the KCRV. The symbol * indicates reported result excluded from the KCRV calculation.

Table A16: Degrees of Equivalence for Hg

NMI/DI	Reported mass fraction, x_i (mg/kg)	Standard uncertainty, u_i (mg/kg)	Difference from KCRV, D_i (mg/kg)	Expanded uncertainty of the difference, $U(D_i)$ (mg/kg)	$D_i/U(D_i)$
INTI	0.439	0.040	-0.040	0.080	-0.49
JSI	0.441	0.015	-0.038	0.040	-0.96
NMISA	0.456	0.017#	-0.023	0.040	-0.58
GLHK	0.474	0.013	-0.005	0.028	-0.17
NMIA	0.478	0.010	-0.001	0.024	-0.03
NIM	0.4830	0.0064	0.0042	0.0172	0.24
HSA	0.4838	0.0032	0.0050	0.0137	0.36
LATU	0.4910	0.0084	0.0122	0.0205	0.60
NIMT	0.4970	0.0171#	0.0182	0.0398	0.46
KRISS	0.5016	0.0169#	0.0228	0.0396	0.58
NIS*	1.116	0.0409#	0.6372	0.0831	7.66

The symbol * indicates reported result excluded from the KCRV calculation.

The values with symbol # correspond to uncertainties including contribution of dark uncertainty.

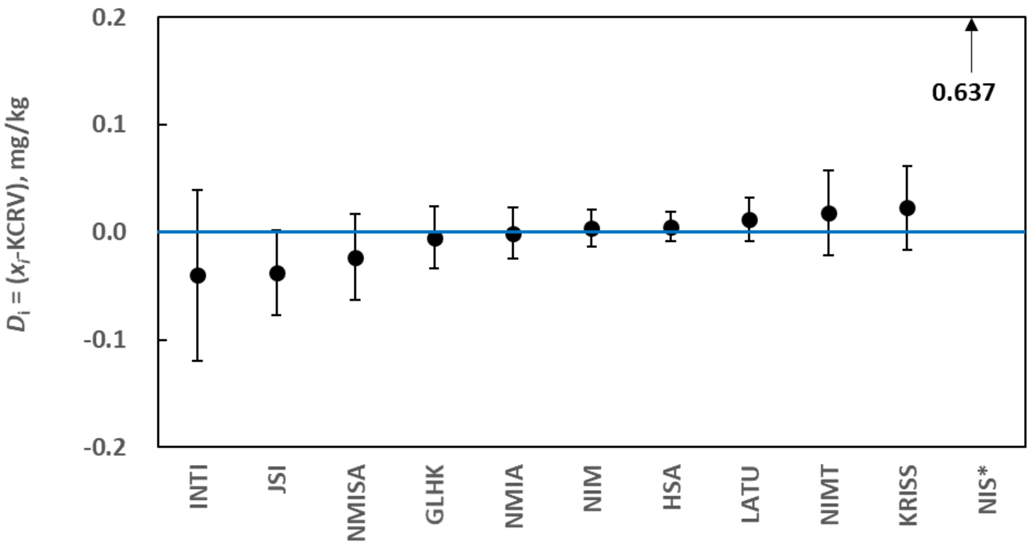


Figure A16: Degrees of Equivalence for Hg associated with the KCRV

Dots represent the D_i, error bars their approximate 95 % expanded uncertainties, $U(D_i)$. The blue horizontal line denotes perfect agreement with the KCRV. The symbol * indicates reported result excluded from the KCRV calculation.

Table A17: Degrees of Equivalence for K

NMI/DI	Reported mass fraction, x_i (mg/kg)	Standard uncertainty, u_i (mg/kg)	Difference from KCRV, D_i (mg/kg)	Expanded uncertainty of the difference, $U(D_i)$ (mg/kg)	$D_i/U(D_i)$
NIMT*	539	$22^{\#}$	-72.6	43.5	-1.67
NIS*	541	40	-70.7	77.9	-0.91
NMISA	583	$13^{\#}$	-28.6	25.2	-1.14
JSI	591	18	-20.6	34.1	-0.60
PTB	609.3	3.9	-2.3	6.7	-0.34
KRISS	613.6	1.9	2.0	4.2	0.48
INMC	617	12	5.2	23.6	0.22
NMIJ	617.2	8.2	5.6	15.2	0.37
LATU	622.0	7.8	10.4	14.6	0.72

The symbol * indicates reported result excluded from the KCRV calculation.

The values with symbol $^{\#}$ correspond to uncertainties including contribution of dark uncertainty.

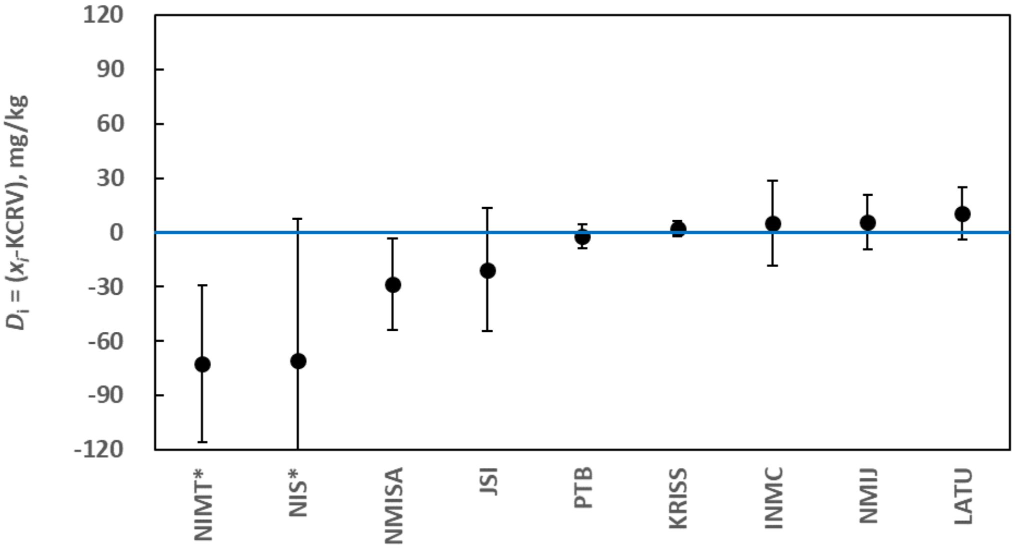


Figure A17: Degrees of Equivalence for K associated with the KCRV

Dots represent the D_i, error bars their approximate 95 % expanded uncertainties, $U(D_i)$. The blue horizontal line denotes perfect agreement with the KCRV. The symbol * indicates reported result excluded from the KCRV calculation.

Table A18: Degrees of Equivalence for Na

NMI/DI	Reported mass fraction, x_i (mg/kg)	Standard uncertainty, u_i (mg/kg)	Difference from KCRV, D_i (mg/kg)	Expanded uncertainty of the difference, $U(D_i)$ (mg/kg)	$D_i/U(D_i)$
NIS*	3.66	$0.12^{\#}$	-1.74	0.27	-6.42
JSI	5.25	0.16	-0.15	0.29	-0.52
KRISS	5.38	0.18	-0.02	0.33	-0.06
NMIJ	5.431	0.090	0.031	0.162	0.19
NMISA	5.45	0.14	0.05	0.24	0.21
NIMT*	8.75	$0.44^{\#}$	3.35	0.87	3.84

The symbol * indicates reported result excluded from the KCRV calculation.

The values with symbol # correspond to uncertainties including contribution of dark uncertainty.

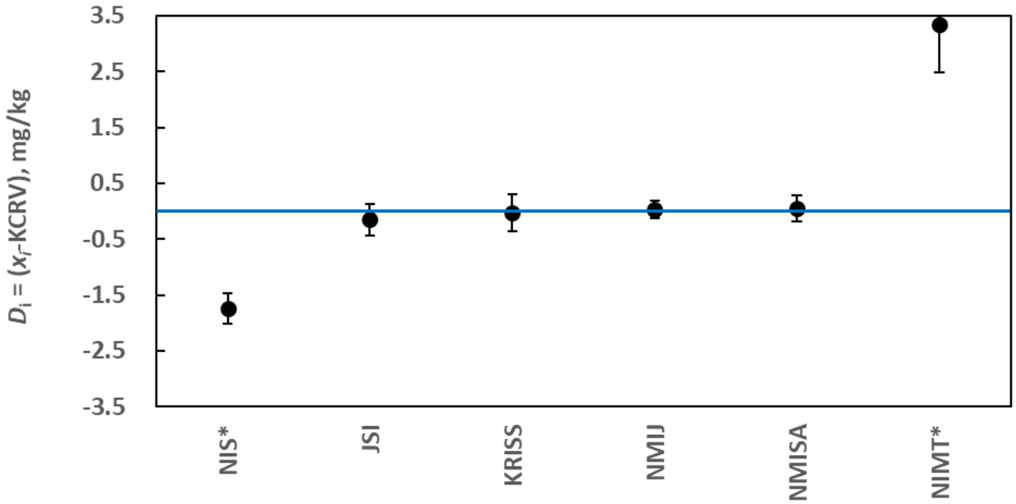


Figure A18: Degrees of Equivalence for Na associated with the KCRV

Dots represent the D_i, error bars their approximate 95 % expanded uncertainties, $U(D_i)$. The blue horizontal line denotes perfect agreement with the KCRV. The symbol * indicates reported result excluded from the KCRV calculation.

Table A19: Degrees of Equivalence for Pb

NMI/DI	Reported mass fraction, x_i (mg/kg)	Standard uncertainty, u_i (mg/kg)	Difference from KCRV, D_i (mg/kg)	Expanded uncertainty of the difference, $U(D_i)$ (mg/kg)	$D_i/U(D_i)$
NMISA	0.1570	0.0170$^{\#}$	-0.0596	0.0372	-1.60
INMC	0.183	0.022$^{\#}$	-0.0336	0.0460	-0.73
METAS	0.198	0.018$^{\#}$	-0.0186	0.0382	-0.49
JSI	0.204	0.006	-0.0126	0.0154	-0.82
GLHK	0.2146	0.0045	-0.0016	0.0099	-0.16
NMIJ	0.2146	0.0028	-0.0016	0.0085	-0.19
NIMT	0.215	0.003	-0.0016	0.0085	-0.19
HSA	0.2168	0.0043	0.0004	0.0105	0.04
LATU	0.2181	0.0033	0.0014	0.0085	0.16
KRISS	0.2186	0.0033	0.0024	0.0109	0.22
PTB	0.2189	0.0022	0.0024	0.0073	0.33
NIS	0.220	0.019	0.0034	0.0379	0.09
NIM	0.221	0.002	0.0044	0.0072	0.60
NMIA	0.2305	0.0173$^{\#}$	0.0134	0.0383	0.35
INTI	0.2415	0.0190$^{\#}$	0.0254	0.0412	0.62
INMETRO	0.2448	0.0175$^{\#}$	0.0284	0.0386	0.74

The symbol * indicates reported result excluded from the KCRV calculation.

The values with symbol $^{\#}$ correspond to uncertainties including contribution of dark uncertainty.

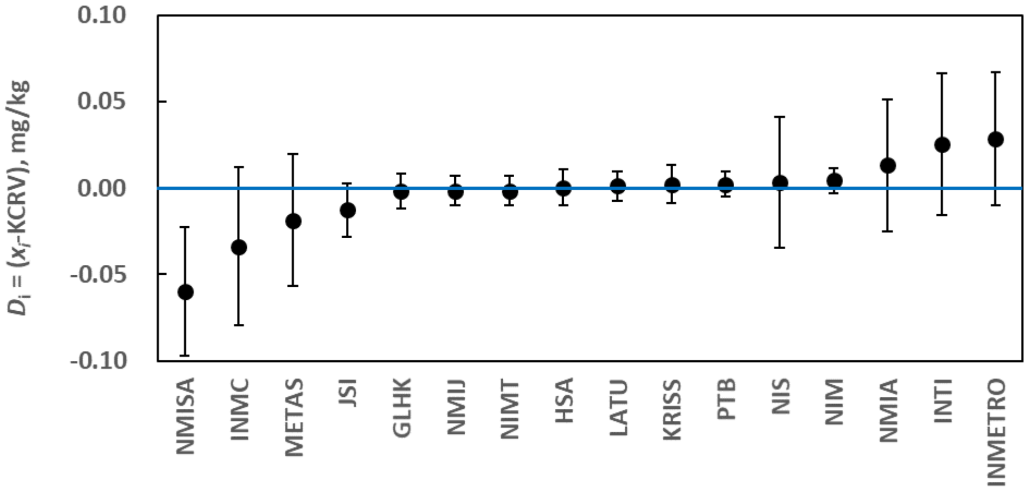


Figure A19: Degrees of Equivalence for Pb associated with the KCRV

Dots represent the D_i, error bars their approximate 95 % expanded uncertainties, $U(D_i)$. The blue horizontal line denotes perfect agreement with the KCRV.

Table A20: Degrees of Equivalence for Sb

NMI/DI	Reported mass fraction, x_i (mg/kg)	Standard uncertainty, u_i (mg/kg)	Difference from KCRV, D_i (mg/kg)	Expanded uncertainty of the difference, $U(D_i)$ (mg/kg)	$D_i/U(D_i)$
NIMT*	0.939	0.021$^\#$	-0.0743	0.0425	-1.75
JSI	0.946	0.033$^\#$	-0.0673	0.0638	-1.05
INTI	0.999	0.038	-0.0143	0.0725	-0.20
GLHK	1.007	0.019	-0.0063	0.0358	-0.18
NMIA	1.011	0.018	-0.0023	0.0340	-0.07
KRISS	1.0115	0.0038	-0.0017	0.0081	-0.21
HSA	1.017	0.018	0.0037	0.0332	0.11
NMIJ	1.0217	0.0066	0.0084	0.0114	0.74

The symbol * indicates reported result excluded from the KCRV calculation.
The values with symbol $^\#$ correspond to uncertainties including contribution of dark uncertainty.

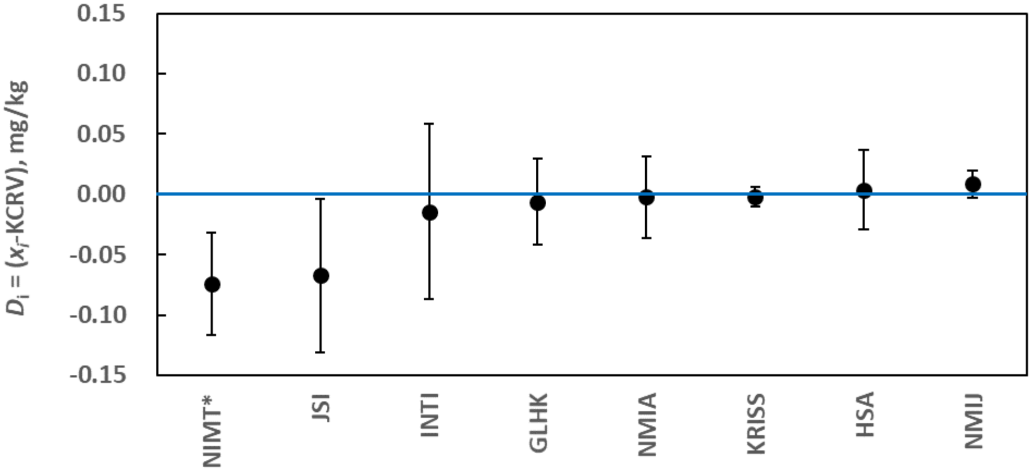


Figure A20: Degrees of Equivalence for Sb associated with the KCRV

Dots represent the D_i, error bars their approximate 95 % expanded uncertainties, $U(D_i)$. The blue horizontal line denotes perfect agreement with the KCRV. The symbol * indicates reported result excluded from the KCRV calculation.

USE OF CCQM K158 PART A IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

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

Successful participation in CCQM-K158 Part A demonstrates measurement capabilities in determining mass fractions of alkali and alkaline earth (K, Na), transition (Cu, Hg, Pb), and metalloid/semi-metal (Sb) elements in mass fraction range from 0.1 mg/kg to 700 mg/kg, which are above 50 µg/kg, in high organic content matrix including grains, beans, and related samples.

Core Capability Table

The measurement space covered by the present study is shown in Table A21 as a part of the IAWG core capability table.

Table A21: Selected IAWG Core Capability Table for CCQM-K158 Part A

Analyte groups	**Matrix challenges**			
	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, …)**
Group I and II: Alkali and Alkaline earth (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba)				
				K158 (K, 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)				
				K158 (Cu, Hg, Pb)
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)				
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)				
				K158 (Sb)
Non-metals (P, S, C, N, O)				
Halogens (F, Cl, Br, I)				
Rare Earth Elements				

(Lanthanides, Actinides)				
Inorganic species (elemental, anions, cations)				
Small organo-metallics				

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

CCQM-K158 Part B

TIMELINE

Table B1 lists the timeline for CCQM-K158 Part B.

Table B1: Timeline for CCQM-K158 Part B

Date	Action
April, 2018	Proposed to CCQM
Oct., 2018	Draft protocol presented to IAWG
April, 2019	IAWG authorized CCQM-K158 Part A & Part B
Feb., 2021	Call for participation to IAWG members
April to May, 2021[*1]	Study samples shipped to participants. The range in shipping times reflects delays from shipping and customs.
March, 2022[*2]	Results due to coordinating laboratory.
April, 2022	Frist discussion in IAWG
Oct to Nov.2022	Second discussion in IAWG, especially for estimating key comparison reference value (KCRV) using NIST decision tree model.
Sep., 2023	Draft A report for Part B distributed to participants
Sep., 2024	Draft A report (Part A & B merged) distributed to participants
Nov., 2024	Draft B report (Part A & B merged) distributed to IAWG
Dec., 2024	Final report approved by IAWG

[*1] National Institute of Standards (NIS, Egypt) received the sample in Dec., 2021, due to delay a custom operation at the airport.

[*2] the reporting deadline had been set at the end of September 2021, but it was extended several times under the COVID-19 pandemic situation. The deadline was finally extended to the end of March 2022.

MEASURANDS

The measurands in Part B are the mass fractions (as As) of total arsenic and inorganic arsenic (As(III) + As(V)). Participation in total arsenic alone was allowed but participation only in inorganic arsenic was not allowed, because participation in total arsenic is mandatory to allow discussion about the extraction efficiencies of inorganic arsenic.

STUDY MATERIALS

The comparison material was polished rice flour, powdering with a freeze-pulverization. The powder was placed into amber glass bottles (20 g each) by using a split method and was sterilized with γ-ray irradiation (^{60}Co, 20 kGy). The bottles were individually vacuum sealed into aluminum bags. The bottles were stored at room temperature.

Each participant received a bottle containing approximately 20 g with the following information: the material containing >0.02 mg/kg of total As and i-As (natural level, no compounds were spiked). The among-bottles homogeneity of the material was <1 % (relative standard deviation) both for total arsenic and inorganic arsenic (As(III) + As(V)), according to the analysis of three subsamples (ca. 0.5 g) taken from each of 10 bottles. The sample after receipt should be kept at laboratory room temperature.

From the point of homogeneity, 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

The moisture content of the rice flour sample should be measured by taking subsamples before and after the subsampling for analyses. The recommended procedure was to dry the sample to constant mass in a desiccator with fresh P_2O_5 at room temperature for at least 7 days. Participant might check if constant mass was reached by extending the drying one more week. A sample size of 0.5 g or more was recommended for the determination of moisture content. The elemental contents determined should be reported on the dry mass basis.

Homogeneity Assessment of Study Material

The homogeneity of the study material was evaluated by one-way ANOVA using data set by analyzing 10 bottles selected from 650 bottles by stratified random sampling. The sample size through the experiment was ca. 0.5 g for both total and inorganic arsenic. The analytical procedures were as follows; for total arsenic, the sample was digested with the mixture of nitric acid, hydrogen peroxide, and hydrofluoric acid using a microwave digestion system. The mass fraction of arsenic was determined by using ICP-MS with a Helium collision mode. For inorganic arsenic, arsenic compounds were thermostatically extracted with a diluted nitric acid at 100 °C using a heat block system. The mass fraction of inorganic arsenic compounds was determined by using an ion-pair chromatograph hyphenated with ICP-MS detection with a helium collision mode.

In the one-way ANOVA, within-bottle mean square (MS_{within}) and between-bottle mean square (MS_{among}) were calculated, then the between-bottle standard deviation (s_{bb}) and the possible between-bottle standard deviation estimated from the influence of analytical repeatability (u_{bb}) were calculated by the following equation (1) and (2) in accordance with ISO Guide 35: 2017.

$$s_{\mathrm{bb}} = \sqrt{\frac{MS_{\mathrm{among}} - MS_{\mathrm{within}}}{n}} \qquad (1)$$

$$u_{\mathrm{bb}} = \sqrt{\frac{MS_{\mathrm{within}}}{\mathrm{n}}}\sqrt[4]{\frac{2}{\nu_{MS_{\mathrm{within}}}}} \qquad (2)$$

In Eq. (2), n is the harmonized mean of analyzed subsample number, and $\nu_{MS_{within}}$ the degree of freedom of MS_{within}.

Table B2: Results of the homogeneity assessment for total and inorganic arsenic in polished rice flour material

Measurand	ANOVA test		Relative standard uncertainties of inhomogeneity, u_{bb} (%)
	F-statistics	F-critical	
Total arsenic	0.65	2.39	0.16
Inorganic arsenic	0.84	2.39	0.16

The values of s_{bb} were invalid for total and inorganic arsenic, and the values of u_{bb} were 0.16 % for total arsenic and 0.16 % for inorganic arsenic. This homogeneity is acceptable for this comparison study because a typical uncertainty of the analytical results for total and inorganic arsenic would be expected around 1 %.

The study material was presumed to be stable at least for 5 years for total and inorganic arsenic analysis under a storage temperature from 5 ℃ to 35 ℃, estimating from the results of the long-term (five years) stability test of NMIJ CRM 7503-a white rice flour, of which the preparation condition is the same as this study material.

PARTICIPANTS, INSTRUCTIONS AND SAMPLE DISTRIBUTION

The call for participation was distributed in Feb. 2021 with the intent to distribute samples in March to May 2021. Table 3 lists the institutions that registered for CCQM-K158 Part B. The sample was dispatched on March 31, 2021, and all the institute, except for NIS, were received by the middle of April 2021. NIS received the sample in Dec., 2021, due to delay a custom operation at the airport. See Table 1 for study timeline. Appendix A reproduces the Call for Participation and the study Protocol.

Table B3: Institutes Receiving CCQM-K158B Sample Materials

Participating NMI/DI	Code	Country	Contact
National Measurement Laboratory, LGC	NML/LGC	United Kingdom	Heidi Goenaga-Infante
National Research Council Canada	NRC	Canada	Patricia Grinberg
National Institute of Metrology (Thailand)	NIMT	Thailand	Nattikarn Ornthai
Government Laboratory Hong Kong	GLHK	Hong Kong, China	TONG Siu-kuen

Participating NMI/DI	Code	Country	Contact
Health Sciences Authority	HSA	Singapore	Richard Shin
Korea Research Institute of Standards and Science	KRISS	Korea	Yong-Hyeon Yim / Kyoung-Seok Lee
Laboratorio Tecnológico del Uruguay	LATU	Uruguay	Ramiro Pérez Zambra / Romina Napoli
Federal Institute of Metrology	METAS	Switzerland	Silvia Mallia
National Measurement Institute, Australia	NMIA	Australia	Jeffrey Merrick
Jožef Stefan Institute	JSI	Slovenia	Radojko Jaćimović
National Metrology Institute of Japan	NMIJ/AIST	Japan	Kazumi Inagaki / Tomoko Ariga
Instituto Nacional de Tecnología Industrial	INTI	Argentina	Osvaldo Acosta / Mabel Puelles
National Institute of Metrology, China	NIM	China	LI Xiao / Ma Qian
National Institute of Standards	NIS	Egypt	Randa N. Yamani
National Metrology Institute of South Africa	NMISA	South Africa	Angelique Botha

The reporting deadline had been set at the end of September 2021, but it had to be extended three times under the COVID-19 pandemic situation. First extension was to the end of October 2021, due to a hard lockdown of some institutes for several months. Second extension was to the end of February 2022, due to the significant delay in the sample receipt of NIS. The final extension was to the end of March 2022, due to delay in shipment of a consumable part for an instrument to NIS under the COVID-19 pandemic situation.

All the results, except for NMISA and NIS, were reported by the end of Feb. 2022. NMISA did not report their results because they found technical issues in their analysis and had not been able to solve them by the final reporting deadline; for the total arsenic quantification, their measurement results maintained a positive bias and read consistently higher than the certified value of NMISA CRM. For the inorganic arsenic, they had to develop the method for a new measurement system, and finally managed to the separation of arsenic species in the chromatography, but their sample was depleted and could not be completed the measurements for the accurate quantification of the inorganic arsenic. NIS also did not report their result for total arsenic because the measured results were near the instrument detection limit and the dispersion of the measurement results was extremely high.

First reporting of the results was done at the spring IAWG meeting on the web in April 2022, and the discussion regarding the estimation of the key comparison reference value including the adaptation of the NIST decision tree model was done at the fall IAWG meeting on the web in Nov. 2022.

RESULTS

Participants were requested to report a single estimate of the mass fraction [mg kg^{-1} as As] for total arsenic (mandatory) and inorganic arsenic (selective). In addition to the quantitative results, participants were instructed to describe their analytical methods and approach to uncertainty estimation. Appendix C reproduces the report form.

The results were reported from thirteen of the fifteen institutions that received samples.

Methods Used by Participants for total arsenic quantification

The measurement methods were left free to be selected by the participant institutes. The analytical techniques adopted by the participants were summarized in Table B4 and B5.

Except for JSI, all the participants used ICP-MS with a microwave assisted digestion. JSI used k_0-INAA with an internal standard.

Table B4: Conditions of sample pretreatment for total As

Participating NMI/DI	Pretreatment technique	Reagents	Sample amount & dilution
LGC	Closed MW digestion	HNO_3, H_2O_2	sample 0.5 g → solution 50 g
NRC	Closed MW digestion	HNO_3, H_2O_2	sample 0.5 g → solution 40 g
NIMT	Closed MW digestion	HNO_3, H_2O_2	sample 0.2 g → solution 40 g
GLHK	Closed MW digestion	HNO_3, H_2O_2	sample 0.5 g → solution 50 g
HSA	Closed MW digestion	HNO_3, HF, H_2O_2	sample 0.5 g → solution 50 g
KRISS	Closed MW digestion	HNO_3	sample 1 g → solution 25 g
LATU	Closed MW digestion	HNO_3, HF, H_2O_2	sample 1 g → solution 30 g
METAS	Closed MW digestion	HNO_3, H_2O_2	sample 0.25 g → solution 40 g
NMIA	Closed MW digestion	HNO_3, H_2O_2	sample 0.5 g → solution 50 g
JSI	Pelletized	Non-destructive	sample 0.42 g
NMIJ	High pressured closed MW digestion	HNO_3, HF, H_2O_2	sample 0.5 g → solution 50 g
INTI	High pressured closed MW digestion	HNO_3	sample 0.5 g → solution 15 g
NIM	Closed MW digestion	HNO_3	sample 0.5 g → solution 50 g

For the sample pretreatment for ICP-MS, most of the participants adopted a closed microwave assisted digestion, but the combinations of acids were different. HSA, LATU, and NMIJ used HF with the mixture of HNO_3 and H_2O_2 for dissolving silicate components. INTI and NIM used only HNO_3. The others used the mixture of HNO_3 and H_2O_2. NMIJ and INTI used a single reaction chamber type microwave digestion system. LGC used a second stage of microwave digestion with addition of extra hydrogen peroxide to reduce residual carbon.

The recommended minimum sample amount for analysis was at least 0.5 g, but NIMT and METAS sub-sampled 0.2 g and 0.25 g in their experiments, respectively.

For eliminating non-spectral interference, all the participants applied an internal standard correction and/or standard addition. In all the cases, the internal standard elements were added before the microwave digestion. The combination of the internal standard elements and adaptation of the standard addition were listed in the Table B5.

For elimination of the effect of spectral interferences, five participants (LGC, NRC, NIMT, HSA and NIM) applied a mass shift mode with oxygen gas using a tandem mass spectrometer, four participants (GLHK, METAS, NMIJ, and INTI) applied a collision mode with helium gas using a single quadrupole mass spectrometer, and three participants (NMIA, KRISS, and LATU) applied a high mass resolution spectral separation using a sector field mass spectrometer.

JSI adopted k_0-INAA after pelletizing of the sample with the addition of an Al-0.1 %Au alloy as a standard.

Table B5: Summary of the measurement methods used for total As

Participating NMI/DI	Measurement method	Internal standard element	Standard addition	Source of traceability	Other information
LGC	ICP-MS/MS with O_2 mode	Ge	---	NIST SRM 3103a	---
NRC	ICP-MS/MS with O_2 mode	---	Yes	NRC HIAS-1 CRM	---
NIMT	ICP-MS/MS with O_2 mode	Rh	Yes	NIST SRM 3103a	---
GLHK	ICP-MS/MS with He mode	Ge	Yes	NIST SRM 3103a	---
HSA	ICP-MS/MS with O_2 mode	Ge, Ga	---	NIST SRM 3103a	---
KRISS	ICP-SFMS with high resolution	Ge	Yes	KRISS arsenic (As) standard solution	As: 99.992 % Ge: 99.9726 % ICP-MS, ICP-OES, GFAAS, and FAAS was used for assessing impurities

Participating NMI/DI	Measurement method	Internal standard element	Standard addition	Source of traceability	Other information
LATU	ICP-SFMS with high resolution	Ge	Yes	NIST SRM 3103a	
METAS	ICP-MS with He mode	---	Yes	NIST SRM 3103a	
NMIA	ICP-SFMS with high resolution	Mg, Mn, Ge, Y	Yes	NIST SRM 3103a	
JSI	k_0-INAA	Al-0.1 %Au alloy	N/A	NIST SRM 3121	Al-0.1 %Au alloy (ERM-EB530A) was validated by NIST SRM 3121 Au Standard Solution
NMIJ	ICP-MS with He mode	Ge, Y	---	JCSS As(III)	
INTI	ICP-MS with He mode	Ge	---	NIST SRM 3103a	
NIM	ICP-MS/MS with O_2 mode	---	Yes	GBW08667	

Methods Used by Participants for inorganic arsenic quantification

The measurement methods were also left free to be selected by the participant institutes. The analytical techniques adopted by the participants were summarized in Table B6 and B7.

Table B6: Conditions of the extraction of inorganic As

Participating NMI/DI	Extraction method and solution	Extraction conditions	Additional preparation
LGC	Thermostatically extracted with 2 % (v/v) HNO_3 and 1 % (v/v) H_2O_2	Vortex (0.5 min) Sonication (5 min) then heating at 75 °C slurry temperature for 2 h	Filtrated, neutralized with 40 µL aqueous ammonia, and diluted with mobile phase of LC
NRC	Thermostatically extracted with 20 mmol L^{-1} trifluoroacetic acid and 2 % H_2O_2	Heating at 95 °C for 1h	Standard addition solutions prior to LC-ICPMS measurements.
NIMT	Thermostatically extracted with 0.15 mol L^{-1} HNO_3	Heating at 100 °C for 2 h	
GLHK	Thermostatically extracted with 0.15 mol L^{-1} HNO_3 and 2 % H_2O_2	Heating at 90 °C for 3 h	

Participating NMI/DI	Extraction method and solution	Extraction conditions	Additional preparation
HSA	Microwave extracted with 10 mL of 1 % HNO_3 and 0.5 mL of 30 % H_2O_2	Heating at 95 °C for 2 h, Power: 900 W	
NMIJ	Thermostatically extracted with 0.15 mol L^{-1} HNO_3	Heating at 100 °C for 2 h	
NIM	Thermostatically extracted with 1 % HNO_3	Heating at 100 °C for 2.5 h	

All the participants used a hyphenation system of a liquid chromatograph-ICP-MS with a thermostatically extraction using diluted acids. In the extraction, various combinations and concentrations of acids were used. LGC and HSA used the mixture of diluted HNO_3 and H_2O_2. NRC used the mixture of diluted trifluoroacetic acid and H_2O_2. The others used only diluted HNO_3. LGC also neutralized a filtrated extractant with an aqueous ammonia and diluted with a mobile phase of LC. The extraction conditions such as temperature and time were also different as were summarized in Table B6.

LGC, NRC, and NIM adopted anion exchange chromatograph with an isocratic elution. GLHK adopted anion exchange chromatograph with a gradient elution. NIMT, HSA, and NMIJ adopted ion pair chromatograph with an isocratic elution. The components of mobile phase and separation columns used were summarized in Table B7.

Table B7: Summary of the measurement methods used for inorganic As

Participating NMI/DI	Measurement method	Analytical column and mobile phase composition	Calibration solution
LGC	Strong anion chromatography hyphenated with ICP-MS/MS detection in O_2 mode	Column: Hamilton PRP-X100 (4.1 mm × 50 mm, 5 µm) Mobile phase: 55 mmol/L NH_4HCO_3 in 1 % v/v CH_3OH, pH 9	NMIJ CRM 7912a
NRC	Strong anion chromatography hyphenated with ICP-MS/MS detection in He mode	column: Hamilton PRP-X100 (4.1 mm × 250 mm, 10 µm) and identical guard column. mobile phase:5 mmol L^{-1} malonic acid pH 5.6 with 5 % MeOH	Commercially available reagents calibrated against the As primary standard solution prepared from NRC HIAS-1 CRM
NIMT	Ion-pair chromatography hyphenated with ICP-MS/MS detection in O_2 mode	column: Shiseido CAPCELL PAK C18 (4.6 mm × 250 mm, 5 µm), mobile phase:10 mmol L^{-1} ammonium nitrate, 2 mmol L^{-1} sodium 1-butanesulfonate and 2 mmol L^{-1} malonic acid (pH 2.5)	CGAS (3)1 for As (III), CGAS (5)1 for As(V) (Inorganic ventures) NMIJ CRM7913-a for DMA
GLHK	Strong anion chromatography hyphenated with ICP-MS/MS detection in He mode	column: Dionex IonPac AS7 (4 mm × 250 mm) mobile phase: water / 200 mmol L^{-1} ammonium carbonate (gradient)	NMIJ CRM 7912a
HSA	Ion-pair chromatography hyphenated with ICP-MS/MS detection in He mode	column: C18 ODS L-column (4.6 mm × 150 mm) mobile phase:10 mmol L^{-1} sodium 1-butanesulfonate, 4 mmol L^{-1} malonic acid, 4 mmol L^{-1} tetramethylammonium hydroxide, 0.05 % methanol (pH 3.0)	NIST SRM 3036
NMIJ	Ion-pair chromatography hyphenated with ICP-MS/MS detection in He mode	column: C18 ODS MG (4.6 mm × 250 mm) mobile phase:10 mmol L^{-1} sodium 1-butanesulfonate / 4 mmol L^{-1} malonic acid / 4 mmol L^{-1} tetramethylammonium hydroxide / 0.05 % methanol (pH 3.0)	JCSS As(III) NMIJ CRM7912-a As(V)
NIM	Strong anion chromatography hyphenated with ICP-MS/MS detection in O_2 mode	column: Hamilton PRP-X100 (4.1 mm × 250 mm, 10 µm) mobile phase:20 mmol L^{-1} $(NH_4)_2HPO_4$, pH 6.0	GBW08666, GBW08667

Calibration Materials Used by Participants

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

The calibration materials used for total arsenic were summarized in Table 5. KRISS prepared a SI traceable calibration standard solution from a high purity material for which they determined the purity themselves. JSI adopted k_0-INAA as a primary method traceable to the SI through NIST, where an 0.1%Au alloy, an absolutely calibrated HPGe detector and calibrated irradiation channel of TRIGA Mark II reactor were utilized in their measurement. The other participants used CRMs issued from NMIs having the required CMC claims.

The calibration materials used for inorganic arsenic were summarized in Table 7. All the calibration solutions, except for NIMT, used were ensured SI-traceability through certified reference materials, having the required CMC claims. NRC used commercially available arsenic compound reagents, for which they calibrated against their CRM HIAS-1 high purity Arsenic. LGC and GLHK used NMIJ CRM7912-a As (V) solution. NMIJ used CRM7912-a and JCSS As (III) solution. HSA used NIST SRM3036 As (V) solution. NIM used GBW08666 As(III) solution and GBW08667 As(V) solution.

NIMT used commercially available arsenic compound reagents but were not ensured SI-traceability in this study. They also used NMIJ CRM7913-a for dimethylarsinic acid (DMA) to validate their analytical result.

Moisture content

All the participants were asked to measure the moisture content in the sample in parallel with sample analyses, and to report the result as the mass fraction (as As) of each measurand on the dry mass basis. The reported results of the moisture content were summarized in Table B8.

Table B8: Reported results of moisture content (%)

Laboratory	Moisture content (%)	Standard deviation	Number of sub-samples
LGC	10.70 %	0.26 %	9
NRC	11.279 %	0.096 %	3
NIMT	10.28 %	0.23 %	6
GLHK	11.96 %	0.11 %	3
HSA	11.20 %	0.12 %	3
JSI	10.99 %	0.19 %	4
NMIJ	11.07 %	0.06 %	3

Laboratory	Moisture content (%)	Standard deviation	Number of sub-samples
NIM	11.04 %	0.10 %	3
KRISS	11.16 %	0.07 %	3
LATU	11.44 %	0.29 %	3
METAS	2.2 %	---	2
NMIA	11.24 %	0.44 %	6
INTI	11.23 %	0.54 %	4

METAS reported a smaller moisture content than the other reported values. After the first discussion in IAWG, METAS found that the moisture content for Part A was also adopted for Part B. The other reported values were within 2 % relative for median, even though rice flour is easy to absorb a moisture in a laboratory environment during a sample preparation. This result indicates that the dry mass correction would be a minor bias source in this comparison study.

Participant Results for total arsenic

The results for the determination of total arsenic are detailed in Table B9 and presented graphically in Figure B1. The values of the degree of freedom were estimated from the reported uncertainty budgets by using the Welch-Satterthwaite equation.

Table B9: Reported results for total As

Participating NMI/DI	Reported mass fraction (mg kg^{-1})	Reported standard uncertainty (mg kg^{-1})	Coverage factor, *k*	Expanded uncertainty (mg kg^{-1})	Degrees of freedom
NIMT	0.093	0.002	2	0.005	5.2
METAS	0.0970	0.0030	2	0.0060	3.0
JSI	0.1037	0.0037	2	0.0074	9.5
LGC	0.1053	0.0012	2	0.0024	21.6
NIM	0.1060	0.0020	2	0.0040	12.6
NMIJ	0.1063	0.0020	2	0.0041	6.5
NMIA	0.1067	0.0029	2.03	0.0059	36.6
KRISS	0.107	0.007	2.57	0.019	5.0
LATU	0.1070	0.0019	2	0.0038	63.5
HSA	0.1072	0.0019	2.57	0.0048	5.9
NRC	0.1075	0.0020	2	0.0040	11.7
GLHK	0.1080	0.0027	2	0.0054	60.0
INTI	0.1094	0.0057	2	0.0115	12.4

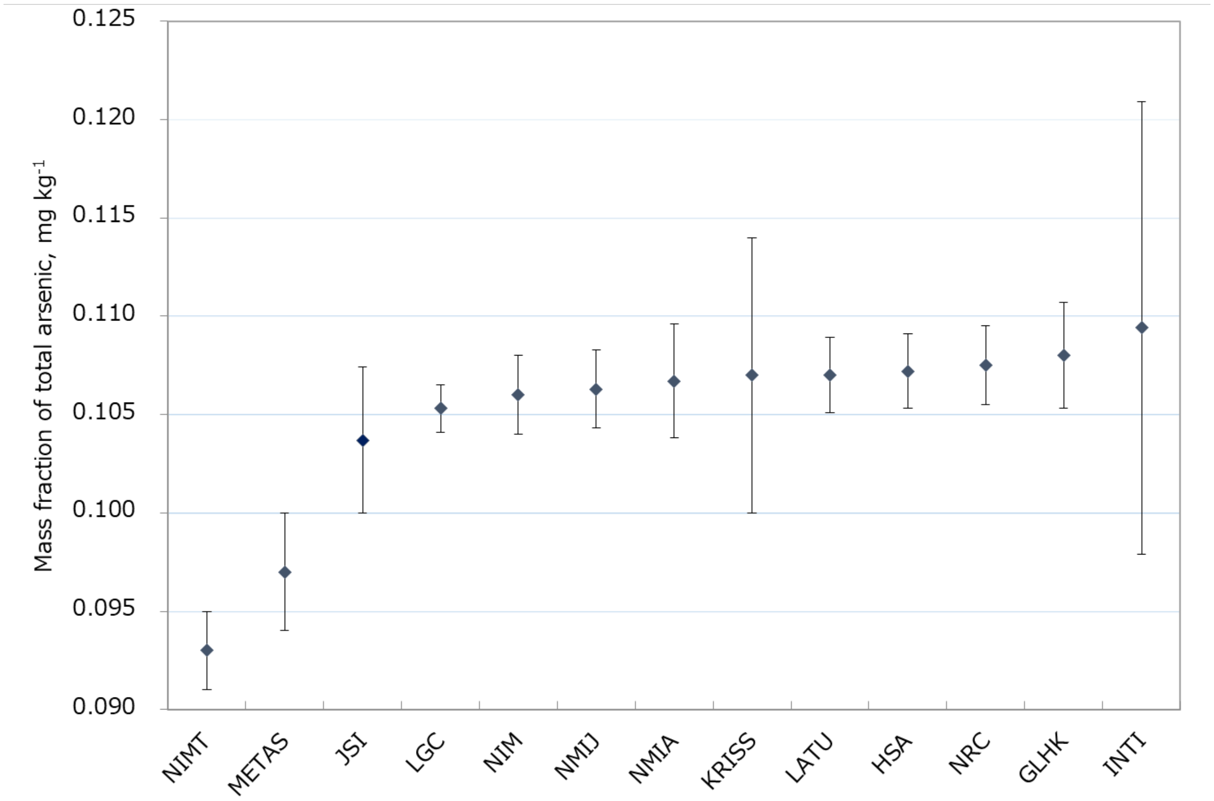


Figure B1: Reported Results for total arsenic, mg kg^{-1}
error bar: reported standard uncertainty

Participant Results for inorganic arsenic

The results for the determination of inorganic arsenic are detailed in Table B10 and presented graphically in Figure B2. The values of the degree of freedom were estimated from the reported uncertainty budgets by using the Welch-Satterthwaite equation.

Table B10: Reported results for inorganic As expressed as the mass fraction of As.

Participating NMI/DI	Reported mass fraction (mg kg^{-1})	Reported standard uncertainty (mg kg^{-1})	Coverage factor, *k*	Expanded uncertainty (mg kg^{-1})	Degrees of freedom
NRC	0.0613	0.0022	2	0.0044	8.0
NIMT	0.0810	0.0050	2	0.010	3.0
GLHK	0.0889	0.0039	2	0.0078	60.0
HSA	0.0896	0.0029	2.57	0.0074	5.6
LGC	0.0901	0.0016	2	0.0032	44.8
NMIJ	0.09070	0.00096	2	0.0024	5.1
NIM	0.0939	0.0015	2	0.0031	46.5

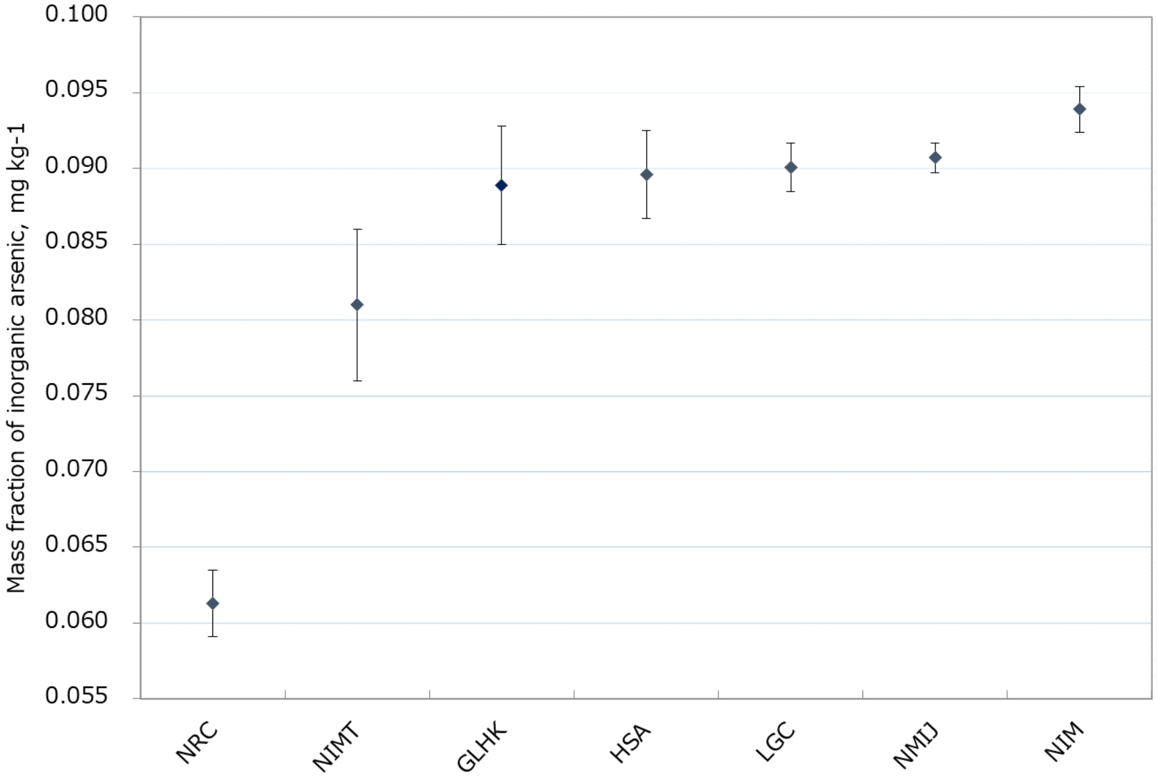


Figure B2: Reported Results for inorganic arsenic, mg kg^{-1} as As
error bar: reported standard uncertainty

Discussion of Results

For total arsenic, two lower results, reported from NIMT and METAS were observed. The other results were within 3 % relative to the median of the results. No dependance for the sample pretreatment and measurement mode of ICP-MS was observed, reflecting that potentially technical issues such as a carbon enhancement effect for arsenic in ICP-MS and spectral interference from argide ion were well addressed in the analytical procedures of the participants. Through the communication between a pilot laboratory (NMIJ) and the participants after the first result report at the IAWG spring meeting in April 2022, NIMT found a mistake in their calculation, missing a dry mass correction. METAS found a mistake in their dry mass correction, a different dry mass correction factor, which is for Part A sample, was used for the Part B sample. After the discussion in IAWG fall meeting in Nov.2022, the results of NIMT and METAS were treated as the outliers, excluding for the calculation of key comparison reference value (KCRV).

For inorganic arsenic, two lower results, reported from NIMT and NRC were observed. The other data were within ± 5 % relative to the median. The result of NIMT was also treated as the outlier, due to the same reason for total arsenic. After the first discussion of the results in the IAWG meeting, NRC re-verified their analytical procedure used in this study by comparing with HNO_3 extraction, where the CRM BARI-1 (rice flour) was used as a quality control material. In the analysis of BARI-1, a discrepancy was not found between the TFA and HNO_3 extraction but found in the analysis of this study's sample. NRC concluded that their reported result in this study had a bias based on the method dependance, agreed on excluding from the calculation of key comparison reference value (KCRV).

KEY COMPARISON REFERENCE VALUE (KCRV)

The choice of appropriate estimators for the key comparison reference value (KCRV) depends upon whether the reported measurement uncertainties are deemed credible for the purpose of establishing the KCRV. If not all is credible, the simplest appropriate estimator is the equally-weighted arithmetic mean and its standard deviation-based uncertainty (Mean) and for study data that may contain values as outliers or have a multi-modal data structure, the use of robust estimators of location and dispersion – such as the median and adjusted median absolute deviation from the median (MAD_E) is a plausible choice.

Table B11 lists the estimated values X, and their standard uncertainties u (X), calculated using the relevant equations for the arithmetic mean and median. The MADe values were calculated by multiplying median absolute deviation (MAD) values with 1.483. The MAD values were calculated using Eq.(5). The median standard uncertainties in Table 11 were calculated using Eq.(6). The arithmetic mean standard uncertainties in Table 11 were calculated using Eq. (7). 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 95 % coverage.

$$MAD = median\ (|x_i - x^*|i_{-1,2,\dots,n}) \tag{5}$$

$$Standard\ uncertainty = 1.25 \times \frac{MADe}{\sqrt{n}} \tag{6}$$

$$Standard\ uncertainty = \frac{Standard\ deviation}{\sqrt{n}} \tag{7}$$

where:

n = the number of participating NMIs/DIs' results included in the calculation

x_i = the participating NMI/DI's result (mg kg^{-1})

x^* = the median (mg kg^{-1})

IAWG has discussed new estimator, NIST decision tree (NDT) [1]. The NDT is a web application that implements the Decision Tree for Key Comparisons, which is intended for use as an aid for generating KCRV. The NDT guides users through a series of hypothesis tests intended to help them in deciding upon an appropriate statistical model for their particular data. The NDT then carries out the preferred statistical procedure, and displays the results include the KCRV estimate and associated uncertainties, an estimate of dark uncertainty (where applicable), and the Degrees of Equivalence and their uncertainties, among other results.

The estimated values calculated by using the NDT were also listed in Table B11. An adaptive weighted average for total arsenic and weighted median for inorganic arsenic were recommended by using the NDT. A dark uncertainty was negligible for the adaptive weighted average for total arsenic. The NDT reports, including other information values were attached as the appendix D.

After the discussion regarding the adoption of the NDT, IAWG decided to accept the estimated values by using the NDT for KCRVs.

Table B11: Candidate Key Comparison Reference Values for total and inorganic arsenic

	Total arsenic, mg kg^{-1}			Inorganic arsenic, mg kg^{-1}		
Estimator	X	$u(X)$	$U_{95}(X)^a$	X	$u(X)$	$U_{95}(X)^a$
Arithmetic mean	0.1067	0.0004	0.0010	0.0906	0.0009	0.0024
Median	0.1070	0.0004	0.0009	0.0901	0.0007	0.0021
Adaptive Weighted Average [b)]	0.1064	0.0006	0.0013	---	---	---
Weighted Median [b)]	---	---	---	0.0903	0.0006	0.0014

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 2.26 for total arsenic and 2.78 for inorganic arsenic.

b) Recommended by using the NDT.

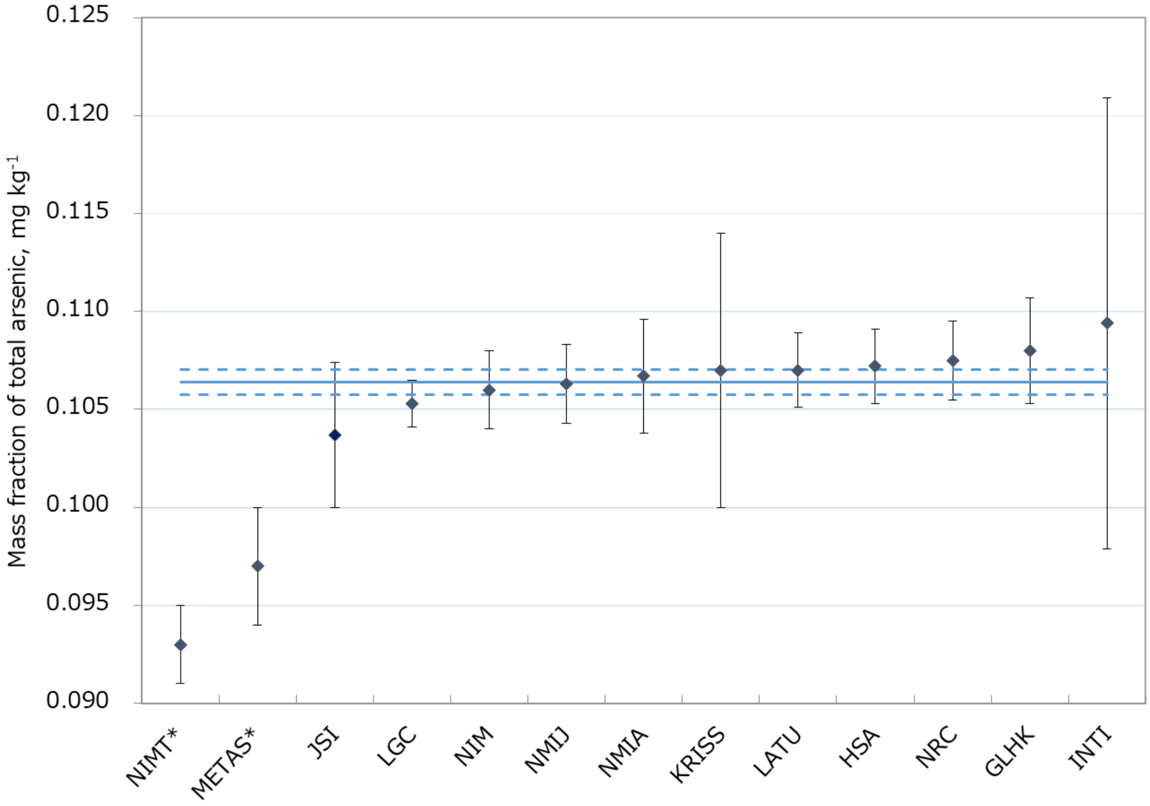


Figure B3: Reported Results with KCRV for total arsenic, mg kg^{-1}

error bar: reported standard uncertainty, solid line: KCRV,
dash lines: standard uncertainty of KCRV, symbol *: indicates reported result excluded from the KCRV calculation

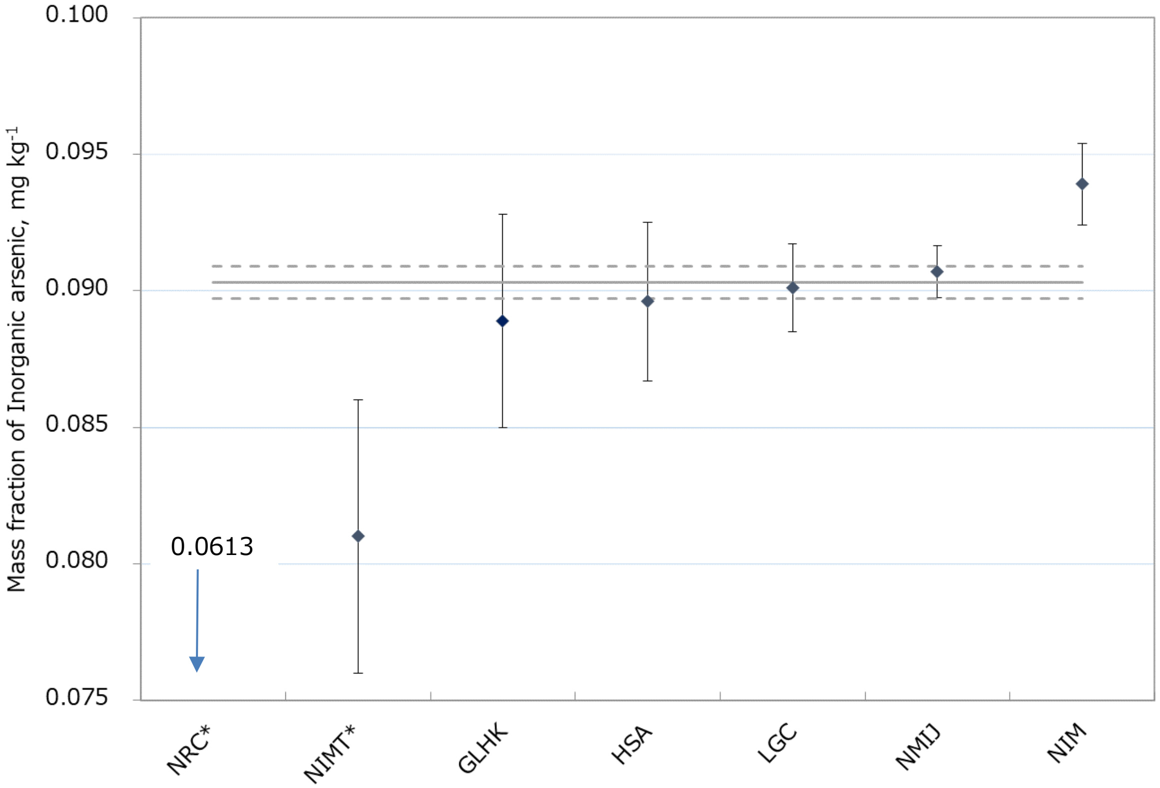


Figure B4: Reported Results with KCRV for inorganic arsenic, mg kg^{-1} as As
error bar: reported standard uncertainty, solid line: KCRV,
dash lines: standard uncertainty of KCRV, symbol *: indicates reported result excluded from the KCRV calculation

DEGREES OF EQUIVALENCE (DoE)

The degrees of equivalence (DoE, d_i) for the participants in CCQM-K158 Part B are estimated as the signed difference between the reported value and the KCRV. The expanded uncertainty in each d_i is estimated by the NDT using statistical bootstrapping as half the shortest interval centered on d_i that includes 95 % of the d_i values. This approach automatically accounts for any covariance between a participant's reported value and the KCRV. The calculation results are summarized in Tables B12 and B13 and Figures B5 and B6. The half of each bar in the Figures indicates U_i.

Table B12 and B13 lists the numeric values of d_i, $U(d_\mathrm{i})$, $d_\mathrm{i}/U(d_\mathrm{i})$ for all participants in total arsenic and inorganic arsenic, respectively.

Table B12: Degrees of Equivalence for total arsenic

Participating NMI/DI	Reported mass fraction, x_i (mg kg^{-1})	Reported standard uncertainty, $u(x_i)$ (mg kg^{-1})	Relative standard uncertainty, %(x_i)	Difference from KCRV, d_i (mg kg^{-1})	Expanded uncertainty of the difference, $U(d_i)$ (mg kg^{-1})	d_i / $U(d_i)$
NIMT*	0.093	0.004$^{\#}$	4.8	-0.0134	0.0041	-0.336
METAS*	0.0970	0.0050$^{\#}$	5.1	-0.0094	0.0060	-0.531
JSI	0.1037	0.0037	3.6	-0.0027	0.0072	-0.375
LGC	0.1053	0.0012	1.1	-0.0010	0.0027	-0.370
NIM	0.1060	0.0020	1.9	-0.0004	0.0042	-0.095
NMIJ	0.1063	0.0020	1.9	-0.0001	0.0041	-0.024
NMIA	0.1067	0.0029	2.7	0.0003	0.0058	0.052
KRISS	0.107	0.007	6.5	0.0006	0.0139	0.043
LATU	0.107	0.0019	1.8	0.0006	0.0041	0.146
HSA	0.1072	0.0019	1.8	0.0008	0.0040	0.200
NRC	0.1075	0.0020	1.9	0.0011	0.0040	0.275
GLHK	0.1080	0.0027	2.5	0.0016	0.0055	0.291
INTI	0.1094	0.0057	5.2	0.0030	0.0114	0.263

The symbol * indicates reported result excluded from the KCRV calculation.
The values with symbol $^{\#}$ correspond to uncertainties including contribution of dark uncertainty.

Table B13: Degrees of Equivalence for inorganic arsenic

Participating NMI/DI	Reported mass fraction, x_i (mg kg^{-1})	Reported standard uncertainty, $u(x_i)$ (mg kg^{-1})	Relative standard uncertainty, %(x_i)	Difference from KCRV, d_i (mg kg^{-1})	Expanded uncertainty of the difference, $U(d_i)$ (mg kg^{-1})	d_i / $U(d_i)$
NRC*	0.0613	0.0103$^{\#}$	17	-0.0290	0.0206	-1.409

Participating NMI/DI	Reported mass fraction, x_i (mg kg^{-1})	Reported standard uncertainty, $u(x_i)$ (mg kg^{-1})	Relative standard uncertainty, %(x_i)	Difference from KCRV, d_i (mg kg^{-1})	Expanded uncertainty of the difference, $U(d_i)$ (mg kg^{-1})	d_i / $U(d_i)$
NIMT*	0.0810	0.0112$^{\#}$	14	-0.0093	0.0224	-0.414
GLHK	0.0889	0.0039	4.4	-0.0014	0.0076	-0.184
HSA	0.0896	0.0029	3.2	-0.0007	0.0058	-0.121
LGC	0.0901	0.0016	1.8	-0.0003	0.0035	-0.086
NMIJ	0.09070	0.000096	1.1	0.0004	0.0023	0.174
NIM	0.0939	0.0015	1.6	0.0036	0.0032	1.125

The symbol * indicates reported result excluded from the KCRV calculation.
The values with symbol $^{\#}$ correspond to uncertainties including contribution of dark uncertainty.

Figure B5 and B6 below graphically illustrates the preferred presentation of both the absolute DoEs for total and inorganic arsenic using the candidate KCRVs estimated by using the NDT, where adaptive weighted average for total arsenic and weighted median for inorganic arsenic were recommended as a statistics model.

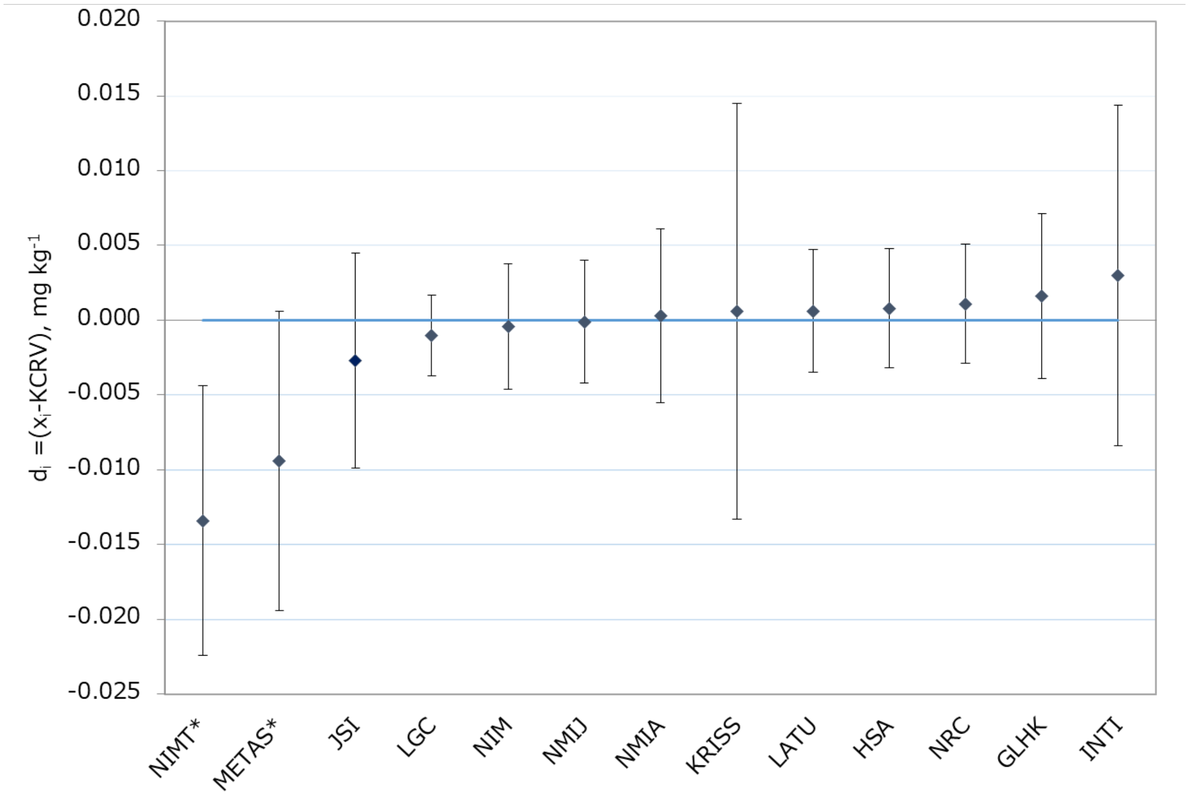


Figure B5: Degrees of Equivalence for total arsenic associated with the candidate KCRVs

Dots represent the d, error bars their approximate 95 % expanded uncertainties, $U_{95}(d)$. The horizontal line denotes perfect agreement with the candidate KCRV. The symbol * indicates reported result excluded from the KCRV calculation.

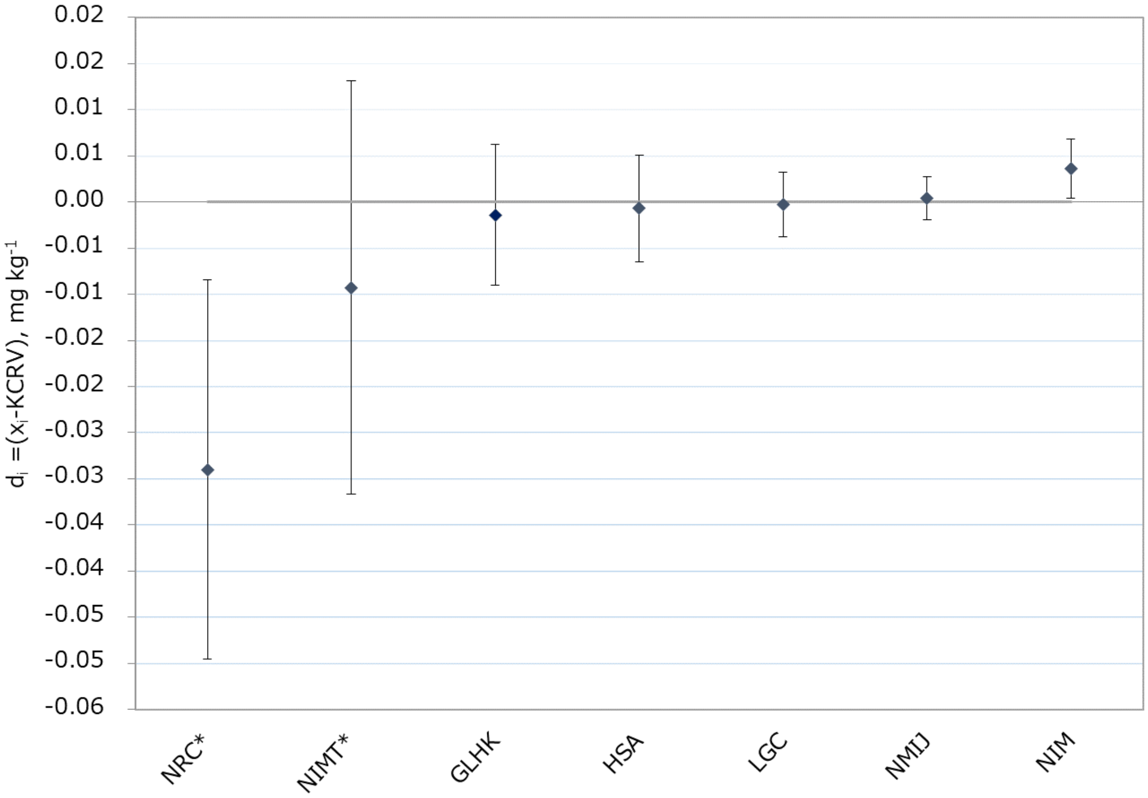


Figure B6: Degrees of Equivalence for inorganic arsenic associated with the candidate KCRVs

Dots represent the *d*, error bars their approximate 95 % expanded uncertainties, $U_{95}(d)$. The horizontal line denotes perfect agreement with the candidate KCRV. The symbol * indicates reported result excluded from the KCRV calculation.

USE OF CCQM-K158 PART B IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

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

Successful participation in CCQM-K158 Part B demonstrates the following measurement capabilities in determining mass fraction of total and water-soluble arsenic species such as inorganic As, DMAA, mono-, tri-, and tetra-methyl arsenic compounds (MAA, TMAO, TeMA), arsenocholine (AsC), and arsenobetaine (AsB), in mass fraction range from 0.05 mg kg^{-1} to 10.0 mg kg^{-1} as As in grains, beans, and related samples.

Table B14: Core Capability Table

Analyte groups	**Matrix challenges**			
	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, …)**
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)				
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)				
				Total As
Inorganic species (elemental, anions, cations)				
				Inorganic arsenic
Small organo-metallics				
				MAA, DMAA, TMAO, TeMA, AsC, AsB

Low level (e.g. below 50 µg/kg)

High level (e.g. above 50 µg/kg)

CONCLUSIONS

Among 17 registered NMIs/DIs for the CCQM-K158 Part A, 16 participants reported their measurement results. The measurands of the Part A are the mass fractions of Cu, Hg, K, Na, Pb, and Sb in rice flour. The KCRVs and associated uncertainties were estimated by using the NIST decision tree (NDT). For K, Na, and Sb, the NDT recommended the adaptive weighted average as the statistical model for fitting the reported results after excluding outliers based on the technical investigations by the relevant participating laboratories. The associated uncertainties of the KCRVs and the dark uncertainties were relatively small and the most of participants demonstrated excellent degrees of equivalence in their measurements. The hierarchical Gauss + Gauss model was recommended for Cu and Hg. Due to dispersion of several reported results with relatively small reported uncertainties, they showed increased dark uncertainties compared with those of K, Na, and Sb. Except for an outlier for each measurand, the most of the reported results showed satisfying degrees of equivalence, of which $D_i/U(D_i)$ values are within the range of ± 1.0. In the case of Pb, more participants' results were deviated from the consensus value and the hierarchical Laplace + Gauss model was used. Due to larger dispersion of participants' results, inclusion of the uncertainty contributions from relatively large dark uncertainty of about 8 % was required for 6 results from total 16 participants to demonstrate the equivalence to the KCRV within the associated uncertainties. For each measurands, one or two participants' results could not satisfy their equivalence to the KCRV even if the contributions of dark uncertainty were included.

Fifteen National Metrology Institutes and Designated Institutes participated in the Part B (Inorganic and total arsenic in polished rice flour). Participants were requested to evaluate the mass fractions, expressed in mg kg^{-1}, of total arsenic and inorganic arsenic (the sum of As (III) and As (V)) in polished rice flour. For total As, thirteen NMIs/DIs reported their analytical results, where all the NMIs/DIs, except for JSI, adopted Inductively coupled plasma mass spectrometry (ICP-MS) with a microwave acid digestion. JSI adopted k_0-INAA after pelletizing of the sample. For inorganic As, seven NMIs/DIs reported their analytical results, where all the NMIs/DIs adopted liquid chromatography-ICP-MS with a thermostatically controlled extraction using diluted acids.

The key comparison reference value (KCRV) and associated uncertainty were estimated by using NIST decision tree (NDT), where adaptive weighted average for total arsenic and weighted median for inorganic arsenic were recommended as a statistics model.

For total As, except for two outliers, all the participating NMIs/DIs' results were found to be consistent according to their equivalence statements with the values of $d_i/U(d_i)$ within ± 0.4, demonstrating their competencies within their level of the uncertainty. For inorganic arsenic, except for two results and two outliers, all the participating NMIs/DIs' results were found to be consistent according to their equivalence statements with the values of $d_i/U(d_i)$ within ± 1.0, demonstrating their competencies within their level of the uncertainty.

ACKNOWLEDGEMENTS

The study coordinators thank the participating NMIs/DIs for their support and providing the requested information used in this study. We'd like to thank Dr. Michael Winchester for his kind support and helpful advice. Special thanks to Dr. Antonio Possolo for his help and useful comments for the statistical analysis of the comparison results using the NDT. We'd like to extend our appreciation to the individuals listed in the following table for their contributions to the study.

NMI/DI	**Additional Contributors**
GLHK	Chun-wai Tse, Hei-shing Chu
HSA	Wesley Yu Zongrong
INMC	Johanna Paola Abella, Fabián Niño Quintero
INMETRO	Marcelo Domingues de Almeida, Vânia Silva de Oliveira
JSI	Darja Mazej, Ermira Begu, Milena Horvat
KRISS	Hana Cho, Jinil Kim, Jean Sun Lim, Sook Heun Kim, Myung Chul Lim, Myung Sub Han, Jung Ki Suh
METAS	Marina Zbinden
NIMT	Usana Thiengmanee, Suttinun Taebunpakul, Nunnapus Laitip
NIS	Moustafa M. Elmasry
NMIA	Ian White, Elizabeth Tully
NRC	Lu Yang
PTB	Ursula Schulz, Jessica Towara, Carola Pape, Samuel Henjes

REFERENCES

[1]. Possolo, A., Koepke, A., Newton, D., Winchester, M. (2021) Decision tree for key comparisons. *J. Res. NIST* 126: 126007. https://doi.org/10.6028/jres.126.007

APPENDIX A: Call for Participation and Technical Protocol

Call for Participants and technical protocol

CCQM-K158 & P200 Elements and Inorganic Arsenic in Rice Flour

(February 1, 2021)

Rationale for the Proposed Comparison

Rice is consumed as the main foodstuff for about half of the world's population, particularly in Asia, where the majority of rice is grown. Therefore, accurate measurement of essential and hazardous elements in rice is important for reliable assessments of nutrition and health hazard. Arsenic contamination is a special concern in rice and rice-based products due to its growing consumption worldwide and higher content of inorganic arsenic species (i-As) with highest toxicity. Food authenticity and traceability are other important issues related to food safety.

KRISS and NMIJ are co-coordinating the CCQM-K158 & P200 on elements and inorganic As. The present comparison supports CMCs within category 11, which corresponds to the sample matrix "High organics content" in the new CC table for broad CMC claiming.

Samples and Measurands

Sample A for elements:
The rice flour material is contained in pre-cleaned amber glass bottles, each accommodating approximately 20 g of rice flour. Most elements are in their natural levels, while six hazardous elements, including As, Cd, Hg, Ni, Sb, and Pb, were spiked. (Cd and Ni measurements were originally thought to be part of the protocol, but have now been excluded.) The analytes are listed in Table 1 with their approximate levels and homogeneities.

Analyte	Approximate Mass fraction (mg/kg)	Between-bottle homogeneity (in % RSD)	Natural/Spiked	Description
Cu	0.5-5	<0.95	Natural	Transition element
Hg	0.5-5	<0.85	Spiked	Toxic element, strong memory effect in ICPMS
K	100-1000	<0.59	Natural	Severe isobaric interferences in ICPMS
Na	2-10	<0.41	Natural	Monoisotopic element

Analyte	Approximate Mass fraction (mg/kg)	Between-bottle homogeneity (in % RSD)	Natural/Spiked	Description
Sb	0.5-5	<0.32	Spiked	Metalloid
Pb	0.1-1	<0.67	Spiked	Toxic element

Each participant will receive two sample bottles, each containing about 20 g of rice flour. The between bottle homogeneity of the sample described in the above table was determined by analyzing a single 0.2 g subsample from each of 12 sample bottles selected at regular intervals during the production batch. ID ICP-MS was used, except for Na, which was analyzed by ICP-OES. Therefore, it is recommended to take subsamples of more than 0.2 g for the analysis.

Sample B for total As & i-As :
The comparison material is polished rice flour, containing >0.02 mg/kg of total As and i-As (natural level, no compounds were spiked). The measurands to be determined are the mass fractions (as As) of inorganic arsenic (As(III) + As(V)) and total arsenic. Participation in total As alone is allowed; but participation only in i-As is not allowed, because participation in total arsenic is mandatory to allow discussion about the extraction efficiencies of inorganic arsenic.

Each participant will receive a sample bottle containing approximately 20 g of polished rice flour. The among-bottles homogeneity of the material was <1 % (rsd) both for inorganic arsenic (As(III) + As(V)) and total arsenic, according to the analysis of three subsamples (ca. 0.5 g) taken from each of 10 bottles. From the viewpoint of homogeneity, the use of more than 0.5 g in each sample for each measurement is strongly recommended. The sample after receipt should be kept at laboratory room temperature.

HFTLS statement

Sample A for elements:
This comparison will support CMCs for Groups I and II elements, transition elements and metalloids/semi-metals in high organics content matrix, including grains, beans and related samples in Category 11.

Sample B for total As & i-As :
This comparison will support CMCs for total As and water-soluble As species, such as inorganic As, DMAA, mono-, tri-, and tetra-methyl arsenic compounds (MAA, TMAO, TeMA), arsenocholine (AsC), and arsenobetaine (AsB), in grains, beans, and related samples in Category 11.

Methods of Measurement

Sample A for elements:

The participants in the key comparison can measure their choice of elements using any method(s) of their choice. It is recommended to take at least 4 subsamples for the measurements of measurands. The calibrations should be carried out by using standards with metrological traceability to the SI, especially for KC participation and use of the comparison results as evidence for future CMC claims. Commercially available calibration materials usually should not be employed if a KC is to be used to support CMC 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.)

Sample B for total As & i-As :

The participants in the key comparison must measure both total inorganic arsenic and total arsenic using any method(s) of their choice. Four measurements for each measurand are to be carried out by each participant. The calibrations should be carried out by using standards with metrological traceability to the SI, especially for KC participation and use of the comparison results as evidence for future CMC claims. Commercially available calibration materials usually should not be employed if a KC is to be used to support CMC 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.)

Determination of moisture content

Sample A & sample B:

The moisture content of the rice flour sample should be measured by taking subsamples at the same time as the subsampling for analyses. It is recommended to take at least 3 subsamples for the measurements of moisture content. The recommended procedure is to dry the sample to constant mass in a desiccator with fresh P_2O_5 at room temperature for 7 days. Participant may check if constant mass is reached by extending the drying one more week. A sample size of 0.5 g or more is recommended for the determination of moisture content. The elemental contents determined should be reported on the basis of dry mass. Do not use the sample, which was used for the determination of moisture content, for analysis.

Reporting

Sample A for elements:

The result should be reported as the mass fraction of each measurand on the dry mass basis, accompanied by a full uncertainty budget. Reporting multiple results using several different methods is allowed for PS participation. For KC, however, one should report only one composite result (e.g., an average value from different methods) or submit only one result from a selected method for KC while reporting the other results from different methods for PS. Reporting the details of the procedure (including details of sample treatment/digestion), the calibration standard and the traceability link, and the instrument(s) used is required. A reporting form will be distributed to participants.

Sample B for total As & i-As :

A value for total arsenic can be reported without reporting a value for inorganic arsenic. However, if inorganic arsenic is reported, then reporting total arsenic is mandatory in order to discuss about the extraction efficiency of arsenic species. The result should be reported as the mass fraction (as As) of each measurand on the dry mass basis, accompanied by a full uncertainty budget. Any participant that chooses to use multiple methods can decide only one composite result (e.g., an average value from different methods) for the KC. If individual results from different methods are reported for a given measurand, then one result must be indicated for the KC, and the other results will be considered for the PS. Reporting the details of the procedure (including details of sample treatment/digestion), the calibration standard and the traceability link, and the instrument(s) used is required. A reporting form will be distributed to participants.

Proposed Schedule

Call for participation: Feb 01, 2021
Deadline of registration: Mar 01, 2021.
Distribution of samples: April 15, 2021
Deadline for submission of results: Aug 31, 2021
First presentation of the results: Autumn meeting 2021

Participants

Participation is open to all interested NMIs or DIs that can perform the determination. Please inform the contact persons of both coordinating laboratories, KRISS and NMIJ, of the contact persons, the shipping address, and the other related information, using the attached registration form. We'll appreciate it very much if you inform us even if you decide not to participate in the comparison.

Coordinating laboratories

The CCQM-K158 and -P200 are co-coordinated by KRISS (Yong-Hyeon Yim and Kyoung-Seok Lee) and NMIJ (Tomoko Ariga, and Kazumi Inagaki).

APPENDIX B: Registration Form

Registration form

CCQM-K158 & P200 Elements and Inorganic Arsenic in Rice Flour
(Feb. 01, 2021)

☐ We would like to participate in the key comparison CCQM-K158 (open only for NMIs or officially designated institutes). The element/species to analyse are listed in the Table below.

☐ We would like to participate in the pilot study CCQM-P200 (open only for NMIs or officially designated institutes). The element/species to analyse are listed in the Table below.

Please complete the registration form and return it to A and B no later than 01 March 2021.

1. Contact Information

Name of institute	
Country/Economy	
Address	
Contact person	
E-mail	

2. Please indicate participation for CCQM-K158 and P200

Sample A:

Proposed elements and expected concentration ranges	Participate in CCQM-K158	Participate in CCQM-P200
Cu: 0.5-5 mg/kg		
Hg: 0.5-5 mg/kg (spiked)		
K: 100-1000 mg/kg		
Na: 2-10 mg/kg		
Sb: 0.5-5 mg/kg (spiked)		
Pb: 0.1-1 mg/kg (spiked)		

Sample B:

Proposed analytes	Participate in CCQM-K158	Participate in CCQM-P200
Total As: >0.02 mg/kg		
Inorganic As (sum of As(III) & As(V)) : >0.02 mg/kg[*1]		

*1 Participants measuring inorganic As must also measure total As.

Contact persons

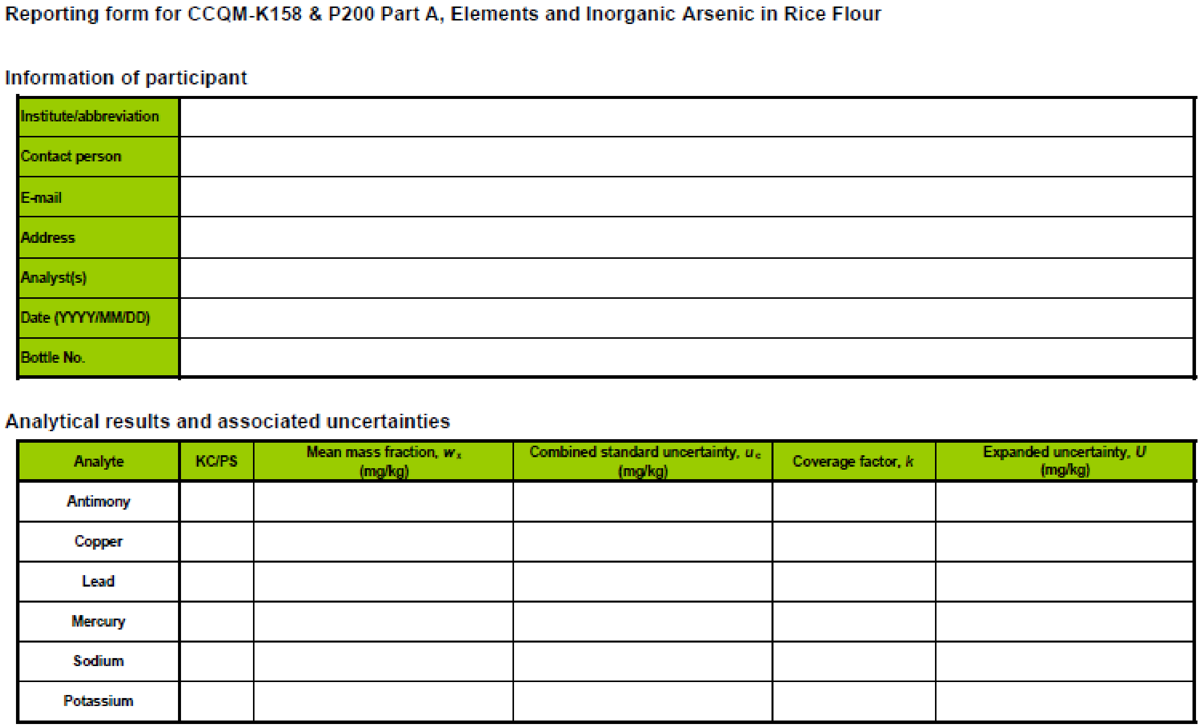
For elemental analysis (Sample A)

Dr. Yong-Hyeon Yim and Dr. Kyoung-Seok Lee, Korea Research Institute of Standards and Science (KRISS)

For total As and i-As (Sample B)

Dr. Tomoko Ariga and Dr. Kazumi Inagaki, National Metrology Institute of Japan (NMIJ)

APPENDIX C: Reporting Form for Part A



Reporting form for CCQM-K158 & P200 Part A, Elements and Inorganic Arsenic in Rice Flour

Information of participant

Institute/abbreviation	
Contact person	
E-mail	
Address	
Analyst(s)	
Date (YYYY/MM/DD)	
Bottle No.	

Analytical results and associated uncertainties

Analyte	KC/PS	Mean mass fraction, w_x (mg/kg)	Combined standard uncertainty, u_c (mg/kg)	Coverage factor, k	Expanded uncertainty, U (mg/kg)
Antimony					
Copper					
Lead					
Mercury					
Sodium					
Potassium					

Antimony (Sb)

Summary of result

Subsample No.	Subsample mass (g)	Mass fraction (mg/kg)
1		
2		
3		
4		
Mean		
Standard deviation		
Standard deviation of the mean		
Combined standard uncertainty, u_c		
Coverage factor, k		
Expanded uncertainty, U		

Analytical method

Sample preparation method

Sample preparation method (e.g., MW-assisted acid digestion)	
Details of sample preparation procedure including reagents, apparatuses and their operating conditions	

Measurement method

Measurement method (e.g., ID ICP-MS, ICP-OES, etc.)	
Analytical instrument (e.g., Thermo Element 2, Agilent 8900, etc.)	
Details of operating conditions of the instrumental technique	
Calibration method (e.g., double ID, standard addition, etc.)	
Reference materials used for calibration purpose (e.g., elemental standard solution, isotopic standard solution, etc)	
Traceability of reference materials used	

Explain sample pretreatment procedure such as matrix separation and preconcentration if it was applied.

Details of the procedure	

Sb

Give your complete equation for the calculation of the mass fraction of arsenic

Parameter	Source of unceratinty	Typical value	Standard uncertainty	Unit	Type

w_x	Mass fraction		mg/kg
u_c	Combined standard uncertainty		mg/kg
k	Coverage factor		
U	Expanded unceratinty		mg/kg

Copper (Cu)

Summary of result

Subsample No.	Subsample mass (g)	Mass fraction (mg/kg)
1		
2		
3		
4		
Mean		
Standard deviation		
Standard deviation of the mean		
Combined standard uncertainty, u_c		
Coverage factor, k		
Expanded uncertainty, U		

Analytical method

Sample preparation method

Sample preparation method (e.g., MW-assisted acid digestion)	
Details of sample preparation procedure including reagents, apparatuses and their operating conditions	

Measurement method

Measurement method (e.g., ID ICP-MS, ICP-OES, etc.)	
Analytical instrument (e.g., Thermo Element 2, Agilent 8900, etc.)	
Details of operating conditions of the instrumental technique	
Calibration method (e.g., double ID, standard addition, etc.)	
Reference materials used for calibration purpose (e.g., elemental standard solution, isotopic standard solution, etc)	
Traceability of reference materials used	

Explain sample pretreatment procedure such as matrix separation and preconcentration if it was applied.

Details of the procedure	

Uncertainty budget

Cu

Give your complete equation for the calculation of the mass fraction of arsenic

Parameter	Source of uceratinty	Typical value	Standard uncertainty	Unit	Type

w_x	Mass fraction		mg/kg
u_c	Combined standard uncertainty		mg/kg
k	Coverage factor		
U	Expanded unceratinty		mg/kg

Lead (Pb)

Summary of result

Subsample No.	Subsample mass (g)	Mass fraction (mg/kg)
1		
2		
3		
4		
Mean		
Standard deviation		
Standard deviation of the mean		
Combined standard uncertainty, u_c		
Coverage factor, *k*		
Expanded uncertainty, *U*		

Analytical method

Sample preparation method

Sample preparation method (e.g., MW-assisted acid digestion)	
Details of sample preparation procedure including reagents, apparatuses and their operating conditions	

Measurement method

Measurement method (e.g., ID ICP-MS, ICP-OES, etc.)	
Analytical instrument (e.g., Thermo Element 2, Agilent 8900, etc.)	
Details of operating conditions of the instrumental technique	
Calibration method (e.g., double ID, standard addition, etc.)	
Reference materials used for calibration purpose (e.g., elemental standard solution, isotopic standard solution, etc)	
Traceability of reference materials used	

Explain sample pretreatment procedure such as matrix separation and preconcentration if it was applied.

Details of the procedure	

Uncertainty budget

Pb

Give your complete equation for the calculation of the mass fraction of arsenic

Parameter	Source of unceratinty	Typical value	Standard uncertainty	Unit	Type

w_x	Mass fraction		mg/kg
u_c	Combined standard uncertainty		mg/kg
k	Coverage factor		
U	Expanded unceratinty		mg/kg

Sodium (Na)

Summary of result

Subsample No.	Subsample mass (g)	Mass fraction (mg/kg)
1		
2		
3		
4		
Mean		
Standard deviation		
Standard deviation of the mean		
Combined standard uncertainty, u_c		
Coverage factor, *k*		
Expanded uncertainty, *U*		

Analytical method

Sample preparation method

Sample preparation method (e.g., MW-assisted acid digestion)	
Details of sample preparation procedure including reagents, apparatuses and their operating conditions	

Measurement method

Measurement method (e.g., ID ICP-MS, ICP-OES, etc.)	
Analytical instrument (e.g., Thermo Element 2, Agilent 8900, etc.)	
Details of operating conditions of the instrumental technique	
Calibration method (e.g., double ID, standard addition, etc.)	
Reference materials used for calibration purpose (e.g., elemental standard solution, isotopic standard solution, etc)	
Traceability of reference materials used	

Explain sample pretreatment procedure such as matrix separation and preconcentration if it was applied.

Details of the procedure	

Na

Give your complete equation for the calculation of the mass fraction of arsenic

Parameter	Source of uncertainty	Typical value	Standard uncertainty	Unit	Type

w_x	Mass fraction		mg/kg
u_c	Combined standard uncertainty		mg/kg
k	Coverage factor		
U	Expanded uncerainty		mg/kg

Potassium (K)

Summary of result

Subsample No.	Subsample mass (g)	Mass fraction (mg/kg)
1		
2		
3		
4		
Mean		
Standard deviation		
Standard deviation of the mean		
Combined standard uncertainty, u_c		
Coverage factor, k		
Expanded uncertainty, U		

Analytical method

Sample preparation method

Sample preparation method (e.g., MW-assisted acid digestion)	
Details of sample preparation procedure including reagents, apparatuses and their operating conditions	

Measurement method

Measurement method (e.g., ID ICP-MS, ICP-OES, etc.)	
Analytical instrument (e.g., Thermo Element 2, Agilent 8900, etc.)	
Details of operating conditions of the instrumental technique	
Calibration method (e.g., double ID, standard addition, etc.)	
Reference materials used for calibration purpose (e.g., elemental standard solution, isotopic standard solution, etc)	
Traceability of reference materials used	

Explain sample pretreatment procedure such as matrix separation and preconcentration if it was applied.

Details of the procedure	

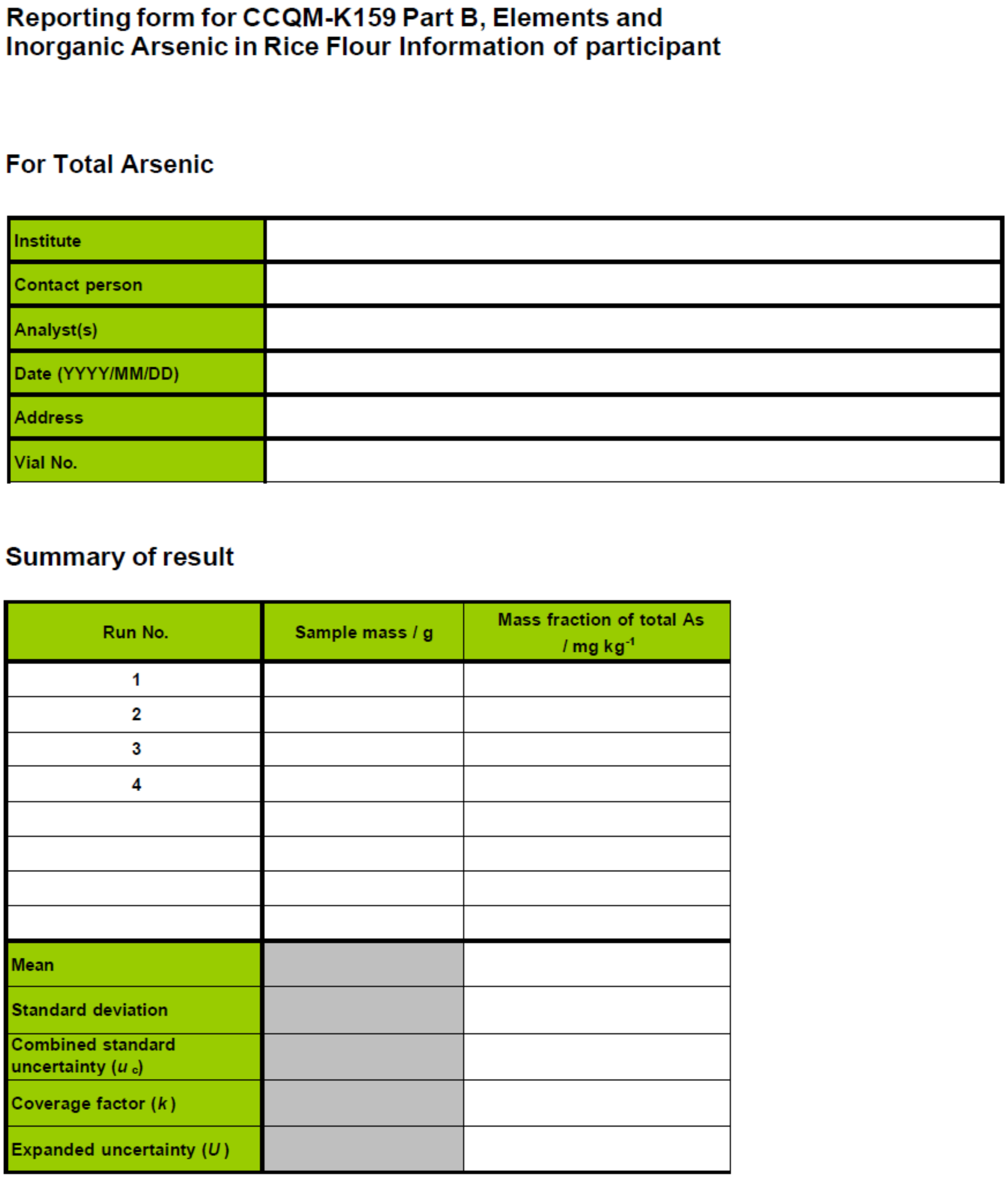
K

Give your complete equation for the calculation of the mass fraction of arsenic

Parameter	Source of unceratinty	Typical value	Standard uncertainty	Unit	Type

w_x	Mass fraction		mg/kg
u_c	Combined standard uncertainty		mg/kg
k	Coverage factor		
U	Expanded unceratinty		mg/kg

APPENDIX D: Reporting Form for Part B



Reporting form for CCQM-K159 Part B, Elements and Inorganic Arsenic in Rice Flour Information of participant

For Total Arsenic

Institute	
Contact person	
Analyst(s)	
Date (YYYY/MM/DD)	
Address	
Vial No.	

Summary of result

Run No.	Sample mass / g	Mass fraction of total As / mg kg^{-1}
1		
2		
3		
4		
Mean		
Standard deviation		
Combined standard uncertainty (u_c)		
Coverage factor (k)		
Expanded uncertainty (U)		

Moisture content

Run No.	Sample mass / g	Mass fraction of moisture / %
1		
2		
3		
Mean		
Standard deviation		

Explain your procedure if you did not apply the recommended procedure for drying.

Summary of analytical method Preparation method

Type of preparation	
Details of sample preparation procedure including reagents, apparatuses and their operating conditions	

Measurement method

Measurement method	
Details of operating conditions of detection tecnique	
Calibration solution	
Purity of material for preparing the calibration solution if you prepared it from a purified material by yourself	
Details of the purity assessment	

Explain pretreatment procedures such as matrix separation and preconcentration if you applied.

Details of the procedure	

Uncertainty budget for Total As

Give your complete equation for the calculation of the mass fraction of arsenic

Parameter	Source of uncertainty	Typical value	Standard uncertainty	Unit	Type

C_x	Mass fraction of total As		mg kg^{-1}
u_c	Combined standard uncertainty		mg kg^{-1}
k	Coverage factor		
U	Expanded unceratinty		mg kg^{-1}

For inorganic Arsenic (i-As)

Institute	
Contact person	
Analyst(s)	
Date (YYYY/MM/DD)	
Address	
Vial No.	

Summary of result

Run No.	Sample mass / g	Mass fraction of inorganic arsenic[*1] as As / mg kg^{-1}
Mean		
Standard deviation		
Combined standard uncertainty (*u* $_c$)		
Coverage factor (*k*)		
Expanded uncertainty (*U*)		

[*1] the sum of As(III) & As(V)

Moisture content

Run No.	Sample mass / g	Mass fraction of moisture / %
Mean		
Standard deviation		

Explain your procedure if you did not apply the recommended procedure for drying.

Summary of analytical method Preparation method

Type of preparation	
Details of sample preparation procedure including reagents, apparatuses and their operating conditions	

Measurement method

Measurement method	
Details of operating conditions of detection tecnique	
Calibration solution	
Purity of material for preparing the calibration solution if you prepared it from a purified material by yourself	
Details of the purity assessment	

Fill up the following columns if you applied LC for the separation of As species,
representative chromatograms of calibration soultion and sample in other sheet "Chromatograms"

Analytical column	
Isocratic or gradient	
Composition of eluent	
Flow rate of eluent	
Others	

Fill up the following columns if you applied SPE for the separation.

Cartridge	
Composition of eluent	
Others	

Explain your procedure if you applied other technique for the separation.

Details of the procedure	

Uncertainty budget
Inorganic arsenic (As(III) + As(V)) as As

Give your complete equation for the calculation of the mass fraction of inorganic arsenic.

Parameter	Source of uncertainty	Typical value	Standard uncertainty	Unit	Type

C_x	Mass fraction of As(III) + As(V) as As		mg kg^{-1}
u_c	Combined standard uncertainty		mg kg^{-1}
k	Coverage factor		
U	Expanded uncertainty		mg kg^{-1}

Elements and Inorganic Arsenic in Rice Flour Chromatograms

Paste the image of a chromatogram of calibration solution

Paste the image of a chromatogram of sample

APPENDIX E: NIST Decision Tree Reports for Part A

NIST Decision Tree Report for Cu

Summary (Cu)

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	NIS*	0.93880	0.03490	60
TRUE	INTI	1.05400	0.05500	60
TRUE	NIMT	1.32200	0.02000	60
TRUE	HSA	1.35200	0.01500	8
TRUE	KRISS	1.36397	0.00621	34
TRUE	NMIJ	1.37400	0.01800	3084
TRUE	LATU	1.38100	0.02000	60
TRUE	NMISA	1.38500	0.03300	60
TRUE	JSI	1.49000	0.06000	5

Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 546
Selected Procedure: Hierarchical Gauss-Gauss Consensus
estimate: 1.345
Standard uncertainty: 0.03024
95% coverage interval: (1.284, 1.406)
Dark uncertainty (tau): 0.0804
Tau posterior 0.025 and 0.975 quantiles: (0.00747,0.1766)

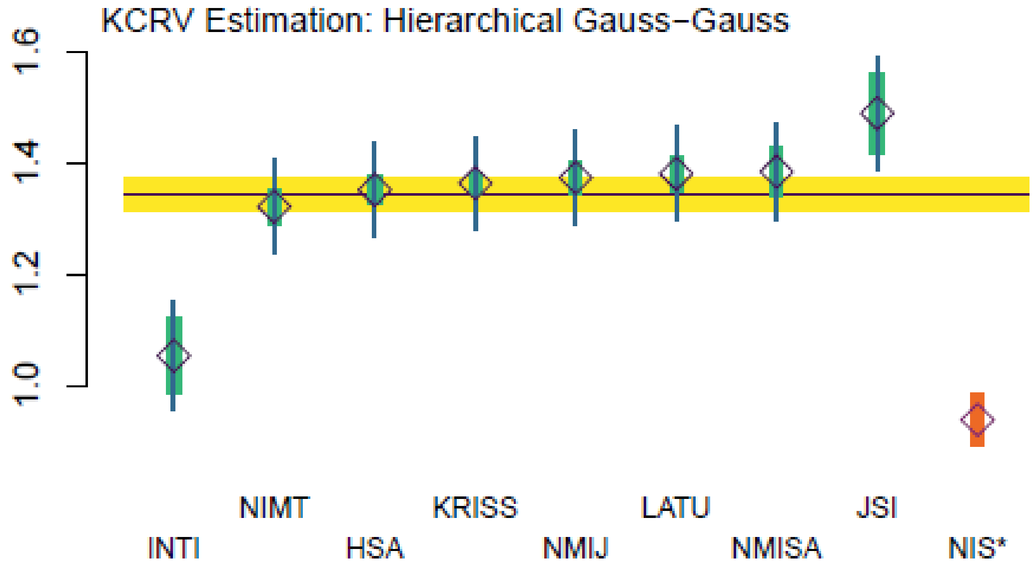
Decision Tree Hypothesis test results (Cu)

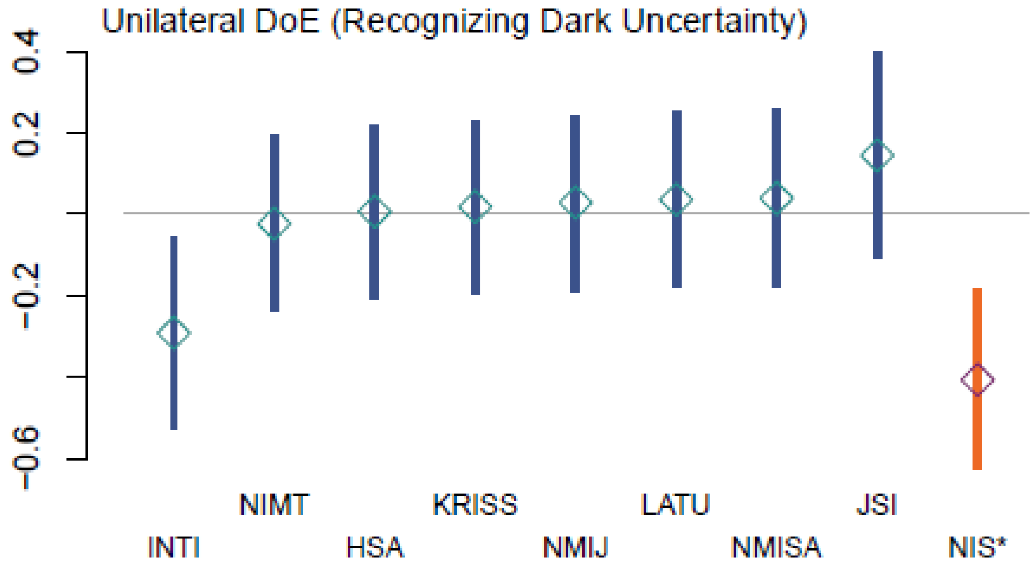
Cochran's test for Homogeneity: p- value: p < 0.001
Q = 42.22 (Reference Distribution: Chi-Square with 7 Degrees of Freedom)
tau est. = 0.03992
tau/median(x) = 0.02916
tau/median(u) = 1.996

Shapiro-Wilk test for Normality: p = 0.2917

Miao-Gel-Gastwirth test of Symmetry: p = 0.4774

Plots (Cu)


KCRV Estimation: Hierarchical Gauss–Gauss
1.6
1.4
1.2
1.0
NIMT
KRISS
LATU
JSI
INTI
HSA
NMIJ
NMISA
NIS*


Unilateral DoE (Recognizing Dark Uncertainty)
0.4
0.2
−0.2
−0.6
NIMT
KRISS
LATU
JSI
INTI
HSA
NMIJ
NMISA
NIS*

DoE Table (Cu)

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
NIS*	NIS*	-0.406300	0.2133	-0.61970	-0.19300
INTI	INTI	-0.291100	0.2289	-0.52010	-0.06222
NIMT	NIMT	-0.023140	0.2071	-0.23020	0.18400
HSA	HSA	0.006857	0.2048	-0.19790	0.21160
KRISS	KRISS	0.018830	0.2040	-0.18520	0.22290
NMIJ	NMIJ	0.028860	0.2073	-0.17840	0.23610
LATU	LATU	0.035860	0.2065	-0.17060	0.24230
NMISA	NMISA	0.039860	0.2118	-0.17200	0.25170
JSI	JSI	0.144900	0.2442	-0.09936	0.38910

Lab Uncertainties Table (Cu)

lab	x	u	nu	ut
NIS*	0.9388	0.03490	60	0.08765
INTI	1.0540	0.05500	60	0.09741
NIMT	1.3220	0.02000	60	0.08285
HSA	1.3520	0.01500	8	0.08179
KRISS	1.3640	0.00621	34	0.08064
NMIJ	1.3740	0.01800	3084	0.08239
LATU	1.3810	0.02000	60	0.08285
NMISA	1.3850	0.03300	60	0.08691
JSI	1.4900	0.06000	5	0.10030

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
NIS*	-0.406300	0.10390	0.2133	-0.61970	-0.19300	0.04607	0.09033	-0.49670	-0.31600
INTI	-0.291100	0.11450	0.2289	-0.52010	-0.06222	0.06543	0.12810	-0.41920	-0.16300
NIMT	-0.023140	0.09983	0.2071	-0.23020	0.18400	0.03631	0.07222	-0.09536	0.04908
HSA	0.006857	0.09918	0.2048	-0.19790	0.21160	0.03489	0.06995	-0.06309	0.07680
KRISS	0.018830	0.09818	0.2040	-0.18520	0.22290	0.03087	0.06247	-0.04364	0.08130
NMIJ	0.028860	0.09949	0.2073	-0.17840	0.23610	0.03517	0.07010	-0.04125	0.09896
LATU	0.035860	0.10000	0.2065	-0.17060	0.24230	0.03649	0.07225	-0.03640	0.10810
NMISA	0.039860	0.10310	0.2118	-0.17200	0.25170	0.04500	0.08880	-0.04894	0.12870
JSI	0.144900	0.12110	0.2442	-0.09936	0.38910	0.07842	0.15610	-0.01126	0.30100

MCMC Sampler Diagnostics Table (Cu) (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	37000
lambda[2]	1.001	50000
lambda[3]	1.001	50000
lambda[4]	1.001	50000
lambda[5]	1.001	34000
lambda[6]	1.001	50000
lambda[7]	1.001	50000
lambda[8]	1.001	40000
mu	1.001	40000
sigma[1]	1.001	50000
sigma[2]	1.001	50000
sigma[3]	1.001	31000
sigma[4]	1.001	34000
sigma[5]	1.001	32000
sigma[6]	1.001	50000
sigma[7]	1.001	50000
sigma[8]	1.001	35000
tau	1.001	20000

NIST Decision Tree Report for Hg

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	INTI	0.4390	0.0400	60
TRUE	JSI	0.4410	0.0150	5
TRUE	NMISA	0.4556	0.0060	60
TRUE	GLHK	0.4740	0.0130	60
TRUE	NMIA	0.4780	0.0100	12.4
TRUE	NIM	0.4830	0.0064	60
TRUE	HSA	0.4838	0.0032	12
TRUE	LATU	0.4910	0.0084	60
TRUE	NIMT	0.4970	0.0050	60
TRUE	KRISS	0.5016	0.0043	717
FALSE	NIS*	1.1160	0.0375	60

Date: 2024-07-11
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty Random Seed:
971
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 0.4788
Standard uncertainty: 0.005914
95% coverage interval: (0.4671, 0.4905) Dark
uncertainty (tau): 0.0163
Tau posterior 0.025 and 0.975 quantiles: (0.008845,0.03122)

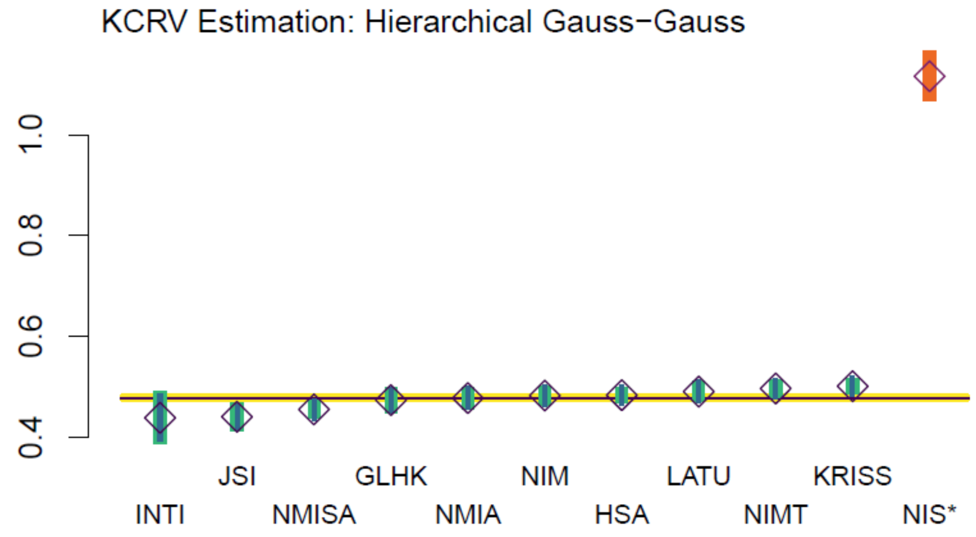
Decision Tree Hypothesis test results

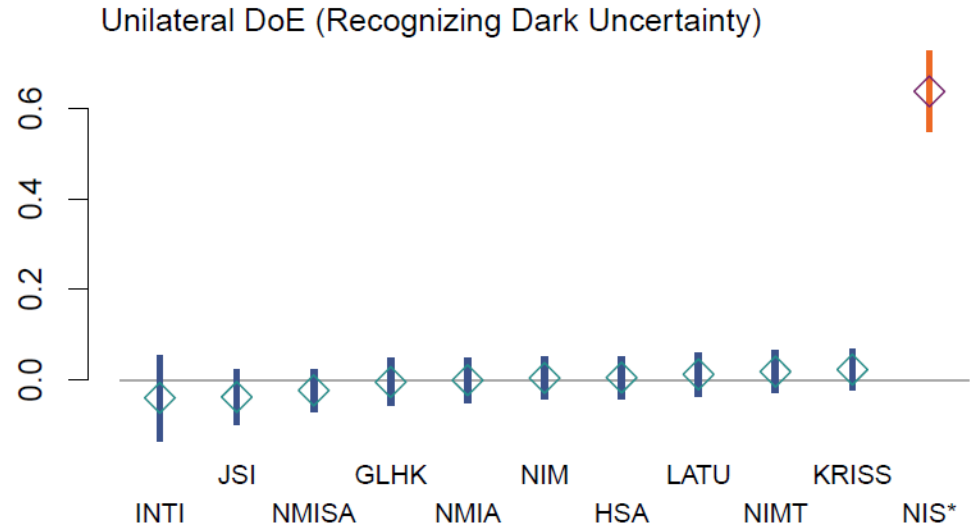
Cochran's test for Homogeneity: p-value: $p < 0.001$
Q = 56.5 (Reference Distribution: Chi-Square with 9 Degrees of Freedom) tau est. = 0.01461
tau/median(x) = 0.03041
tau/median(u) = 1.974

Shapiro-Wilk test for Normality: p = 0.9766 Miao-Gel-

Gastwirth test of Symmetry: p = 0.032

Plots


KCRV Estimation: Hierarchical Gauss−Gauss
0.4
0.6
0.8
1.0
JSI
GLHK
NIM
LATU
KRISS
INTI
NMISA
NMIA
HSA
NIMT
NIS*


Unilateral DoE (Recognizing Dark Uncertainty)
0.0
0.2
0.4
0.6
JSI
GLHK
NIM
LATU
KRISS
INTI
NMISA
NMIA
HSA
NIMT
NIS*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
INTI	INTI	-0.039830	0.08805	-0.12790	0.04823
JSI	JSI	-0.037830	0.05404	-0.09186	0.01621
NMISA	NMISA	-0.023230	0.03994	-0.06317	0.01672
GLHK	GLHK	-0.004826	0.04593	-0.05075	0.04110
NMIA	NMIA	-0.000826	0.04341	-0.04424	0.04259
NIM	NIM	0.004174	0.04031	-0.03614	0.04449
HSA	HSA	0.004974	0.03949	-0.03451	0.04446
LATU	LATU	0.012170	0.04162	-0.02945	0.05380
NIMT	NIMT	0.018170	0.03978	-0.02161	0.05795
KRISS	KRISS	0.022770	0.03957	-0.01679	0.06234
NIS*	NIS*	0.637200	0.08314	0.55400	0.72030

Lab Uncertainties Table

lab	x	u	nu	ut
INTI	0.4390	0.0400	60.0	0.04320
JSI	0.4410	0.0150	5.0	0.02215
NMISA	0.4556	0.0060	60.0	0.01737
GLHK	0.4740	0.0130	60.0	0.02085
NMIA	0.4780	0.0100	12.4	0.01913
NIM	0.4830	0.0064	60.0	0.01752
HSA	0.4838	0.0032	12.0	0.01662
LATU	0.4910	0.0084	60.0	0.01834
NIMT	0.4970	0.0050	60.0	0.01705
KRISS	0.5016	0.0043	717.0	0.01686
NIS*	1.1160	0.0375	60.0	0.04089

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
INTI	-0.039830	0.04475	0.08805	-0.12790	0.04823	0.040960	0.08089	-0.120700	0.041060
JSI	-0.037830	0.02713	0.05404	-0.09186	0.01621	0.019780	0.03944	-0.077270	0.001619
NMISA	-0.023230	0.02009	0.03994	-0.06317	0.01672	0.008520	0.01679	-0.040020	-0.006431
GLHK	-0.004826	0.02319	0.04593	-0.05075	0.04110	0.014420	0.02835	-0.033180	0.023530
NMIA	-0.000826	0.02183	0.04341	-0.04424	0.04259	0.012100	0.02389	-0.024720	0.023070
NIM	0.004174	0.02024	0.04031	-0.03614	0.04449	0.008778	0.01724	-0.013060	0.021410
HSA	0.004974	0.01951	0.03949	-0.03451	0.04446	0.006911	0.01367	-0.008696	0.018640
LATU	0.012170	0.02092	0.04162	-0.02945	0.05380	0.010420	0.02045	-0.008272	0.032620
NIMT	0.018170	0.01992	0.03978	-0.02161	0.05795	0.007829	0.01539	0.002786	0.033560
KRISS	0.022770	0.01961	0.03957	-0.01679	0.06234	0.007298	0.01437	0.008399	0.037150
NIS*	0.637200	0.04223	0.08314	0.55400	0.72030	0.037870	0.07453	0.562600	0.711700

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	21000
lambda[2]	1.001	46000
lambda[3]	1.001	50000
lambda[4]	1.001	39000
lambda[5]	1.001	50000
lambda[6]	1.001	50000
lambda[7]	1.001	50000
lambda[8]	1.001	50000
lambda[9]	1.001	43000
lambda[10]	1.001	34000
mu	1.001	50000
sigma[1]	1.001	50000
sigma[2]	1.001	50000
sigma[3]	1.001	17000
sigma[4]	1.001	50000
sigma[5]	1.001	50000
sigma[6]	1.001	19000
sigma[7]	1.001	46000
sigma[8]	1.001	50000
sigma[9]	1.001	17000
sigma[10]	1.001	33000
tau	1.001	50000

NIST Decision Tree Report for K

Summary (K)

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	NIMT*	539.0000	21.4000	60
FALSE	NIS*	540.9000	39.7000	60
TRUE	NMISA	583.0000	12.0000	60
TRUE	JSI	591.0000	18.0000	8
TRUE	PTB	609.3000	3.9000	180
TRUE	KRISS	613.5816	1.8658	230
TRUE	INMC	616.8000	12.3000	238
TRUE	NMIJ	617.1600	8.2200	77774209
TRUE	LATU	622.0000	7.8000	60

Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 956
Selected Procedure: Adaptive Weighted Average Consensus estimate: 611.6
Standard uncertainty: 3.177
Standard uncertainty (using parametric bootstrap): 3.281
95% coverage interval: (605.3, 617.8)
95% coverage interval (using parametric bootstrap): (604.8, 618.4)
Dark uncertainty (tau): 4.9

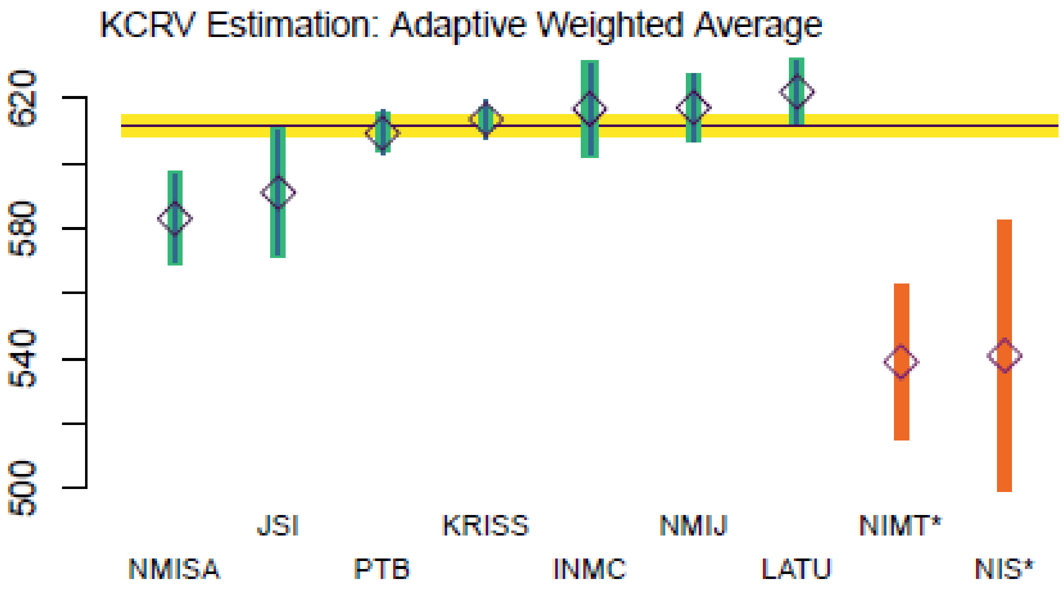
Decision Tree Hypothesis test results (K)

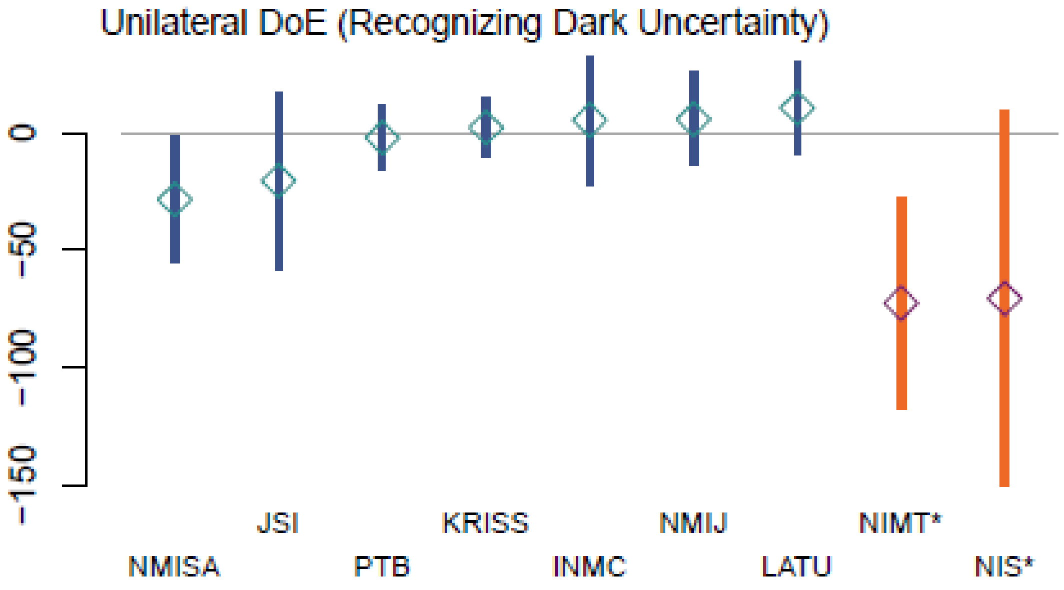
Cochran's test for Homogeneity: p-value: 0.11
Q = 10.39 (Reference Distribution: Chi-Square with 6 Degrees of Freedom)
tau est. = 4.9
tau/median(x) = 0.007986
tau/median(u) = 0.5962

Shapiro-Wilk test for Normality: p = 0.6815

Miao-Gel-Gastwirth test of Symmetry: p = 0.0632

Plots (K)


KCRV Estimation: Adaptive Weighted Average
620
580
540
500
JSI
KRISS
NMIJ
NIMT*
NMISA
PTB
INMC
LATU
NIS*


Unilateral DoE (Recognizing Dark Uncertainty)
0
−50
−100
−150
JSI
KRISS
NMIJ
NIMT*
NMISA
PTB
INMC
LATU
NIS*

DoE Table (K)

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
NMISA	NMISA	-28.570	25.17	-53.740	-3.403
JSI	JSI	-20.570	36.05	-56.620	15.480
PTB	PTB	-2.269	11.96	-14.230	9.691
KRISS	KRISS	2.012	11.04	-9.023	13.050
INMC	INMC	5.231	25.72	-20.490	30.950
NMIJ	NMIJ	5.591	18.27	-12.680	23.860
LATU	LATU	10.430	17.98	-7.554	28.420
NIMT*	NIMT*	-72.570	43.53	-116.100	-29.040
NIS*	NIS*	-70.670	78.68	-149.300	8.007

Lab Uncertainties Table (K)

lab	x	u	nu	ut
NIMT*	539.0	21.400	60	21.950
NIS*	540.9	39.700	60	40.000
NMISA	583.0	12.000	60	12.960
JSI	591.0	18.000	8	18.660
PTB	609.3	3.900	180	6.263
KRISS	613.6	1.866	230	5.244
INMC	616.8	12.300	238	13.240
NMIJ	617.2	8.220	77770000	9.570
LATU	622.0	7.800	60	9.212

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
NIMT*	-28.570	12.930	25.17	-53.740	-3.403	11.870	22.970	-51.540	-5.598
NIS*	-20.570	18.400	36.05	-56.620	15.480	17.690	34.130	-54.700	13.560
NMISA	-2.269	5.910	11.96	-14.230	9.691	3.520	6.691	-8.960	4.421
JSI	2.012	5.011	11.04	-9.023	13.050	1.832	4.151	-2.139	6.164
PTB	5.231	13.170	25.72	-20.490	30.950	12.180	23.610	-18.380	28.840
KRISS	5.591	9.183	18.27	-12.680	23.860	7.695	15.150	-9.558	20.740
INMC	10.430	9.043	17.98	-7.554	28.420	7.465	14.580	-4.151	25.010
NMIJ	-72.570	22.210	43.53	-116.100	-29.040	21.480	42.110	-114.700	-30.460
LATU	-70.670	40.140	78.68	-149.300	8.007	39.750	77.900	-148.600	7.232

MCMC Sampler Diagnostics Table (K) (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.

NIST Decision Tree Report for Na

Summary (Na)

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	NIS*	3.66	0.12	60
TRUE	JSI	5.25	0.16	8
TRUE	KRISS	5.38	0.18	4
TRUE	NMIJ	5.43	0.09	1905
TRUE	NMISA	5.45	0.14	60
FALSE	NIMT*	8.75	0.44	60

Date: 2023-10-22
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 728
Selected Procedure: Adaptive Weighted Average Consensus
estimate: 5.399
Standard uncertainty: 0.06397
Standard uncertainty (using parametric bootstrap): 0.06927
95% coverage interval: (5.274, 5.524)
95% coverage interval (using parametric bootstrap): (5.262, 5.536)
Dark uncertainty (tau): 0

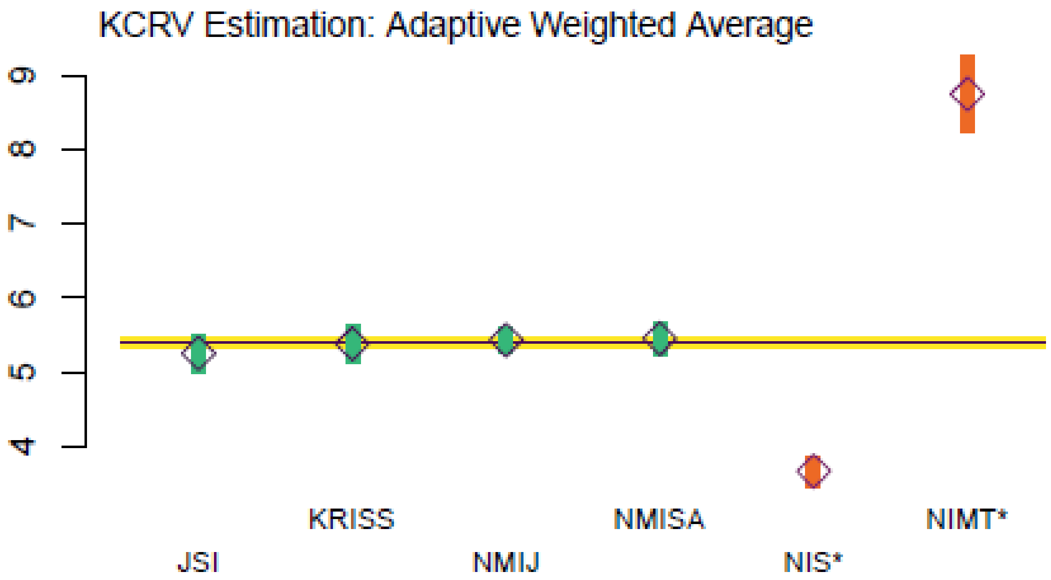
Decision Tree Hypothesis test results (Na)

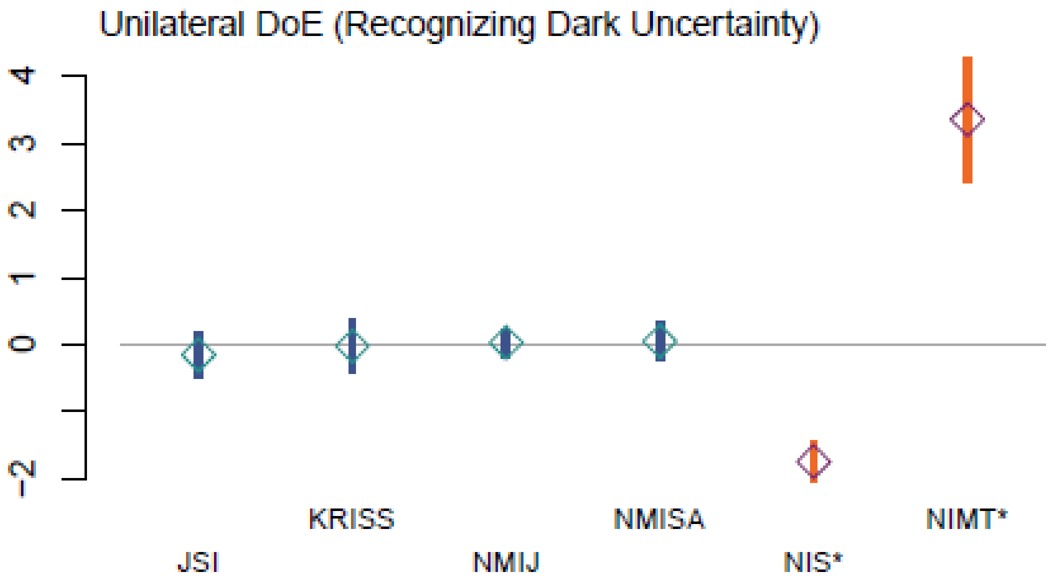
Cochran's test for Homogeneity: p-value: 0.77
Q = 1.13 (Reference Distribution: Chi-Square with 3 Degrees of Freedom)
tau est. = 0
tau/median(x) = 0
tau/median(u) = 0

Shapiro-Wilk test for Normality: p = 0.2303

Miao-Gel-Gastwirth test of Symmetry: p = 0.1194

Plots (Na)


KCRV Estimation: Adaptive Weighted Average
4
5
6
7
8
9
JSI
KRISS
NMIJ
NMISA
NIS*
NIMT*


Unilateral DoE (Recognizing Dark Uncertainty)
−2
0
1
2
3
4
JSI
KRISS
NMIJ
NMISA
NIS*
NIMT*

DoE Table (Na)

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
JSI	JSI	-0.14910	0.2881	-0.4372	0.1390
KRISS	KRISS	-0.01909	0.3304	-0.3495	0.3113
NMIJ	NMIJ	0.03091	0.1639	-0.1329	0.1948
NMISA	NMISA	0.05091	0.2425	-0.1916	0.2934
NIS*	NIS*	-1.73900	0.2708	-2.0100	-1.4680
NIMT*	NIMT*	3.35100	0.8728	2.4780	4.2240

Lab Uncertainties Table (Na)

lab	x	u	nu	ut
NIS*	3.66	0.12	60	0.12
JSI	5.25	0.16	8	0.16
KRISS	5.38	0.18	4	0.18
NMIJ	5.43	0.09	1905	0.09
NMISA	5.45	0.14	60	0.14
NIMT*	8.75	0.44	60	0.44

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
NIS*	-0.14910	0.14620	0.2881	-0.4372	0.1390	0.14490	0.2858	-0.4349	0.1367
JSI	-0.01909	0.16840	0.3304	-0.3495	0.3113	0.16790	0.3300	-0.3491	0.3109
KRISS	0.03091	0.07797	0.1639	-0.1329	0.1948	0.07617	0.1616	-0.1307	0.1925
NMIJ	0.05091	0.12430	0.2425	-0.1916	0.2934	0.12280	0.2388	-0.1879	0.2897
NMISA	-1.73900	0.13820	0.2708	-2.0100	-1.4680	0.13770	0.2700	-2.0090	-1.4690
NIMT*	3.35100	0.44530	0.8728	2.4780	4.2240	0.44520	0.8725	2.4780	4.2230

MCMC Sampler Diagnostics Table (Na) (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.

NIST Decision Tree Report for Pb

Summary (Pb)

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	NMISA	0.157	0.003	60
TRUE	INMC	0.183	0.014	238
TRUE	METAS	0.198	0.005	60
TRUE	JSI	0.204	0.006	5
TRUE	GLHK	0.215	0.004	60
TRUE	NMIJ	0.215	0.003	46
TRUE	NIMT	0.215	0.003	60
TRUE	HSA	0.217	0.004	12
TRUE	LATU	0.218	0.003	60
TRUE	KRISS	0.219	0.004	7
TRUE	PTB	0.219	0.002	29
TRUE	NIS	0.220	0.019	60
TRUE	NIM	0.221	0.002	60
TRUE	NMIA	0.230	0.004	8
TRUE	INTI	0.242	0.009	60
TRUE	INMETRO	0.245	0.005	60

Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty Random Seed: 789
Selected Procedure: Hierarchical Laplace-Gauss
Consensus estimate: 0.2166
Standard uncertainty: 0.003043
95% coverage interval: (0.2106, 0.2227) Dark uncertainty (tau): 0.01678
Tau posterior 0.025 and 0.975 quantiles: (0.01007,0.02959)

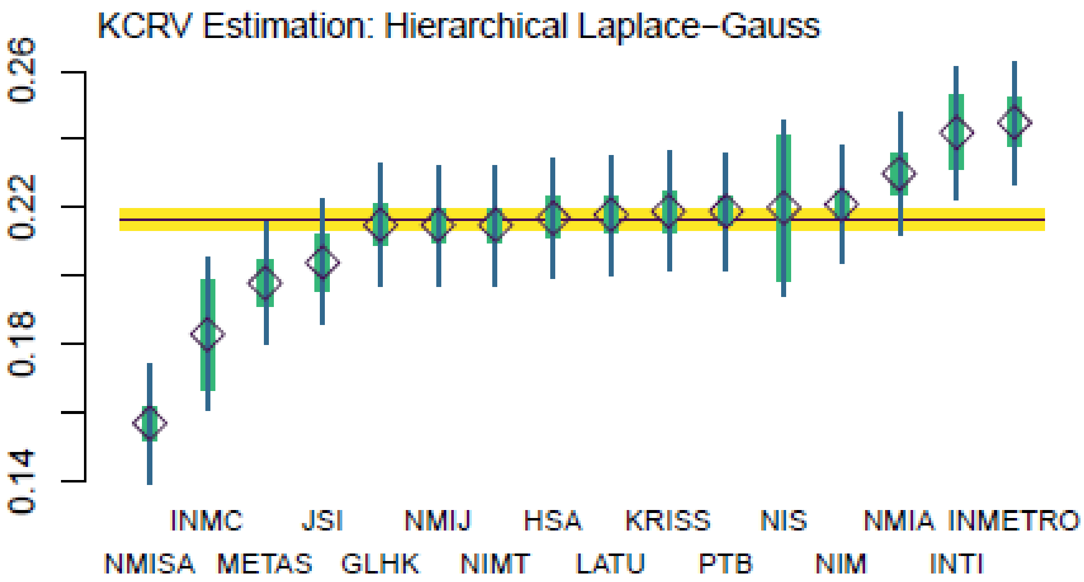
Decision Tree Hypothesis test results (Pb)

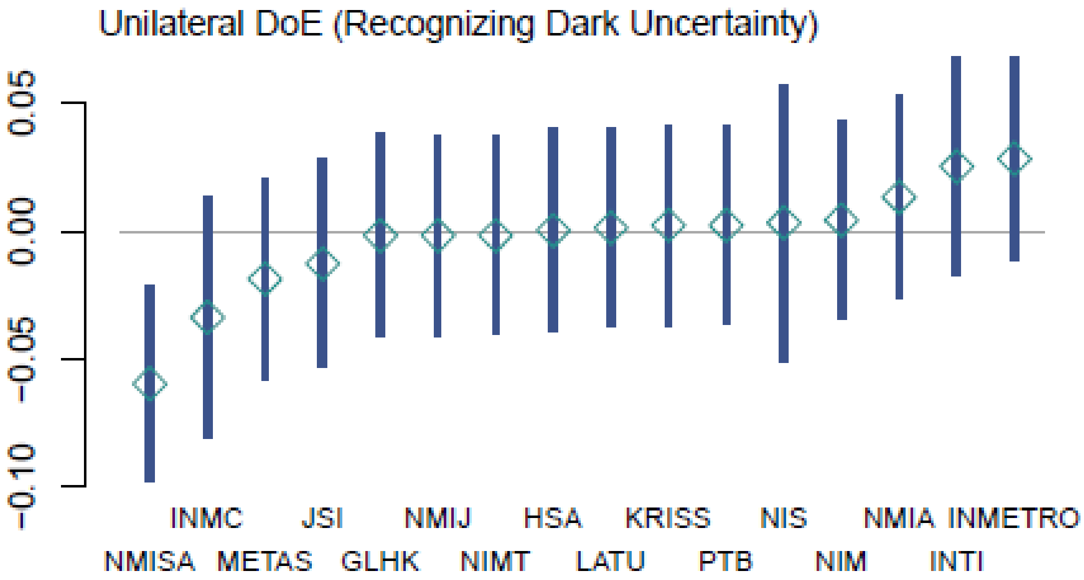
Cochran’s test for Homogeneity: p-value: p < 0.001
Q = 465.6 (Reference Distribution: Chi-Square with 15 Degrees of Freedom)
tau est. = 0.01958
tau/median(x) = 0.09001
tau/median(u) = 4.894

Shapiro-Wilk test for Normality: p = 8.855e-05

Miao-Gel-Gastwirth test of Symmetry: p = 0.2846

Plots (Pb)


KCRV Estimation: Hierarchical Laplace−Gauss
0.14
0.18
0.22
0.26
NMISA
INMC
METAS
JSI
GLHK
NMIJ
NIMT
HSA
LATU
KRISS
PTB
NIS
NIM
NMIA
INTI
INMETRO


Unilateral DoE (Recognizing Dark Uncertainty)
−0.10
−0.05
0.00
0.05
NMISA
INMC
METAS
JSI
GLHK
NMIJ
NIMT
HSA
LATU
KRISS
PTB
NIS
NIM
NMIA
INTI
INMETRO

DoE Table (Pb)

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
NMISA	NMISA	-0.0596200	0.03724	-0.09686	-0.02237
INMC	INMC	-0.0336200	0.04602	-0.07964	0.01240
METAS	METAS	-0.0186200	0.03817	-0.05679	0.01955
JSI	JSI	-0.0126200	0.03942	-0.05204	0.02680
GLHK	GLHK	-0.0016170	0.03829	-0.03991	0.03667
NMIJ	NMIJ	-0.0016170	0.03798	-0.03960	0.03636
NIMT	NIMT	-0.0016170	0.03734	-0.03895	0.03572
HSA	HSA	0.0003828	0.03834	-0.03796	0.03872
LATU	LATU	0.0013830	0.03733	-0.03595	0.03872
KRISS	KRISS	0.0023830	0.03800	-0.03562	0.04038
PTB	PTB	0.0023830	0.03742	-0.03504	0.03980
NIS	NIS	0.0033830	0.05266	-0.04928	0.05604
NIM	NIM	0.0043830	0.03760	-0.03321	0.04198
NMIA	NMIA	0.0133800	0.03825	-0.02487	0.05164
INTI	INTI	0.0253800	0.04120	-0.01582	0.06658
INMETRO	INMETRO	0.0283800	0.03861	-0.01023	0.06699

Lab Uncertainties Table (Pb)

lab	x	u	nu	ut
NMISA	0.157	0.003	60	0.01704
INMC	0.183	0.014	238	0.02185
METAS	0.198	0.005	60	0.01751
JSI	0.204	0.006	5	0.01782
GLHK	0.215	0.004	60	0.01725
NMIJ	0.215	0.003	46	0.01704
NIMT	0.215	0.003	60	0.01704
HSA	0.217	0.004	12	0.01725
LATU	0.218	0.003	60	0.01704
KRISS	0.219	0.004	7	0.01725
PTB	0.219	0.002	29	0.01690
NIS	0.220	0.019	60	0.02535
NIM	0.221	0.002	60	0.01690
NMIA	0.230	0.004	8	0.01725
INTI	0.242	0.009	60	0.01904
INMETRO	0.245	0.005	60	0.01751

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
NMISA	-0.05962	0.01867	0.03724	-0.09686	-0.02237	0.00433	0.008515	-0.06813	-0.0511
INMC	-0.03362	0.02336	0.04602	-0.07964	0.0124	0.01444	0.02841	-0.06202	-0.00521
METAS	-0.01862	0.01914	0.03817	-0.05679	0.01955	0.00591	0.0116	-0.03022	-0.00702
JSI	-0.01262	0.01973	0.03942	-0.05204	0.0268	0.00775	0.01543	-0.02805	0.002814
GLHK	-0.00162	0.01902	0.03829	-0.03991	0.03667	0.005065	0.009944	-0.01156	0.008327
NMIJ	-0.00162	0.0188	0.03798	-0.0396	0.03636	0.004326	0.008531	-0.01015	0.006914
NIMT	-0.00162	0.01866	0.03734	-0.03895	0.03572	0.004298	0.008529	-0.01015	0.006912
HSA	0.000383	0.01907	0.03834	-0.03796	0.03872	0.005284	0.01046	-0.01007	0.01084
LATU	0.001383	0.01871	0.03733	-0.03595	0.03872	0.004327	0.008482	-0.0071	0.009865
KRISS	0.002383	0.01895	0.038	-0.03562	0.04038	0.005498	0.01089	-0.00851	0.01328
PTB	0.002383	0.01853	0.03742	-0.03504	0.0398	0.003689	0.007326	-0.00494	0.009709
NIS	0.003383	0.02662	0.05266	-0.04928	0.05604	0.01923	0.03785	-0.03447	0.04123
NIM	0.004383	0.01863	0.0376	-0.03321	0.04198	0.00367	0.007246	-0.00286	0.01163
NMIA	0.01338	0.01907	0.03825	-0.02487	0.05164	0.005484	0.01081	0.002573	0.02419
INTI	0.02538	0.02067	0.0412	-0.01582	0.06658	0.009592	0.01887	0.006513	0.04425
INMETRO	0.02838	0.01916	0.03861	-0.01023	0.06699	0.005936	0.01163	0.01675	0.04002

MCMC Sampler Diagnostics Table (Pb) (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	16000
lambda[2]	1.001	40000
lambda[3]	1.001	50000
lambda[4]	1.001	49000
lambda[5]	1.001	35000
lambda[6]	1.001	50000
lambda[7]	1.001	32000
lambda[8]	1.001	23000
lambda[9]	1.001	35000
lambda[10]	1.001	50000
lambda[11]	1.001	43000
lambda[12]	1.001	47000
lambda[13]	1.001	24000
lambda[14]	1.001	50000
lambda[15]	1.001	50000
lambda[16]	1.001	50000
mu	1.001	34000
sigma[1]	1.001	50000
sigma[2]	1.001	31000
sigma[3]	1.001	35000
sigma[4]	1.001	50000
sigma[5]	1.001	43000
sigma[6]	1.001	30000
sigma[7]	1.001	24000
sigma[8]	1.001	50000
sigma[9]	1.001	50000
sigma[10]	1.001	50000
sigma[11]	1.001	23000
sigma[12]	1.001	50000
sigma[13]	1.001	13000
sigma[14]	1.001	50000
sigma[15]	1.001	50000
sigma[16]	1.001	32000
Tau	1.001	20000

NIST Decision Tree Report for Sb

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	NIMT*	0.93900	0.02100	60
TRUE	JSI	0.94600	0.03300	8
TRUE	INTI	0.99900	0.03800	60
TRUE	GLHK	1.00700	0.01900	60
TRUE	NMIA	1.01100	0.01800	24
TRUE	KRISS	1.01154	0.00379	1003
TRUE	HSA	1.01700	0.01800	7
TRUE	NMIJ	1.02170	0.00660	869

Date: 2024-07-11
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty Random
Seed: 880
Selected Procedure: Adaptive Weighted Average Consensus
estimate: 1.013
Standard uncertainty: 0.003541
Standard uncertainty (using parametric bootstrap): 0.004961 95%
coverage interval: (1.006, 1.02)
95% coverage interval (using parametric bootstrap): (1.003, 1.023) Dark
uncertainty (tau): 0.002442

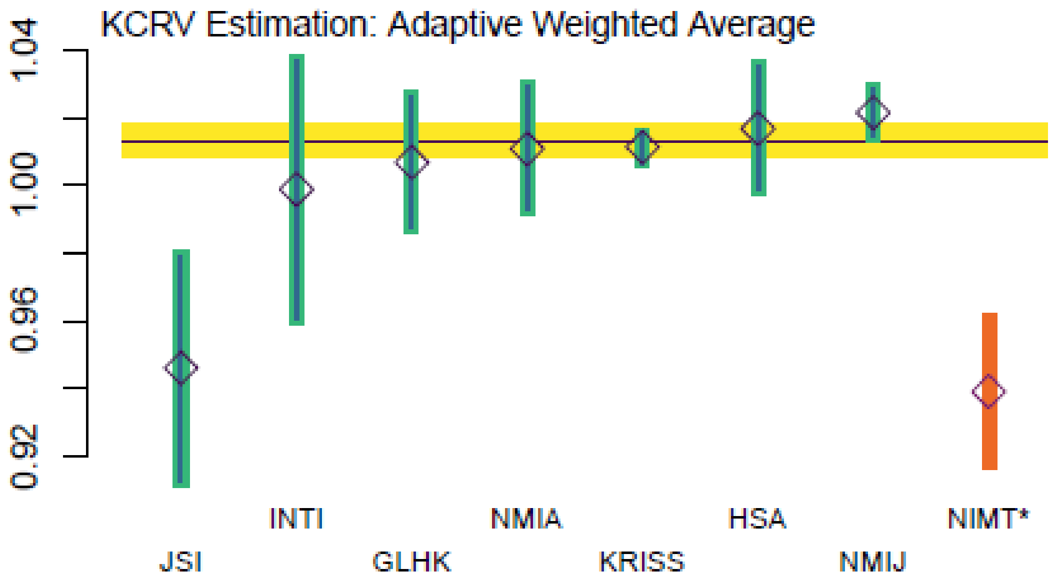
Decision Tree Hypothesis test results

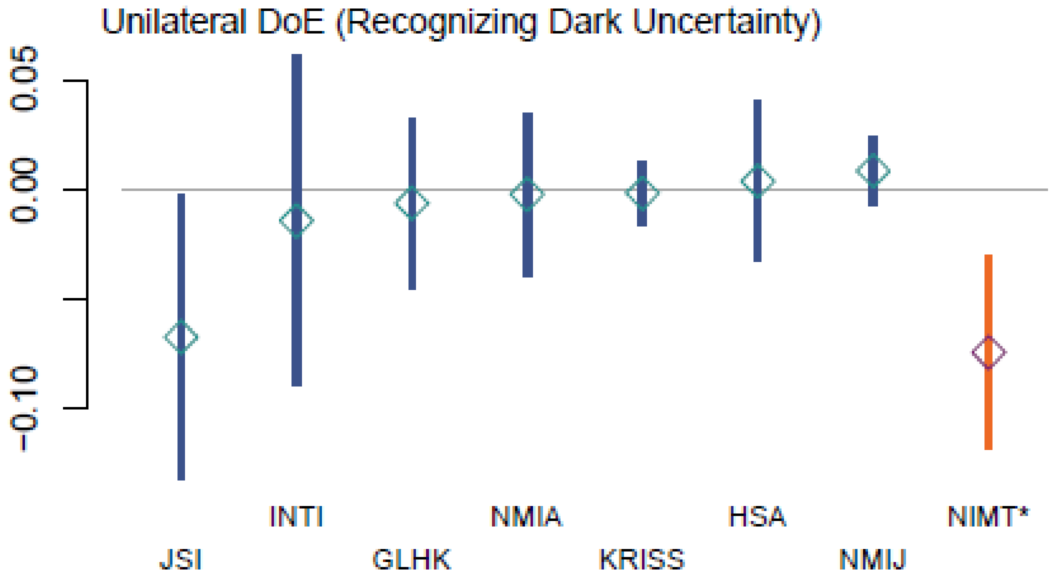
Cochran's test for Homogeneity: p-
value: 0.39
Q = 6.303 (Reference Distribution: Chi-Square with 6 Degrees of Freedom) tau est. =
0.002442
tau/median(x) = 0.002416
tau/median(u) = 0.1357

Shapiro-Wilk test for Normality: p = 0.4148

Miao-Gel-Gastwirth test of Symmetry: p = 0.0926

Plots


KCRV Estimation: Adaptive Weighted Average
1.04
1.00
0.96
0.92
INTI
NMIA
HSA
NIMT*
JSI
GLHK
KRISS
NMIJ


Unilateral DoE (Recognizing Dark Uncertainty)
0.05
0.00
-0.10
INTI
NMIA
HSA
NIMT*
JSI
GLHK
KRISS
NMIJ

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
JSI	JSI	-0.067280	0.06382	-0.131100	-0.003463
INTI	INTI	-0.014280	0.07401	-0.088290	0.059720
GLHK	GLHK	-0.006285	0.03722	-0.043500	0.030930
NMIA	NMIA	-0.002285	0.03548	-0.037770	0.033200
KRISS	KRISS	-0.001745	0.01262	-0.014370	0.010880
HSA	HSA	0.003715	0.03509	-0.031380	0.038810
NMIJ	NMIJ	0.008415	0.01462	-0.006203	0.023030
NIMT*	NIMT*	-0.074280	0.04252	-0.116800	-0.031770

Lab Uncertainties Table

lab	x	u	nu	ut
NIMT*	0.939	0.02100	60	0.021140
JSI	0.946	0.03300	8	0.033090
INTI	0.999	0.03800	60	0.038080
GLHK	1.007	0.01900	60	0.019160
NMIA	1.011	0.01800	24	0.018160
KRISS	1.012	0.00379	1003	0.004509
HSA	1.017	0.01800	7	0.018160
NMIJ	1.022	0.00660	869	0.007037

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
NIMT*	-0.074280	0.021690	0.04252	-0.116800	-0.031770	0.021330	0.041800	-0.116100	-0.032490
JSI	-0.067280	0.032760	0.06382	-0.131100	-0.003463	0.032350	0.063540	-0.130800	-0.003742
INTI	-0.014280	0.037860	0.07401	-0.088290	0.059720	0.037450	0.072530	-0.086810	0.058240
GLHK	-0.006285	0.019110	0.03722	-0.043500	0.030930	0.018390	0.035790	-0.042070	0.029500
NMIA	-0.002285	0.018210	0.03548	-0.037770	0.033200	0.017280	0.034010	-0.036290	0.031720
KRISS	-0.001745	0.005738	0.01262	-0.014370	0.010880	0.003627	0.008139	-0.009884	0.006394
HSA	0.003715	0.018070	0.03509	-0.031380	0.038810	0.017240	0.033190	-0.029470	0.036900
NMIJ	0.008415	0.007493	0.01462	-0.006203	0.023030	0.005842	0.011350	-0.002932	0.019760

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.

APPENDIX F: NIST Decision Tree Reports for Part B

NIST Decision Tree Report for total As

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	NIMT	0.0930000	0.0020000	5.20
FALSE	METAS	0.0970000	0.0030000	3.00
TRUE	JSI	0.1037000	0.0037000	9.54
TRUE	LGC	0.1053462	0.0012084	21.60
TRUE	NIM	0.1060000	0.0020000	12.60
TRUE	NMIJ	0.1063000	0.0020000	6.50
TRUE	NMIA	0.1067000	0.0029000	36.60
TRUE	KRISS	0.1070000	0.0070000	5.00
TRUE	LATU	0.1070000	0.0019000	63.50
TRUE	HSA	0.1072000	0.0019000	5.93
TRUE	NRC	0.1075000	0.0020000	11.70
TRUE	GLHK	0.1080000	0.0027000	60.00
TRUE	INTI	0.1094000	0.0057000	12.40

Date: 2023-09-07
Version Number: 1.0.2
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty Random
Seed: 601
Selected Procedure: Adaptive Weighted Average
Consensus estimate: 0.1064
Standard uncertainty: 0.0006497
Standard uncertainty (using parametric bootstrap): 0.0006992 95% coverage interval: (0.1051, 0.1077)
95% coverage interval (using parametric bootstrap): (0.105, 0.1077) Dark uncertainty (tau): 0

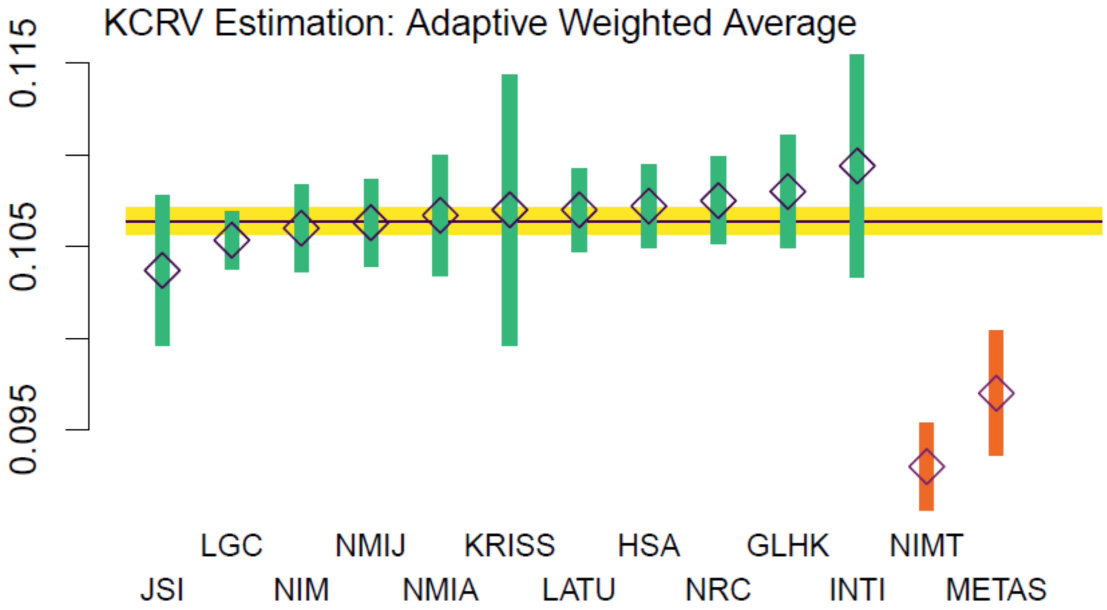
Decision Tree Hypothesis test results

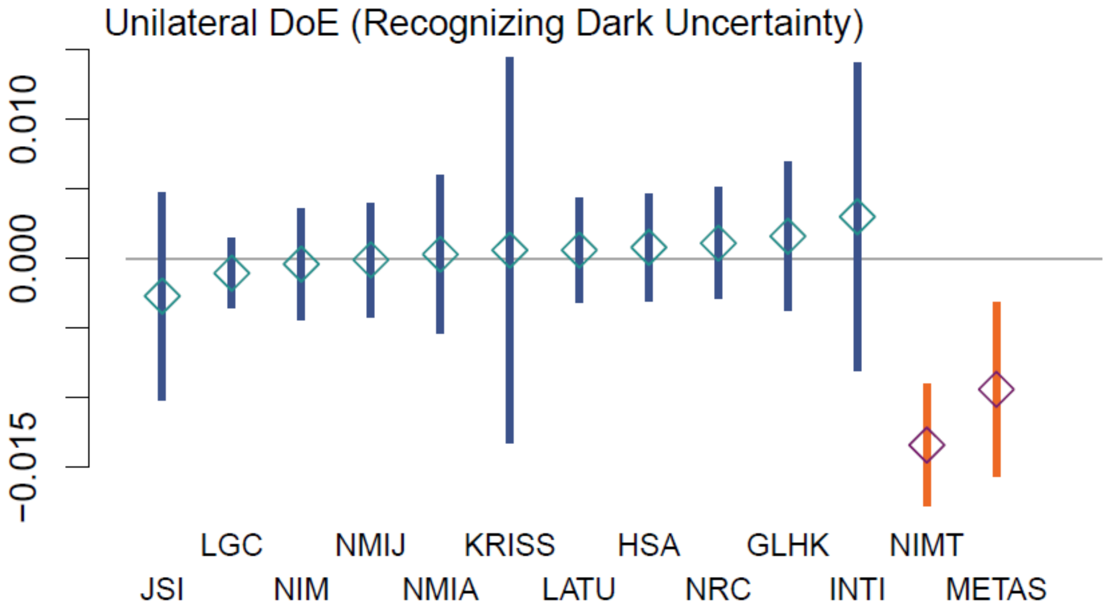
Cochran’s test for Homogeneity:
p-value: 0.99
Q = 2.561 (Reference Distribution: Chi-Square with 10 Degrees of Freedom) tau est. = 0
tau/median(x) = 0
tau/median(u) = 0

Shapiro-Wilk test for Normality: p = 0.2184

Miao-Gel-Gastwirth test of Symmetry: p = 0.36

Plots


KCRV Estimation: Adaptive Weighted Average
0.095
0.105
0.115
LGC
NMIJ
KRISS
HSA
GLHK
NIMT
JSI
NIM
NMIA
LATU
NRC
INTI
METAS


Unilateral DoE (Recognizing Dark Uncertainty)
−0.015
0.000
0.010
LGC
NMIJ
KRISS
HSA
GLHK
NIMT
JSI
NIM
NMIA
LATU
NRC
INTI
METAS

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
JSI	JSI	-0.002691	0.007193	-0.009884	0.004502
LGC	LGC	-0.001045	0.002265	-0.003310	0.001220
NIM	NIM	-0.000391	0.003709	-0.004100	0.003318
NMIJ	NMIJ	-0.000091	0.003850	-0.003941	0.003759
NMIA	NMIA	0.000309	0.005452	-0.005143	0.005761
KRISS	KRISS	0.000609	0.013560	-0.012950	0.014170
LATU	LATU	0.000609	0.003525	-0.002916	0.004134
HSA	HSA	0.000809	0.003612	-0.002803	0.004421
NRC	NRC	0.001109	0.003722	-0.002613	0.004831
GLHK	GLHK	0.001609	0.005060	-0.003451	0.006669
INTI	INTI	0.003009	0.010840	-0.007836	0.013850
NIMT	NIMT	-0.013390	0.004155	-0.017550	-0.009236
METAS	METAS	-0.009391	0.006039	-0.015430	-0.003352

Lab Uncertainties Table

lab	x	u	nu	ut
NIMT	0.0930	0.0020	5.20	0.0020
METAS	0.0970	0.0030	3.00	0.0030
JSI	0.1037	0.0037	9.54	0.0037
LGC	0.1053	0.0012	21.60	0.0012
NIM	0.1060	0.0020	12.60	0.0020
NMIJ	0.1063	0.0020	6.50	0.0020
NMIA	0.1067	0.0029	36.60	0.0029
KRISS	0.1070	0.0070	5.00	0.0070
LATU	0.1070	0.0019	63.50	0.0019
HSA	0.1072	0.0019	5.93	0.0019
NRC	0.1075	0.0020	11.70	0.0020
GLHK	0.1080	0.0027	60.00	0.0027
INTI	0.1094	0.0057	12.40	0.0057

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
NIMT	-0.0027	0.0037	0.0072	-0.0099	0.0045	0.0038	0.0074	-0.0101	0.0047
METAS	-0.0010	0.0011	0.0022	-0.0032	0.0011	0.0014	0.0027	-0.0038	0.0017
JSI	-0.0004	0.0019	0.0037	-0.0041	0.0033	0.0021	0.0042	-0.0046	0.0038
LGC	-0.0001	0.0019	0.0037	-0.0037	0.0036	0.0021	0.0041	-0.0042	0.0040
NIM	0.0003	0.0028	0.0055	-0.0052	0.0058	0.0030	0.0059	-0.0056	0.0062
NMIJ	0.0006	0.0070	0.0139	-0.0133	0.0145	0.0071	0.0140	-0.0134	0.0146
NMIA	0.0006	0.0018	0.0036	-0.0030	0.0042	0.0020	0.0039	-0.0033	0.0045
KRISS	0.0008	0.0018	0.0036	-0.0028	0.0044	0.0020	0.0040	-0.0032	0.0048
LATU	0.0011	0.0019	0.0037	-0.0026	0.0048	0.0022	0.0042	-0.0031	0.0053
HSA	0.0016	0.0026	0.0051	-0.0035	0.0068	0.0028	0.0055	-0.0039	0.0071
NRC	0.0030	0.0056	0.0111	-0.0080	0.0141	0.0058	0.0114	-0.0084	0.0144
GLHK	-0.0134	0.0021	0.0042	-0.0175	-0.0092	0.0021	0.0042	-0.0175	-0.0092
INTI	-0.0094	0.0031	0.0060	-0.0154	-0.0034	0.0031	0.0060	-0.0154	-0.0034

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.

NIST Decision Tree Report for inorganic As

Summary

Include	Laboratory	Result	Uncertainty	Degrees of Freedom
FALSE	NRC	0.06130	0.00220	7.99
FALSE	NIMT	0.08100	0.00500	3.00
TRUE	GLHK	0.08890	0.00391	60.00
TRUE	HSA	0.08960	0.00290	5.64
TRUE	LGC	0.09006	0.00160	44.80
TRUE	NMIJ	0.09070	0.00096	5.09
TRUE	NIM	0.09390	0.00150	46.50

Date: 2023-09-07
Version Number: 1.0.2
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty Random
Seed: 541
Selected Procedure: Weighted Median
Consensus estimate: 0.09034
Standard uncertainty: 0.0005511
95% coverage interval: (0.08893, 0.0917)

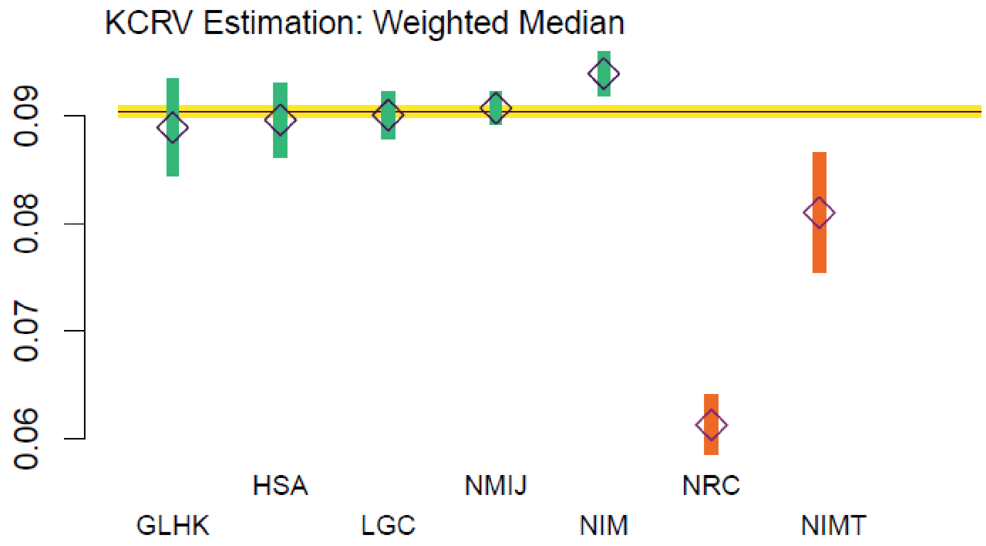
Decision Tree Hypothesis test results

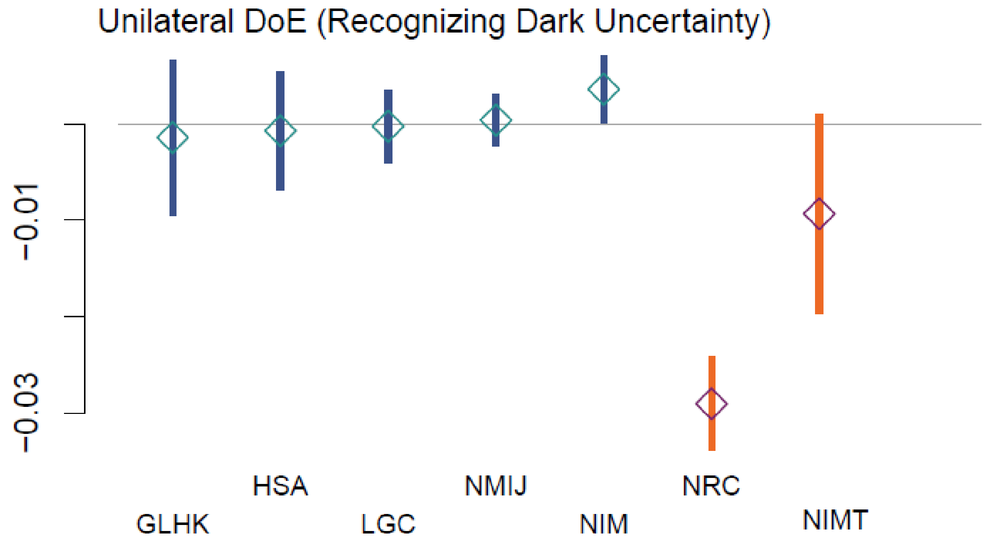
Cochran's test for Homogeneity:
p-value: 0.32
Q = 4.661 (Reference Distribution: Chi-Square with 4 Degrees of Freedom) tau est. = 0.0006949
tau/median(x) = 0.007716
tau/median(u) = 0.4343

Shapiro-Wilk test for Normality: p = 0.06622

Miao-Gel-Gastwirth test of Symmetry: p = 0.183

Plots


KCRV Estimation: Weighted Median
0.06
0.07
0.08
0.09
GLHK
HSA
LGC
NMIJ
NIM
NRC
NIMT


Unilateral DoE (Recognizing Dark Uncertainty)
−0.03
−0.01
GLHK
HSA
LGC
NMIJ
NIM
NRC
NIMT

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
NRC	NRC	-0.0290400	0.004583	-0.0336200	-0.0244600
NIMT	NIMT	-0.0093420	0.010030	-0.0193700	0.0006859
GLHK	GLHK	-0.0014420	0.007731	-0.0091730	0.0062900
HSA	HSA	-0.0007415	0.005820	-0.0065620	0.0050790
LGC	LGC	-0.0002815	0.003472	-0.0037530	0.0031900
NMIJ	NMIJ	0.0003585	0.002313	-0.0019540	0.0026710
NIM	NIM	0.0035580	0.003159	0.0003995	0.0067180

Lab Uncertainties Table

lab	x	u	nu	ut
NRC	0.0613	0.0022	7.99	0.0022
NIMT	0.0810	0.0050	3.00	0.0050
GLHK	0.0889	0.0039	60.00	0.0039
HSA	0.0896	0.0029	5.64	0.0029
LGC	0.0901	0.0016	44.80	0.0016
NMIJ	0.0907	0.0010	5.09	0.0010
NIM	0.0939	0.0015	46.50	0.0015

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
NRC	-0.0290	0.0023	0.0044	-0.0335	-0.0246	0.0023	0.0044	-0.0335	-0.0246
NIMT	-0.0093	0.0051	0.0100	-0.0193	0.0006	0.0051	0.0100	-0.0193	0.0006
GLHK	-0.0014	0.0039	0.0076	-0.0091	0.0062	0.0039	0.0076	-0.0091	0.0062
HSA	-0.0007	0.0030	0.0058	-0.0065	0.0050	0.0030	0.0058	-0.0065	0.0050
LGC	-0.0003	0.0017	0.0035	-0.0037	0.0032	0.0017	0.0035	-0.0037	0.0032
NMIJ	0.0004	0.0012	0.0023	-0.0020	0.0027	0.0012	0.0023	-0.0020	0.0027
NIM	0.0036	0.0017	0.0032	0.0003	0.0068	0.0017	0.0032	0.0003	0.0068

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.