CCQM-K155
Elements and Tributyltin in Seawater

Key Comparison

Final Report

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Authors:
Wai-hong Fung[1], Süleyman Z. Can[2], Kelvin Chun-wai Tse[1], Yuk-tai Tsoi[1], Wan-waan Lee[1], Betül Arı[2], Murat Tunç[2], Jeffrey Merrick[3], Rodrigo Caciano de Sena[4], Kenny Nadeau[5], Juris Meija[5], Lu Yang[5], Zoltan Mester[5], Soraya Sandoval Riquelme[6], Javier Vera Maldonado[6], Jingbo Chao[7], Qian Wang[7], Shanjun Song[7], Paola Fisicaro[8], Yanbei Zhu[9], Yong-Hyeon Yim[10], Kyoung-Seok Lee[10], Evaldas Naujalis[11], Michał Strzelec[12], Aleksey Stakheev[13], Anatoliy Krylov[14], Egor Sobina[15], Richard Shin[16], Fransiska Dewi[16], Sim Lay Peng[16], Leung Ho Wah[16], Wesley Yu[16], Radojko Jaćimović[17], Tea Zuliani[17], Conny Haraldsson[18], Sutthinun Taebunpakul[19]

1. Government Laboratory, Hong Kong, China
2. TUBITAK Ulusal Metroloji Enstitüsü, Türkiye
3. National Measurement Institute, Australia
4. Instituto Nacional de Metrologia, Qualidade e Tecnologia, Brazil
5. National Research Council Canada, Canada
6. Instituto de Salud Pública de Chile, Chile
7. National Institute of Metrology, China
8. Laboratoire National de Métrologie et d'Essais, France
9. National Metrology Institute of Japan, Japan
10. Korea Research Institute of Standards and Science, Korea (Republic of)
11. Center for Physical Sciences And Technology, Lithuania
12. Central Office of Measures, Poland
13. Russian Metrological Institute of Technical Physics and Radio Engineering, Russian Federation
14. D.I. Mendeleyev Institute for Metrology, Rosstandart, Russian Federation
15. UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology, Russian Federation
16. Health Sciences Authority, Singapore
17. Jožef Stefan Institute, Slovenia
18. RISE Research Institutes of Sweden AB, Sweden
19. National Institute of Metrology (Thailand), Thailand

Coordinators:
Wai-hong Fung, Kelvin Chun-wai Tse, Yuk-tai Tsoi and Wan-waan Lee
Süleyman Z. Can, Betül Arı Engin, and Murat Tunç

SUMMARY

Twenty National Metrology Institutes and Designated Institutes registered in the CCQM Key Comparison of CCQM-K155 “Elements and Tributyltin in Seawater” and nineteen institutes submitted their results. Participants were requested to evaluate the mass fractions, expressed in ng/g, of arsenic, cadmium, copper, lead, nickel, zinc and ng/kg level of tributyltin in seawater. Key Comparison Reference Values (KCRVs) are assigned to the various measurands by the NIST decision tree approach (NDT). Participants used analytical methods of their choice. Most participants employed dilution or co-precipitation for sample treatment and analyzed the samples using Isotope Dilution Mass Spectrometry (IDMS) or standard addition method with ICP-MS, applying various interference removing techniques for different elements. For tributyltin, most participants utilized derivatization followed by liquid-liquid extraction, with analysis conducted using isotope dilution GC-ICP-MS.

Measurand	**KCRV ($\overline{X}_{NDT}$)**	**$u(\overline{X}_{NDT})$**	**Dark uncertainty (τ)**	**NDT estimator**
Arsenic	3.832 ng/g	0.050 ng/g	0.102 ng/g	Adaptive Weighted Average (AWA)
Cadmium	0.2283 ng/g	0.0044 ng/g	0.0101 ng/g	Hierarchical Laplace + Gauss (HLG)
Copper	3.099 ng/g	0.035 ng/g	0.068 ng/g	Hierarchical Gauss + Gauss (HGG)
Lead	1.067 ng/g	0.012 ng/g	0.021 ng/g	Hierarchical Gauss + Gauss (HGG)
Nickel	4.549 ng/g	0.027 ng/g	0.052 ng/g	Hierarchical Gauss + Gauss (HGG)
Zinc	8.540 ng/g	0.042 ng/g	0.037 ng/g	Adaptive Weighted Average (AWA)
Tributyltin	7.020 ng/kg	0.557 ng/kg	1.318 ng/kg	Hierarchical Laplace + Gauss (HLG)

Successful participation in CCQM-K155 demonstrates measurement capabilities for determining mass fraction of transition elements (excluding mercury) and metalloids/semi-metals, with mass fractions ranging from 0.1 ng/g to 50 ng/g. Additionally, it covers small organo-tin and organo-mercury compounds with mass fractions from 1 ng/kg to 50 ng/g in a high-salt content matrix (seawater).

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ACRONYMS/SYMBOLS

AWA	Adaptive Weighted Average
NH_4OH	ammonium hydroxide
ANOVA	analysis of variance
u_{bb}	between-bottle (in)homogeneity
CCQM	Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology
CMC	calibration and measurement capability
CWA	Clean Water Act
tau	dark uncertainty
°C	degree Celsius
DoE	degree of equivalence
DI	designated institute
D_i	difference from KCRV
DRC	dynamic reaction cell
EQS	environmental quality standards
EC	European Community
EU	European Union
$U(D_i)$	expanded uncertainty of the difference
GC-ICP-MS	gas chromatography – inductively coupled plasma – mass spectrometry
GC-MS	gas chromatography – mass spectrometry
HGG	Hierarchical Gauss-Gauss
HLG	Hierarchical Laplace-Gauss
HDPE	high density polyethylene
HMI	high matrix introduction
ICP-HR-MS	high resolution – inductively coupled plasma – mass spectrometry
HVG-AAS	hydride-vapor generation – flame atomic absorption spectrometry
GC	gas chromatography
IAWG	Inorganic Analysis Working Group
ICP-MS	inductively coupled plasma – mass spectrometry
IS/ISTD	internal standard
IDMS	isotope dilution mass spectrometry
ISO	International Organization for Standardization
KC	Key Comparison
KCRV	Key Comparison Reference Value
kGy	kilogray
KED	kinetic energy discrimination
L	litre
µg/kg	microgram per kilogram
µg/L	microgram per litre
µm	micrometre
mL	millilitre
ng/g	nanogram per gram
ng/kg	nanogram per kilogram
NMI	national metrology institute
NDT	NIST Decision Tree
HNO_3	nitric acid
%	percentage

PES	polyethersulfone
PET	polyethylene terephthalate
pH	decimal logarithm of the reciprocal of the hydrogen ion activity
PS	Pilot Study
PTFE	polytetrafluoroethylene
psu	pressure status unit
SA	standard addition
u(KCRV)	standard uncertainty of the Key Comparison Reference Value
TMAH	tetramethyl ammonium hydroxide
TBT	tributyltin
TEA	triethylamine
QQQ-ICP-MS	triple quadrupole inductively coupled plasma – mass spectrometry
TDS	total dissolved solid
UHP	ultra high purity
USEPA	United States Environmental Protection Agency
WFD	Water Framework Directive

1. INTRODUCTION

Monitoring trace elements and tributyltin in seawater is crucial for determining environmental baselines, measuring environmental changes, and assessing the overall ecosystem. This information can greatly benefit the management and protection of marine resources, as well as safeguard human health. In line with this objective, the European Union (EU) has implemented Directive 2000/60/EC (Water Framework Directive or WFD), which aims to achieve long-term high-level protection from chemical pollution in the aquatic environment, covering lakes, groundwater, and coastal waters. The WFD establishes a list of priority substances while the daughter Directive 2013/39/EU sets environmental quality standards (EQS) for priority substances and other pollutants, with the goal of achieving good chemical status in surface waters. For instance, the WFD sets maximum allowable concentrations of cadmium in seawater ranging from 0.45 µg/L to 1.5 µg/L, depending on water hardness classes. In the United States, the Clean Water Act (CWA) provides the basic framework for regulating the discharge of pollutants into waters, including seawater, and establishing quality standards. The United States Environmental Protection Agency (USEPA) develops Water Quality Criteria that accurately reflect the latest scientific knowledge on the impacts of pollutants on human health and the environment, encompassing both freshwater and saltwater environments. Arsenic, cadmium, chromium (VI), copper, lead, nickel, selenium, silver, and zinc are recommended pollutants listed in the table for saltwater. The use of reliable methods to measure trace elements in seawater is essential to safeguard the ecosystem and public health. Achieving accurate measurements at the ng/g level for arsenic, cadmium, copper, lead, nickel, and zinc, as well as at the ng/kg level for tributyltin in seawater, pose important challenges for reference material producers and providers of measurement services, including proficiency testing schemes. To adequately support calibration and measurement capability (CMC) claims made by national metrology institutes (NMIs) and designated institutes (DIs), evidence of successful participation in relevant international comparisons is required.

According to the IAWG's five-year plan, it is recommended to have a key comparison under the measurement service category of high salt content for the year 2019. In this regard, the National Metrology Institute of Türkiye (TUBITAK UME or shortly UME) and the Government Laboratory of Hong Kong, China (GLHK) proposed to coordinate a new key comparison study for the determination of trace elements and tributyltin in seawater at the CCQM IAWG Meeting in September 2017. In March 2018, the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) approved the Key Comparison (KC) and parallel Pilot Study (PS) of CCQM-K155/-P196 "Elements and Tributyltin in Seawater". CCQM-K155/-P196 was designed to assess participants' capabilities for measuring the mass fractions of the analytes at ng/g levels in a test sample of high salt content (seawater) by various analytical techniques. CCQM-K155/-P196 was further discussed at the CCQM IAWG Meeting in April 2018. Lead, mercury, nickel, and zinc have been selected as the measurands in Sample A prepared by UME, whereas arsenic, cadmium, copper have been selected as the measurands in Sample B prepared by GLHK, and tributyltin in Sample C prepared by UME. It was the first KC for trace elements in seawater (high salt) matrix.

The following sections of this report document the timeline of CCQM-K155, the measurands, study material, participants, results, and the measurement capability claims that participation in CCQM-K155 can support. The Appendices reproduce the official communication materials and summaries of information about the results provided by the participants.

2. TIMELINE

Table 1 lists the timeline for CCQM-K155.

Table 1. Timeline for CCQM-K155.

Date	Action
Sep 2017	Proposed to CCQM
Apr 2018	Draft protocol presented to IAWG
Oct 2018	IAWG authorized CCQM-K155/P196
Feb 2019	Call for participation to IAWG members
Oct 2019	Study samples shipped to participants. The range in shipping times reflects delays from shipping and customs.
Jan 2020	Results due to pilot institute (for tributyltin)
Jun 2020	Results due to pilot institutes (for elements)
Jan 2024	Draft A report distributed to participants
Oct 2024	Draft A2 report distributed to participants
Oct 2024	Draft B report distributed to IAWG
Jan 2025	Final report approved by CCQM

3. MEASURANDS

Participating laboratories were given different volumes of seawater for samples A, B, and C. Sample A consisted of about 250 mL of seawater, while sample B had about 100 mL, and sample C contained about 1 L. The expected mass fractions of the measurands are provided in Table 2.

Table 2. Measurands and mass fractions in the sample A, sample B and sample C.

Sample identity	Measurand	Expected mass fraction (unit)
Sample A (prepared by UME)	lead	0.5 ng/g – 10 ng/g
	mercury*	0.1 ng/g – 2 ng/g
	nickel	1 ng/g – 20 ng/g
	zinc	1 ng/g – 20 ng/g
Sample B (prepared by GLHK)	arsenic	1 ng/g – 20 ng/g
	cadmium	0.1 ng/g – 2 ng/g
	copper	1 ng/g – 20 ng/g
Sample C (prepared by UME)	tributyltin	1 ng/kg – 20 ng/kg

Note *: According to the decision made in Nov 2020 IAWG Meeting, mercury was removed as a measurand due to instability in the sample.

4. STUDY MATERIALS

Sample A: lead, mercury, nickel and zinc

The sampling of seawater (sample A) was performed from the Marmara Sea (40 31,423 N; 027 11, 333 E), Türkiye by research vessel of TUBITAK Marmara Research Center. About 100 L of seawater was acidified by subboiled HNO_3 to adjust the pH to 1.6. The salinity and total dissolved solid (TDS) of the water is 27 psu and 1.7 %, respectively. Whole processing of reference materials including cleaning of bottles and processing equipment, spiking, homogenization and filling had been taken in ISO 6 Clean Chemical Laboratory. Approximately 100 L raw material was transferred into pre-cleaned 114 L HDPE drum, and was homogenized for 4 hours after spiking. The whole batch was filtered from one drum to another via 0.8/0.2 µm (Pall Corp, Supor® Membrane, AcroPackTM 1000, PN 12992) which also used for removing bacterial retention. Materials were filled into 250 mL low density polyethylene bottles manually in ISO 6 clean laboratory. Bottles were irradiated using a gamma source at a dose of about 25 kGy. All the bottles were placed into aluminized PET sachets after gamma irradiation, and placed in 4 °C temperature room.

Sample B: arsenic, cadmium and copper

About 12 L of seawater was collected from the Victoria Harbour in Hong Kong, China. The material has a salinity of about 28. It was filtered through 0.45 µm PES filters (HPWP, Millipore) and 0.22 µm PES filters (GPWP, Millipore) into a pre-cleaned 15 L polypropylene carboy. The seawater was then acidified to a pH of around 1.5 using ultrapure nitric acid. The material was spiked and confirmed to contain varying amounts of arsenic, cadmium and copper. A mechanical stirrer was used to thoroughly mix the material for one week to ensure homogenization. Afterward, the material was irradiated with a gamma source at a dose of approximately 10 kGy for disinfection purposes. The irradiated material was packed into pre-cleaned and nitrogen-flushed 125 mL high-density polyethylene bottles, with each bottle holding around 100 mL. A total of 110 bottles of samples were prepared. Finally, each bottle of sample was vacuum-sealed in a polypropylene bag and stored in a refrigerator at 4 °C until distribution or use.

Sample C: tributyltin

Due to the limited stability of tributyltin in sea water, inter-comparison samples were prepared shortly before the distribution. The sampling was performed from the coast of Marmara Sea. The samples were filtered through 0.2 µm filters (ISOLAB) into a pre-cleaned 20 L glass bottle. After homogenization, sea water was filled into 1 L amber glass bottles with PTFE septum caps. All the bottles were stored in 4 °C refrigerator prior to distribution.

Homogeneity Assessment of Study Material

Sample A: lead, mercury, nickel and zinc

The homogeneity study was performed using 10 bottles. Three independent subsamples were taken from each unit using 5.0 g of sample. As co-precipitation was applied with isotope dilution mass spectrometry technique (IDMS) for determination of lead, nickel and zinc, cold vapor IDMS was applied for the measurements of mercury determination.

Trend analysis were performed for both filling sequence and analytical sequence order. Assessment of homogeneity data was performed by one-way ANOVA, and results were given in Table 3a.

Sample B: arsenic, cadmium and copper

The homogeneity study was conducted after the testing material had been bottled and irradiated. Ten bottles of the test material, stored in a 4 °C refrigerator, were randomly selected from the entire batch. Two 10 g samples were taken from each bottle for analysis. The samples were analyzed using validated procedures, including gravimetric standard additions with ICP-MS for arsenic and copper and co-precipitation with double isotope dilution ICP-MS for cadmium. The between-bottle (in)homogeneity was assessed using ANOVA technique in accordance with ISO Guide 35:2017. The results are summarized in Table 3a.

Based on the results, it can be concluded that the bottles were sufficiently homogeneous, and no trend for filling sequence was observed at a 95 % confidence level. The results of the homogeneity study indicated that there was no significant inhomogeneity in the test material. Therefore, the test material was considered suitable for the purpose of the key comparison.

Table 3a. Results of the homogeneity assessment for sample A and sample B.

Sample identity	**Measurand**	**ANOVA test**		**Relative standard uncertainty due to between-bottle (in)homogeneity, u_{bb} (%)**
		***F*-statistics**	**Critical value at 95 % confidence level**	
Sample A	lead	0.96	2.39	0.08
	mercury	0.68	2.42	1.52
	nickel	1.67	2.39	0.11
	zinc	0.07	2.42	1.62
Sample B	arsenic	1.16	3.02	1.11
	cadmium	1.59	3.02	0.73
	copper	0.51	3.02	1.04

Sample C: tributyltin

Seawater collected from Marmara Sea was filtered through 0.22 µm filters (GPWP, Millipore) into a pre-cleaned 20 L glass bottle and was homogenized for five hours after spiking. Materials were filled into 1000 mL amber glass bottles with PTFE/silicone septum cap. The homogeneity assessment was performed through five bottles. Three independent subsamples were taken from each unit, and isotope dilution GC-ICPMS method was applied for the measurements.

Trend analysis were performed for both filling sequence and analytical sequence order. Assessment of homogeneity data was performed by one way ANOVA, and results are given in Table 3b. Based on the results, the bottles were sufficiently homogeneous and no trend for filling sequence was observed at a 95 % confidence level.

Table 3b. Results of the homogeneity for sample C.

Sample identity	**Measurand**	**ANOVA test**		**Relative standard uncertainty due to between-bottle (in)homogeneity, u_{bb} (%)**
		***F*-statistics**	**Critical value at 95 % confidence level**	
Sample C	tributyltin	1.42	3.48	0.98

Stability Assessment of Study Material

Sample A: lead, mercury, nickel and zinc

Both short and long-term stability analysis were performed using an isochronous approach over the determined time periods.

For the short-term stability (STS) measurements, according to the designed test temperatures and time points, 14 units were selected by RSS from the whole batch produced. The tests were performed for one, two and four weeks at pre-defined test temperatures, +18 °C and +60 °C. Two units for each time period were used. The bottles kept at test temperatures for defined time periods were transferred to reference temperature, +4 °C where "reference" units were already kept. For Zn, 30 °C and 40 °C temperatures were also studied as the slopes of regression line was significantly different from zero at 60 °C. Table 4a(i) summarizes the Student's *t*-test results of the short-term stability assessment for sample A.

Table 4a(i). Results of the short-term stability assessment for sample A.

Measurand	**STS 18 °C**	**STS 60 °C**	**STS 30 °C**	**STS 40 °C**	***t*-crit at 95 % confidence level**
	Student's *t*-test	**Student's *t*-test**	**Student's *t*-test**	**Student's *t*-test**	
	***t*-calc**	***t*-calc**	***t*-calc**	***t*-calc**	
lead	1.32	0.60	-	-	2.07
nickel	0.06	0.14	-	-	2.07
zinc	1.96	11.8	0.06	2.70	2.07

For the long-term stability study (LTS), two units for each storage time period [(0, 2, 4, 6, 9, 12 and 15) months] and three replicates from each unit were measured for LTS analysis. The reference temperature was set to 4 °C, and each unit were transferred to reference temperature at the end of the period spent at 18 °C. Table 4a(ii) summarizes the Student's *t*-test results of the long-term stability assessment for sample A.

Table 4a(ii). Results of the long-term stability assessment for sample A.

Measurand	**Student's *t*-test**	
	***t*-calc**	***t*-crit at 95 % confidence level**
lead	1.29	2.02
nickel	1.62	2.02
zinc	0.36	2.02

Thus, the statistical evaluation of the data shows that the study material was stable during the course of comparison for all three measurands.

Sample B: arsenic, cadmium and copper

For the short-term stability test, the study was conducted using an isochronous approach over a 4-week period. The simulated transport temperature was set at 40 °C ± 5 °C, while the reference temperature remained at about 4 °C. The same analytical procedures as the homogeneity study were applied. At three different time points (1 week, 2 weeks, and 4 weeks), two bottles of sample were randomly transferred from the reference temperature to the simulated transport temperature. Duplicate analyses were performed on each bottle to monitor the stability of the samples. To assess the stability of the test material at 40 °C, the slope β_1 of the regression line (mass fraction of analyte versus time) should not be significantly different from zero, as per the trend-analysis technique proposed by ISO Guide 35:2017. The summarized results can be found in Table 4b(i).

Table 4b(i). Results of the short-term stability assessment for sample B.

Measurand	***p*-value for significance test for β_1**
	40 °C
arsenic	0.320
cadmium	0.979
copper	0.859

The *p*-value (> 0.05) indicates that the regression is insignificant. Therefore, the samples were considered to be adequately stable.

For the long-term stability, the study was conducted using a classical approach, starting from the date of the homogeneity study and continuing until the deadline for submission of results. The test material was stored at a temperature of about 4 °C. The analytical procedures used were the same as those for the homogeneity study. A total of 4 monitoring points were included in the study, with the last monitoring point occurring on 12 October 2020. The stability of the test material was assessed using the trend-analysis technique proposed by ISO Guide 35:2017. Student's *t*-test was applied to the slope of the linear regression, and no significant instability of the comparison material was observed since $|b_1| < t_{95,n-2} \times s(b_1)$, and the slope β_1 of the regression line (mass fraction of analyte versus time) should not be significantly different from zero. The results are summarized in Table 4b(ii).

Table 4b(ii). Results of the long-term stability assessment for sample B.

Measurand	$\lvert b_1 \rvert$	$t_{95,n-2} \times s(b_1)$	p-value for significance test for β_1
arsenic	0.60×10^{-4}	3.47×10^{-4}	0.537
cadmium	1.11×10^{-4}	1.88×10^{-4}	0.127
copper	1.19×10^{-5}	2.59×10^{-5}	0.188

The *p*-value (> 0.05) indicates that the regression is insignificant. The test samples were considered to be adequately stable.

Sample C: tributyltin

A short-term stability study using isochronous design was carried out over a period of 4 weeks. Two randomly selected bottles were transferred from the reference temperature of 4 °C to 23 °C and 45 °C over the study period. Using Student's *t*-test on the slope of the linear regression at 95 % level of confidence, no significant instability of tributyltin in the comparison material was observed. Table 4c(i) summarizes the Student's *t*-test results of the short-term stability assessment for sample C.

Table 4c(i). Results of the short-term stability assessment for sample C.

Measurand	Short-term stability 23 °C		Short-term stability 45 °C	
	Student's *t*-test		Student's *t*-test	
	t-calc	*t*-crit at 95 % confidence level	*t*-calc	*t*-crit at 95 % confidence level
tributyltin	0.86	2.08	0.85	2.10

Thus, the material is assumed to be adequately stable during the dispatch period.

The long-term stability study for sample C was conducted using a classical approach, starting from the date of the homogeneity study until the deadline for submission of results. The test material was stored at a temperature of about 4 °C (reference temperature). The results are given in Table 4c(ii) below.

Table 4c(ii). Results of the long-term stability assessment for sample C.

Week	Tributyltin (%)	RSD (%)
0	100 (spike amount)	-
3	99.9	1.5
12	100.6	1.2
16	81.0	2.1
38	96.0	5.3

The trend observed during the measurement period is not significant considering the known stability limitations of the material. Thus, the deviation from the starting mass fraction during the course of measurement period is low enough for possibly associating with the reported measurement results.

5. PARTICIPANTS, INSTRUCTIONS AND SAMPLE DISTRIBUTION

The call for participation was sent out in February 2019, with the intention of distributing samples in October 2019. The deadline for submitting results for TBT was 31 January 2020, while the deadline for elements was extended to 30 June 2020. Discussions of the results were held during the IAWG meetings. Please refer to Table 1 for the study timeline. Appendix A includes the Call for Participation and the study Protocol. A total of twenty (20) institutes registered for CCQM-K155, and the registered institutes for the comparison study are listed in Table 5.

Table 5. Institutes registered for CCQM-K155 (in alphabetical order by the name of member state/ associate).

Number	Member State/ Associate	NMI or DI	Institute code	Measurands registered	Contact
1	Australia	National Measurement Institute, Australia	NMIA	Cu, Ni	Jeffrey Merrick
2	Brazil	Instituto Nacional de Metrologia, Qualidade e Tecnologia	INMETRO	As, Cd, Cu, Hg, Ni, Pb, Zn	Rodrigo Caciano de Sena
3	Canada	National Research Council Canada	NRC	As, Ni, Zn	Kenny Nadeau, Juris Meija, Lu Yang and Zoltan Mester
4	Chile	Instituto de Salud Pública de Chile	ISP	As, Cd, Cu, Pb, Zn	Soraya Sandoval Riquelme and Javier Vera Maldonado
5	China	National Institute of Metrology, China	NIM	As, Cd, Cu, Hg, Ni, Pb, Zn, TBT	Jingbo Chao
6	Finland	Finnish Environment Institute	SYKE	Hg, Pb	Teemu Näykki
7	France	Laboratoire National de Métrologie et d'Essais	LNE	As, Hg, TBT	Paola Fisicaro
8	Hong Kong, China	Government Laboratory	GLHK	As, Cd, Cu, Pb	Alvin Wai-hong Fung, Yuk-tai Tsoi and Kelvin Chun-wai Tse
9	Japan	National Metrology Institute of Japan	NMIJ	As, Cd, Cu, Hg, Ni, Pb, Zn	Yanbei Zhu

Number	Member State/ Associate	NMI or DI	Institute code	Measurands registered	Contact
10	Korea (Republic of)	Korea Research Institute of Standards and Science	KRISS	As, Cd, Cu, Hg, Ni, Pb, Zn	Yong-Hyeon Yim and Kyoung-Seok Lee
11	Lithuania	Center for Physical Sciences And Technology	FTMC	As, Cd, Cu, Hg, Ni, Pb, Zn	Evaldas Naujalis
12	Poland	Central Office of Measures	GUM	As, Cd, Cu	Michał Strzelec
13	Russian Federation	Russian Metrological Institute of Technical Physics and Radio Engineering	VNIIFTRI	As, Cd, Cu, Hg, Ni, Pb, Zn	Aleksey Stakheev
14	Russian Federation	D.I. Mendeleyev Institute for Metrology, Rosstandart	VNIIM	TBT	Anatoliy Krylov
15	Russian Federation	Ural Scientific Research Institute for Metrology (UNIIM - Affiliated branch of the D.I. Mendeleyev Institute for Metrology since 2020)	VNIIM-UNIIM (in this report is indicated as UNIIM)	As, Cd, Cu, Hg, Ni, Pb, Zn	Egor Sobina
16	Singapore	Health Sciences Authority	HSA	As, Cd, Cu, Hg, Pb	Richard Shin
17	Slovenia	Jožef Stefan Institute	JSI	Hg, Ni, Zn, TBT	Radojko Jaćimović
18	Sweden	Research Institutes of Sweden AB	RISE	Hg, Ni, Pb, Zn	Conny Haraldsson
19	Thailand	National Institute of Metrology (Thailand)	NIMT	As, Cd, Cu, Hg, Ni, Pb, Zn, TBT	Sutthinun Taebunpakul
20	Türkiye	TUBITAK Ulusal Metroloji Enstitüsü	UME	As, Cd, Cu, Hg, Ni, Pb, Zn, TBT	Süleyman Z. Can, Betül Arı Engin and Murat Tunç

Each participant received one bottle of sample A, B and/or C, depending on their registration. Participants were free to use their preferred analytical methods for the analysis. Upon receiving the samples, they were recommended to be stored in a refrigerator at around 4 °C. Before opening, the samples were recommended to be mixed thoroughly by hand-shaking for approximately 30 seconds and allowed to settle for one minute. Participants were then asked to perform at least three independent measurements on three separate portions of the sample to determine the mass fractions of the analytes.

To monitor the highest temperature that the test material was exposed to during transportation, temperature recording strips were included with the test material provided to the participating institutes. According to the information filled out by the participants on the sample receipt forms for sample B, the test material never experienced temperatures exceeding 40 ºC. For

sample A and C, the highest recorded temperature was reported as 29 ºC. Thus, temperatures were within the safe conditions as tested by the short-term stability tests, and no stability concerns were raised from the sample transportation.

A reporting form was given to participants after distributing the test materials. Participants were required to provide a clear description of their analytical methods, including sample preparation methods, calibration methods, and the instruments used. They should also give details about the evaluation of uncertainty, providing complete specifications of the measurement equations and describing all sources of uncertainty and their typical values. For each analyte, participants must report the mean value from at least three independent measurements on three separate portions of the sample, along with the associated measurement uncertainty. All analytical calibrations should be performed using metrologically traceable standards. Additionally, participants need to provide information about the sources, purity, and traceability of the reference materials used for calibration purposes.

6. RESULTS

A Report Form was provided to the participating NMIs/DIs for completion. The NMIs/DIs were expected to report their results based on a minimum of three subsamples for each measurand. Only one result, calculated from the average of the measurements, was requested for each measurand. The results were reported in ng/g for lead, nickel, zinc, arsenic, cadmium, copper and in ng/kg for tributyltin, and included standard and expanded uncertainties (95 % confidence level) for the mean of the replicate determinations.

The NMIs/DIs were reminded to ensure the metrological traceability of their results to the International System of Units (SI) through direct realization using primary methods, certified reference materials (CRMs) from NMIs/DIs with appropriate CMC claims, or by preparing their own calibration standards using commercially available high purity materials whose purity they have determined.

Furthermore, the NMIs/DIs were requested to provide information on the measurement procedure (including the sample treatment method, calibration method, internal standard, quality control, analytical instruments used, etc.), result calculation, and evaluation of measurement uncertainty in the Report Form. The completed form was to be submitted to the organizers on or before the assigned deadline. Appendix C includes a reproduction of the Report Form.

Table 6a summarizes the number of participants registered and submitted results for each measurand. Table 6b summarizes the institutes did not submit results.

Table 6a. Summary of registration and result submission.

Sample I.D.	Measurand	Number of institutes registered for the measurand	Number of institutes submitted result for the measurand
A	lead	14	13
	nickel	13	11
	zinc	13	8
B	arsenic	15	12
	cadmium	13	12
	copper	14	12
C	tributyltin	6	5

Table 6b. Registered institutes did not submit any result.

Sample I.D.	Measurand	NMI/DI
A	lead	SYKE
	nickel	INMETRO, ISP, JSI
	zinc	FTMC, INMETRO, ISP, JSI, NIMT
B	arsenic	KRISS, INMETRO, VNIIFTRI
	cadmium	INMETRO
	copper	INMETRO, NIMT
C	tributyltin	NIMT

ISP reported that they were unable to analyze nickel and zinc due to analytical difficulties and quality assay control. INMETRO stated that they did not have enough time to develop a method for cleaning up and preconcentrating the elements in the sample, and only reported the measurement result for lead. KRISS mentioned that they were unable to measure arsenic due to limited resources. NIMT found the determination of copper and zinc challenging and did not report the measurement results. JSI mentioned that they were unable to analyze sample A and B in their lab due to lab renovations and the COVID-19 pandemic. FTMC did not report the measurement result for zinc. NIMT did not report the measurement result for tributyltin. SYKE did not report the measurement result for lead. VNIIFTRI did not report the measurement result for arsenic.

Methods Used by Participants

For arsenic measurement, most participants used dilution for sample preparation and determined it using the standard addition calibration method with inductively coupled plasma mass spectrometry (ICP-MS) combined with various interference removal techniques. For the measurements of cadmium, copper, lead, nickel, and zinc, most participants used either the dilution or co-precipitation technique for sample preparation and determined them using either ID-MS or the standard addition calibration method with ICP-MS, again employing various interference removal techniques. For tributyltin measurement, most participants employed the derivatization method for sample preparation and determined it using ID-MS with the GC-ICP-MS technique. The measurement methods used by the participants for each analyte are summarized in Table 7.

Table 7. Summary of measurement methods.

Institute code	Sample treatment	Calibration method	Analytical instrument
NMIA	Cu: HMI dilution Ni: 1/10 dilution with UHP water.	Cu: d-IDMS Ni: IDMS (reference isotopes: ^{63}Cu, ^{60}Ni; spiked isotopes: ^{65}Cu, ^{61}Ni)	Cu: ICP-MS-CRC-MS (He Gas) Ni: HR-ICP-MS (med. res.)
INMETRO	Pb: No treatment was applied	Standard addition with internal standard	ICP-MS
NRC	As: 10-fold dilution Ni, Zn: Column separation	As: Standard addition Ni, Zn: Double IDMS (reference isotopes: ^{60}Ni, ^{66}Zn; spiked isotopes: ^{61}Ni, ^{67}Zn)	As: O_2 mode with QQQ ICP-MS Ni, Zn: HR-ICP-MS
ISP	As, Cd, Cu, Pb: Microwave digestion with HNO_3	As, Cd, Cu, Pb: Internal standard / addition standard external	ICP-MS
NIM	As, Cd, Cu, Pb, Ni, Zn: Dilution with Milli-Q water, HMI dilution when determination TBT: Liquid-liquid extraction after borohydride derivatization	As: Standard addition Cd, Cu, Pb, Ni, Zn: IDMS and Standard addition (reference isotopes: ^{110}Cd, ^{63}Cu, ^{208}Pb, ^{60}Ni, ^{66}Zn; spiked isotopes: ^{111}Cd, ^{65}Cu, ^{207}Pb, ^{61}Ni, ^{67}Zn) TBT: Primary tributyltin as calibration standard and determined by species-specific IDMS method	As, Cd: QQQ-ICP-MS Cu, Pb, Ni, Zn: ICP-MS TBT: GC-ICP-MS
LNE	As: Sample dilution in acidified Milli-Q water TBT: Acidic solid-liquid extraction followed by liquid – liquid extraction	As: Standard addition TBT: Species-specific double isotope dilution mass spectrometry	As: HR-ICP-MS TBT: GC-ICP-MS

Institute code	Sample treatment	Calibration method	Analytical instrument
GLHK	As: 10-fold dilution Cd, Cu: Co-precipitation by NH_4OH and TMAH Pb: 4-fold dilution with discrete sampling method	As, Pb: Gravimetric standard addition Cd, Cu: IDMS (reference isotopes: ^{114}Cd, ^{63}Cu; spiked isotopes: ^{111}Cd, ^{65}Cu)	As, Cd, Cu, Pb: ICP-CRC-MS (He)
NMIJ	As: 1/50 dilution with 2 % nitric acid and 5 % ethanol Cd, Cu, Pb, Ni: Solid phase extraction with chelating resin Zn: 1/50 dilution with 2 % nitric acid	As, Zn: Standard addition Cd, Cu, Pb, Ni: ID-MS (reference isotopes: ^{110}Cd, ^{63}Cu, ^{208}Pb, ^{60}Ni; spiked isotopes: ^{111}Cd, ^{65}Cu, ^{206}Pb, ^{61}Ni)	QQQ-ICP-MS
KRISS	Cd, Cu, Pb, Ni, Zn: Co-precipitation by NH_4OH and TMAH	Cd, Cu, Pb, Ni, Zn: IDMS (reference isotopes: ^{110}Cd, ^{63}Cu, ^{208}Pb, ^{62}Ni, ^{66}Zn; spiked isotopes: ^{111}Cd, ^{65}Cu, ^{206}Pb, ^{60}Ni, ^{68}Zn)	Cd, Pb: HR-ICP-MS (low res.) Cu, Ni, Zn: HR-ICP-MS (med. res.)
FTMC	As: 1/10 dilution, standard addition Cd, Cu, Pb, Ni: 1/10 dilution	As: Standard addition, single-point calibration Cd, Cu, Pb, Ni: Single-point calibration	ICP-MS
GUM	As, Cd, Cu, Pb, Ni, Zn: Direct analysis after acidification and dilution	As, Cd, Cu, Pb, Ni, Zn: External, calibration curve	ICP-MS
VNIIFTRI	Cd, Cu, Pb, Ni, Zn: 1:30 dilution	Cd, Cu, Pb, Ni, Zn: IS+SA	ICP-MS
VNIIM	TBT: Derivatization (10 % Sodium Tetraethylborate in tetrahydrofuran) and extraction to organic phase.	Internal Standard (IS) calibration (IS is Triphenyltin - TPhT). Single-point calibration	GC-MS Agilent Technologies 7890B/5977B MSD

Institute code	Sample treatment	Calibration method	Analytical instrument
UNIIM	As, Cd, Cu, Pb, Ni, Zn: Dilution (HNO_3 1 %) 1/5; 1/10; 1/20	As: (KED ICP-MS SAM) Cd, Pb: IDMS (STD ID-ICP-MS) Cu, Ni: IDMS (KED ID-ICP-MS) Zn: IDMS (DRC + KED ID-ICP-MS)	ICP-MS
HSA	As, Cd, Cu, Pb: Samples were diluted 10-fold	As: Gravimetric standard addition using gallium as internal standard Cd: IDMS using ^{111}Cd (96.44%) isotopic spike Cu: IDMS using ^{65}Cu (99.70%) isotopic spike Pb: IDMS using ^{206}Pb (99.76 %) isotopic spike	As: HR-ICP-MS Cd, Cu, Pb: ICP-MS
JSI	TBT: Liquid-liquid extraction	Isotope dilution	GC-ICP-MS
RISE	Pb, Ni, Zn: Preconcentration and matrix separation using Chelex column	Pb, Ni, Zn: Single point external calibration	ICP-MS
NIMT	As: Ten-time dilution of seawater with 2 % nitric acid Cd: The mixed solution is ten-fold diluted with 2 % HNO_3 Pb, Ni: Direct analysis after spiking and DI water dilution	As: Gravimetric standard addition with addition of ISTD Cd, Pb, Ni: IDMS (reference isotopes: ^{114}Cd, ^{208}Pb, ^{60}Ni; spiked isotopes: ^{106}Cd, ^{206}Pb, ^{61}Ni)	As, Cd: ICP-MS Pb, Ni: HR-ICPMS
UME	As: 10 fold dilution with 1.0 % HNO_3 Cd, Cu, Pb, Ni, Zn: Co-precipitation TBT: Liquid-liquid extraction after Sodium Tetraethylborate derivatization	As: Standard addition Cd, Cu, Pb, Ni, Zn: ID-ICP-MS (reference isotopes: ^{114}Cd, ^{63}Cu, ^{208}Pb, ^{60}Ni, ^{66}Zn; spiked isotopes: ^{111}Cd, ^{65}Cu, ^{206}Pb, ^{62}Ni, ^{68}Zn) TBT: Species-specific triple isotope dilution mass spectrometry	As, Cd, Cu, Pb, Ni, Zn: QQQ-ICP-MS TBT: GC-ICP-MS

Calibration Materials Used by Participants

The sources of traceability used by the participants for each analyte are summarized in Table 8a and 8b. Most of the participating NMIs/DIs used the following standard solutions from NIST: SRM 3103a Arsenic, SRM 3108 Cadmium, SRM 3114 Copper, SRM 3128 Lead, SRM 3136 Nickel, SRM 3168a Zinc. The institutes of NRC, NIM, NMIJ and KRISS employed their own standards with CMCs underpinned. GUM employed SMU Standards of Arsenic, Cadmium, Copper, Lead, Nickel and Zinc with CMCs underpinned. UNIIM employed PRM Standards of Cadmium, Copper, Lead, Nickel and Zinc with CMCs underpinned, and an in-house validated reference material for arsenic. VNIIFTRI employed GSO Standards of Cadmium and Lead with CMCs underpinned, and in-house standards for copper, nickel and zinc. FTMC employed NIST SRM 3103a Arsenic, combined with a freshwater matrix CRM from NIST and a seawater matrix CRM from NMIA as a single point calibration standard.

Table 8a. Sources of traceability for the measurements of arsenic, cadmium, copper, lead, nickel and zinc.

Institute Code	**Reference materials used for calibration (traceability)**
NMIA	Cu: NIST SRM 3114; Ni: NIST SRM 3136
INMETRO	Pb: NIST SRM 3128
NRC*	NRC standards of As (HIAS-1 https://doi.org/10.4224/crm.2020.hias-1), Ni (HINI-1 https://doi.org/10.4224/crm.2020.hini-1) and Zn (HIZN-1 https://doi.org/10.4224/crm.2020.hizn-1)
ISP	As: NIST SRM 3103a; Cd: NIST SRM 3108; Cu: NIST SRM 3114; Pb: NIST SRM 3128
NIM	As: GBW (E) 080117; Cd: GBW (E) 080119, Cu: GBW (E) 080122 Pb: GBW (E) 080129; Ni: GBW (E) 080128; Zn: GBW 08620 GBW 04441 ^{111}Cd, GBW 04463 ^{65}Cu, GBW 04442 ^{207}Pb, GBW 04464 ^{67}Zn spike solution
LNE	As: NIST SRM 3103a
GLHK	As: NIST SRM 3103a; Cd: NIST SRM 3108, Cu: NIST SRM 3114; Pb: NIST SRM 3128
NMIJ*	JCSS guaranteed solutions of As, Cd, Cu, Pb, Ni and Zn
KRISS*	KRISS standard solutions of Cd, Cu, Pb, Ni, and Zn
FTMC	NIST SRM 3103a; NIST SRM 1643f and CRM NMIA MX014#
GUM	As: SMU B03; Cd: SMU B08; Cu: SMU B12; Pb: SMU B26; Ni: SMU B24; Zn: SMU B37
VNIIFTRI	Cd: GSO 11406-2019; Cu: in-house standard; Pb: GSO 11409-2019: Ni: in-house standard; Zn: in-house standard
UNIIM	As: in-house reference material *(validated in-house)*; PRM-1.4-176-038-2017-Cd; PRM-1.4-176-039-2017-Cu; PRM-1.4-176-035-2017-PbO; PRM-1.4-176-036-2017-Ni; PRM-1.4-176-043-2017-Zn
HSA	As: NIST SRM 3103a; Cd: NIST SRM 3108; Cu: NIST SRM 3114; Pb: NIST SRM 3128
RISE	Pb: NIST SRM 3128, Ni: NIST SRM 3136; Zn: NIST SRM 3168a
NIMT	As: NIST SRM 3103a; Cd: NIST SRM 3108; Pb: NIST SRM 3128; Ni: NIST SRM 3136
UME	As: NIST SRM 3103a; Cd: NIST SRM 3108; Cu: NIST SRM 3114; Pb: NIST SRM 3128; Ni: NIST SRM 3136; Zn: NIST SRM 3168a

Notes:

1. *The symbol * indicates the institutes have the relevant CMCs recorded in KCDB.*
2. *The symbol # indicates the reference material is a matrix material and with no CMC support.*

Table 8b. Sources of traceability for the measurements of tributyltin.

Institute code	Reference material of tributyltin
NIM	GBW 08710 tributyltin (as $C_{12}H_{27}Sn^{+}$) in methanol
LNE	1. Tributyltin chloride standard checked for purity 2. Tributyltin internal standard solution enriched in the tin isotope 119 checked for isotopic composition at LNE
VNIIM	Pure tributyltin chloride (98.6 % ± 0.24 %), certified in-house
JSI	TBT-chloride solution (purity checked in-house)
UME	GBW 08710 tributyltin (as $C_{12}H_{27}Sn^{+}$) in methanol

Two participants used a calibrant produced by NIM China, GBW 08710 as their source of traceability. The remaining three participants claimed the in-house certified materials.

Participant Results for Arsenic, Cadmium, Copper, Lead, Nickel, Zinc and Tributyltin

The results for CCQM-K155 for the determination of arsenic, cadmium, copper, lead, nickel, zinc and tributyltin are detailed in Tables 9 to 15 and presented graphically in Figures 1 to 7. Participants' results are displayed with error bars representing reported standard uncertainties. Blue data point represents the reported value (x_i) of each participant, and blue bar represents its standard uncertainty, $u(x_i)$. The degrees of freedom (DoF) were estimated from the reported coverage factor at 95 % confidence level.

Table 9. Reported results for arsenic.

Institute	Reported mass fraction (x_i), ng/g	Reported standard uncertainty $u(x_i)$, ng/g	Coverage factor, k	Expanded uncertainty, ng/g	DoF
FTMC	2.65	0.49	2.262	1.12	9
UME	3.59	0.09	2	0.18	60
HSA	3.77	0.10	2.57	0.26	5
NIMT	3.79	0.10	2	0.20	60
NIM	3.798	0.071	2	0.142	60
NRC	3.82	0.08	2	0.16	60
LNE	3.82	0.24	2	0.47	60
ISP	3.88	0.2469	2.78	0.69	4
GUM	3.88	0.19	2	0.38	60
GLHK	3.90	0.14	2	0.28	60
UNIIM	4.1	0.25	2	0.5	60
NMIJ	4.21	0.13	2	0.27	60

Figure 1. Dot-and-bar display of reported results for arsenic in units of ng/g.

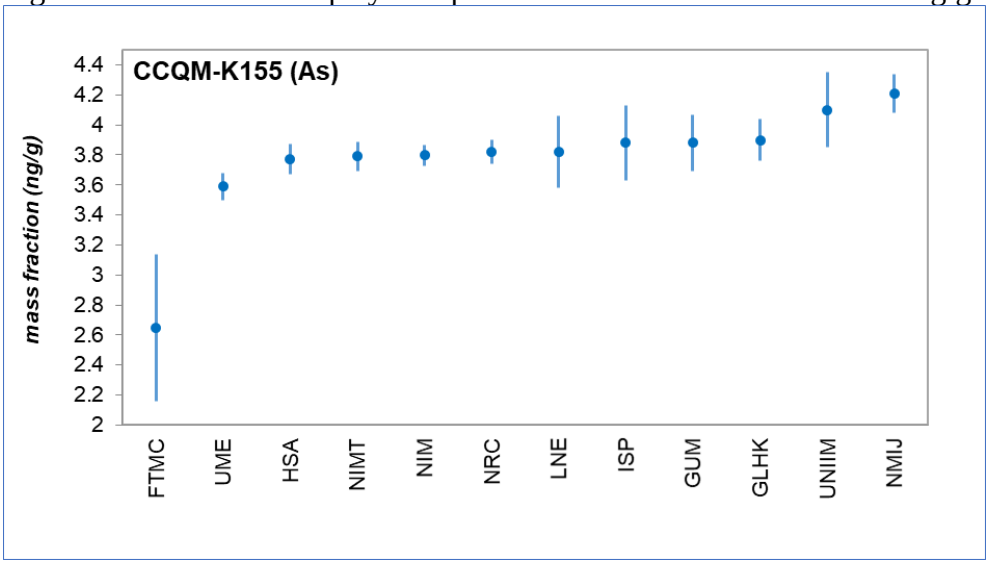


Table 10. Reported results for cadmium.

Institute	Reported mass fraction (x_i), ng/g	Reported standard uncertainty $u(x_i)$, ng/g	Coverage factor, k	Expanded uncertainty, ng/g	DoF
ISP	0.194	0.0069	4.3	0.030	2
NMIJ	0.219	0.005	2	0.010	60
UME	0.2232	0.0028	2	0.0055	60
NIM	0.225	0.006	2	0.011	60
GLHK	0.2254	0.0042	2	0.0083	60
HSA	0.2301	0.0042	2	0.0084	60
GUM	0.232	0.014	2	0.029	60
NIMT	0.258	0.006	2	0.012	60
UNIIM	0.26	0.015	2	0.03	60
KRISS	0.28	0.007	2.78	0.019	4
FTMC	0.329	0.037	2.262	0.083	9
VNIIFTRI	0.535	0.038	2	0.076	60

Figure 2a. Dot-and-bar display of reported results for cadmium in units of ng/g.

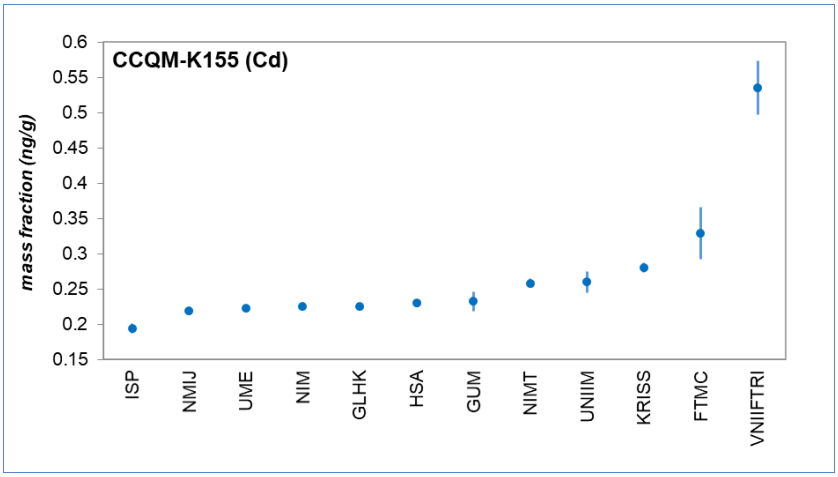


Figure 2b. Dot-and-bar display of reported results for cadmium in units of ng/g (enlarged).

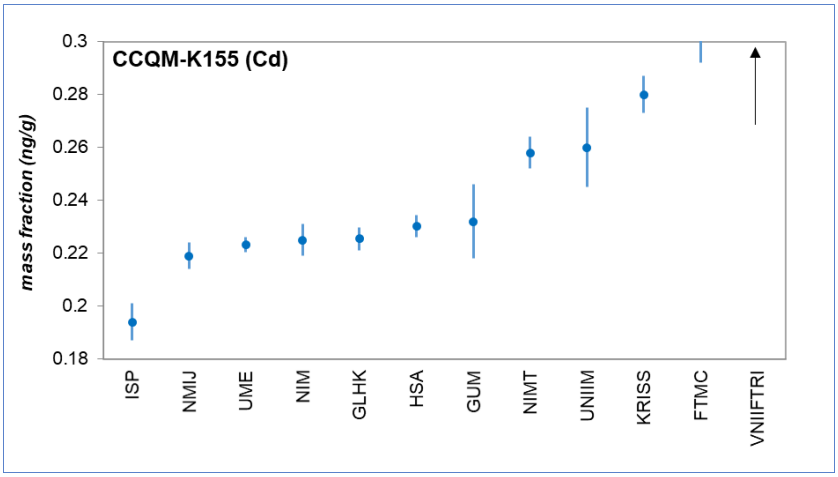


Table 11. Reported results for copper.

Institute	Reported mass fraction (x_i), ng/g	Reported standard uncertainty $u(x_i)$, ng/g	Coverage factor, k	Expanded uncertainty, ng/g	DoF
ISP	2.95	0.11	2.36	0.26	7
GUM	3.00	0.16	2	0.32	60
UME	3.022	0.022	2	0.043	60
NMIJ	3.05	0.04	2	0.08	60
GLHK	3.09	0.05	2	0.10	60
KRISS	3.093	0.008	2.01	0.016	50
HSA	3.107	0.082	2	0.165	60
NIM	3.269	0.061	2	0.122	60
NMIA	3.28	0.14	2.04	0.29	30
FTMC	3.31	0.31	2.262	0.69	9
UNIIM	4.0	0.4	2	0.8	60
VNIIFTRI	7.93	0.49	2	0.98	60

Figure 3a. Dot-and-bar display of reported results for copper in units of ng/g.

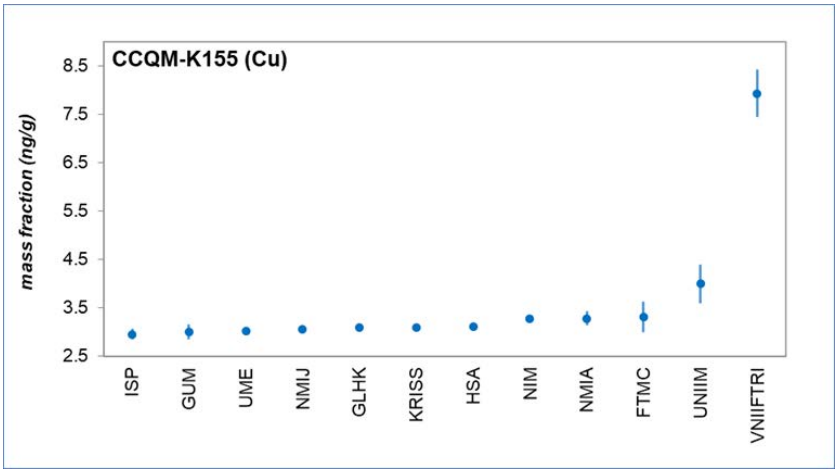


Figure 3b. Dot-and-bar display of reported results for copper in units of ng/g (enlarged).

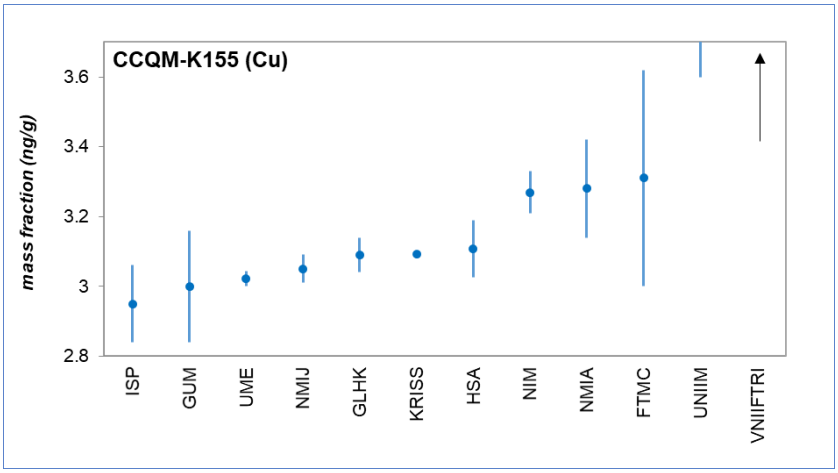


Table 12. Reported results of lead.

Institute	Reported mass fraction (x_i), ng/g	Reported standard uncertainty $u(x_i)$, ng/g	Coverage factor, k	Expanded uncertainty, ng/g	DoF
ISP	0.543	0.01787	2.78	0.050	4
INMETRO	0.982	0.041	2	0.082	60
RISE	1.006	0.039	2	0.078	60
NIMT	1.02	0.023	2	0.05	60
UME	1.068	0.008	2	0.016	60
NMIJ	1.07	0.03	2	0.06	60
HSA	1.073	0.023	2.31	0.053	8
GLHK	1.084	0.035	2	0.069	60
NIM	1.088	0.017	2	0.034	60
KRISS	1.113	0.026	2.78	0.073	4
UNIIM	1.3	0.1	2	0.2	60
FTMC	1.36	0.13	2.262	0.30	9
VNIIFTRI	1.68	0.11	2	0.22	60

Figure 4a. Dot-and-bar display of reported results for lead in units of ng/g.

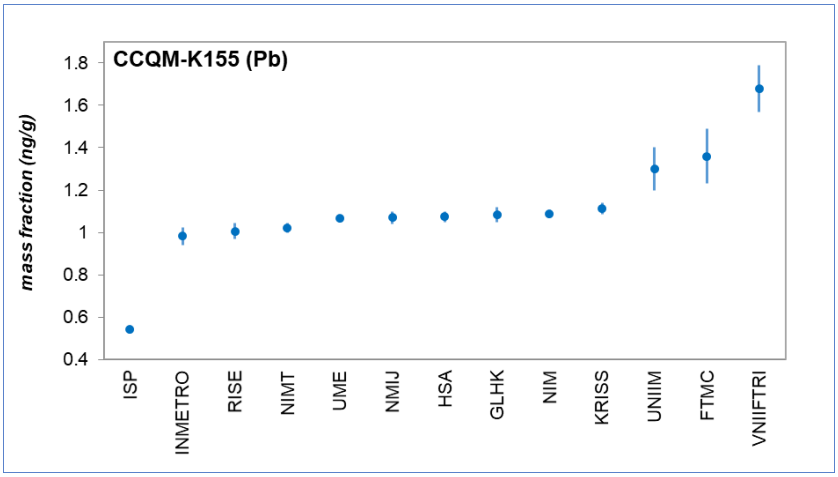


Figure 4b. Dot-and-bar display of reported results for lead in units of ng/g (enlarged).

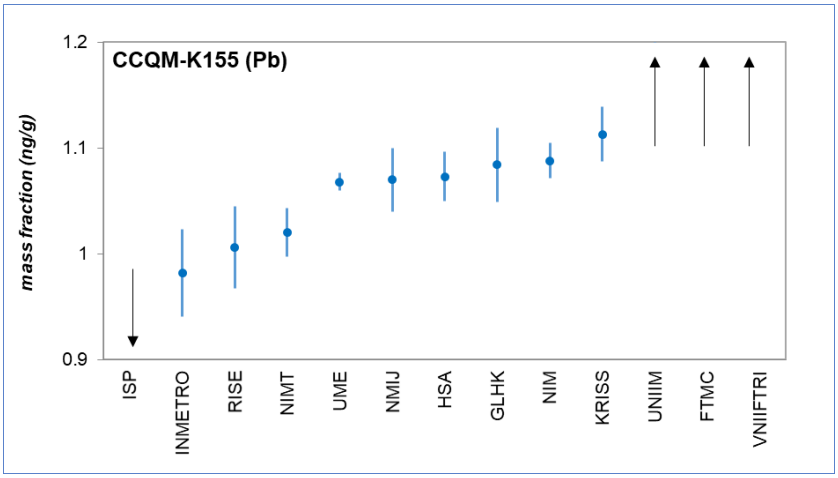


Table 13. Reported results for nickel.

Institute	Reported mass fraction (x_i), ng/g	Reported standard uncertainty $u(x_i)$, ng/g	Coverage factor, k	Expanded uncertainty, ng/g	DoF
FTMC	4.28	0.65	2.262	1.46	9
NIMT	4.32	0.071	2	0.15	60
RISE	4.48	0.15	2	0.31	60
NRC	4.522	0.022	2	0.044	60
KRISS	4.534	0.020	2.31	0.045	8
UME	4.568	0.019	2	0.037	60
NMIA	4.58	0.07	2.02	0.14	40
NMIJ	4.62	0.06	2	0.13	60
UNIIM	4.7	0.45	2	0.9	60
NIM	4.744	0.090	2	0.181	60
VNIIFTRI	6.67	0.38	2	0.76	60

Figure 5a. Dot-and-bar display of reported results for nickel in units of ng/g.

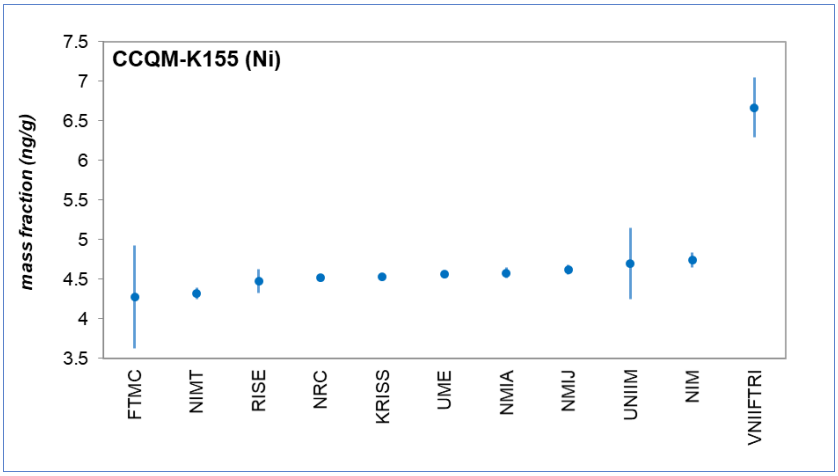


Figure 5b. Dot-and-bar display of reported results for nickel in units of ng/g (enlarged).

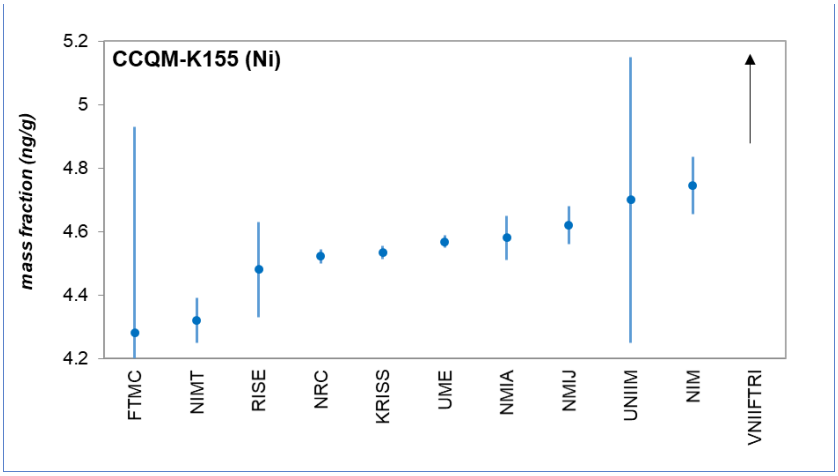


Table 14. Reported results for zinc.

Institute	Reported mass fraction (x_i), ng/g	Reported standard uncertainty $u(x_i)$, ng/g	Coverage factor, k	Expanded uncertainty, ng/g	DoF
RISE	8.10	0.35	2	0.69	60
KRISS	8.30	0.45	1.97	0.89	200
NMIJ	8.31	0.15	2	0.30	60
UME	8.521	0.038	2	0.075	60
NRC	8.572	0.034	2	0.068	60
UNIIM	8.6	0.5	2	1.0	60
NIM	8.764	0.162	2	0.324	60
VNIIFTRI	13.54	0.96	2	1.92	60

Figure 6a. Dot-and-bar display of reported results for zinc in units of ng/g.

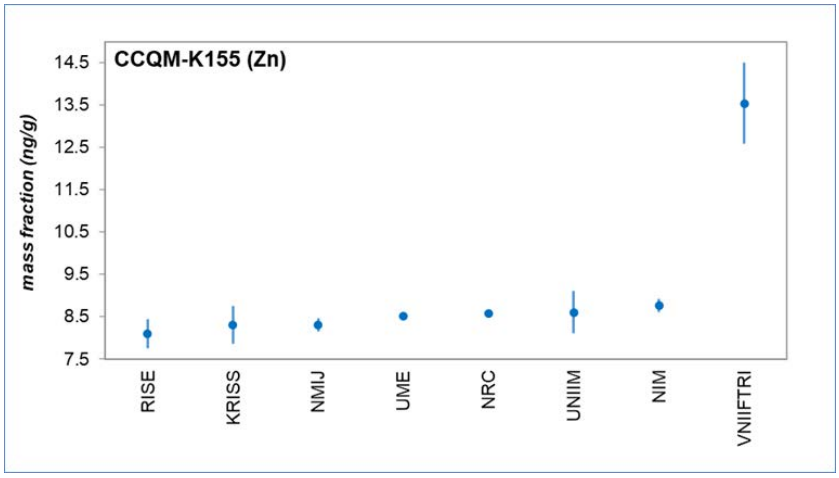


Figure 6b. Dot-and-bar display of reported results for zinc in units of ng/g (enlarged).

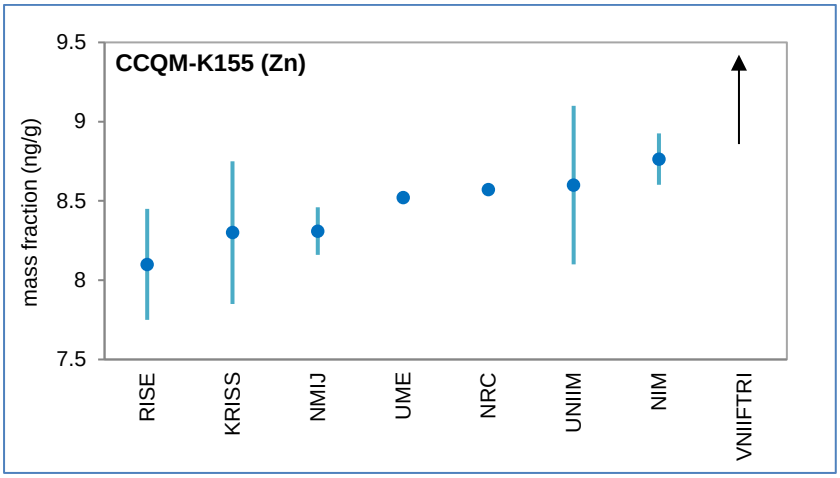
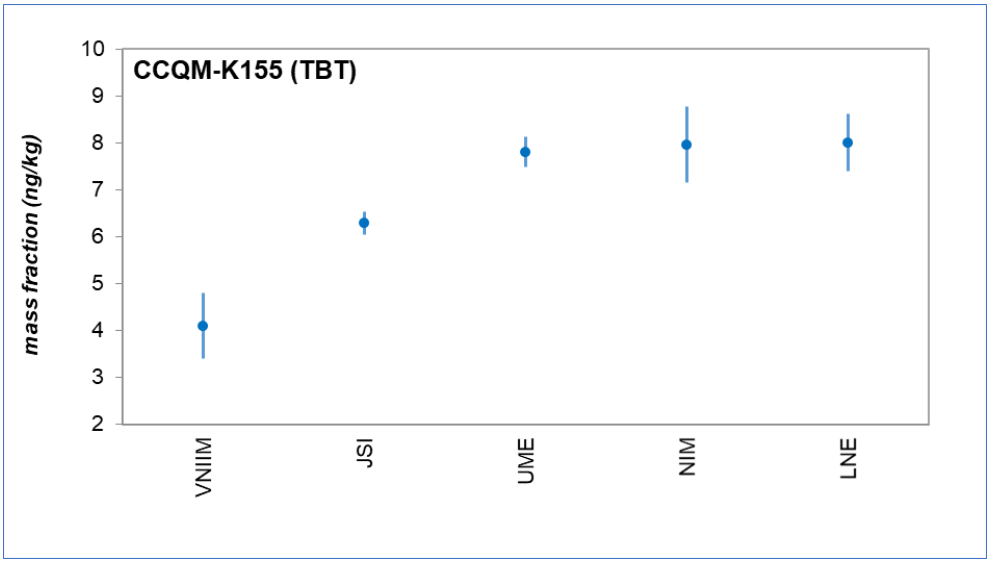


Table 15. Reported results for tributyltin.

Institute	Reported mass fraction (x_i), ng/kg	Reported standard uncertainty $u(x_i)$, ng/kg	Coverage factor, k	Expanded uncertainty, ng/kg	DoF
VNIIM	4.1	0.7	2	1.4	60
JSI	6.285	0.250	2	0.500	60
UME	7.81	0.33	2	0.67	60
NIM	7.96	0.81	2	1.61	60
LNE	8.02	0.61	2	1.23	60

Figure 7. Dot-and-bar display of reported results for tributyltin in units of ng/kg.



Discussion of Results

Evaluation of results for KCRV calculation

Mercury in sample A was abandoned due to its instability. The pilot institutes, UME and GLHK, circulated the Initial Result Summary to participants on 29 October 2020 for error checking. Participating institutes were instructed to review their own results and inform the coordinating laboratory of any measurement problems that may have led to errors in the reported results.

VNIIFTRI reported instrumentation problems in their measurement results. UME and GLHK discussed the results and participant feedback at the CCQM IAWG Meeting (02 to 04 November 2020). Based on the decision made during the meeting, VNIIFTRI's results were excluded from the KCRV calculation.

At the CCQM IAWG Meeting in May 2021, there was a discussion about the use of a freshwater matrix CRM as a single point calibration standard for ICP-MS. The working group considered this calibration approach to be inappropriate and decided to exclude FTMC's measurement results from the KCRV calculation.

During the CCQM IAWG Meeting in November 2021, the results submitted by ISP raised concerns due to data transcription errors for cadmium and lead. ISP provided revised results on 02 June 2021.

Measurand	**Reported mass fraction (x_i), ng/g**	**Reported standard uncertainty $u(x_i)$, ng/g**	**Coverage factor, k**	**Expanded uncertainty, ng/g**	**DoF**
cadmium	0.223	0.041	2	0.081	60
lead	1.02	0.13	2	0.25	60

The working group decided at the meeting that the original reported data for cadmium and lead by ISP would not be used for the KCRV calculation, but it should be included in the DoE based on the original values.

According to the minutes of the CCQM IAWG meeting held on 11 to 13 April 2022, there was a discussion about the results submitted by JSI about the traceability of tributyltin calibrants. JSI replied that they checked the purity internally and the purity was further shown to be stable for the period of the comparison.

NIMT responded to the organizer's inquiry about their cadmium measurement on 18 Nov 2022 as follows: *"As the reported result of cadmium (IDMS) was 0.258 ng/g +/- 0.012 ng/g (k=2). It seems to be 5% expanded uncertainty. You are right. Your suggestion is worthwhile for us to work more carefully in detail. After result scrutiny, there could be a method bias from the study on matrix CRM used (NMIA MX014) around 10%, that we missed the calculation of uncertainty type B arising from recovery into account."* Consequently, their measurement result of cadmium has been excluded for KCRV calculation.

Table 16 summarizes the measurements of those institutes that have been excluded from the calculation of KCRVs for each measurand.

Table 16. Summary of the institute's measurements excluded from calculation of KCRVs.

Measurand	**Institute's measurement excluded from calculation of the KCRV**
arsenic	FTMC
cadmium	VNIIFTRI, ISP, FTMC, NIMT
copper	VNIIFTRI, FTMC
lead	VNIIFTRI, ISP, FTMC
nickel	VNIIFTRI, FTMC
zinc	VNIIFTRI

A check of mutual consistency of the data sets was performed by applying the Cochran's Q Test, the outcome was summarized in Table 17.

Table 17. Summary of the data set evaluation.

Measurand	**n**	**$Q\ (\chi^2_{obs})$**	**$\chi^2_{0.05,\ m-1}$**	**Data set consistency**
arsenic	11	17.66	18.31	No evidence of significant inconsistency
cadmium	8	66.82	14.07	Evidence of significant mutual inconsistency
copper	10	28.06	16.92	Evidence of significant mutual inconsistency
lead	10	21.31	16.92	Evidence of significant mutual inconsistency
nickel	9	19.91	15.51	Evidence of significant mutual inconsistency
zinc	7	7.237	12.59	No evidence of significant inconsistency
tributyltin	5	34.53	9.49	Evidence of significant mutual inconsistency

7. KEY COMPARISON REFERENCE VALUE (KCRV) and DEGREE OF EQUIVALENCE (DoE)

As per the agreement made by the IAWG, the NIST decision tree (NDT) (version 1.0.4, accessed on Nov 2023 and Apr 2024) was used to calculate the KCRV and the degrees of equivalence (DoEs) of participants. The NDT requires the identification of participants, reported results, uncertainties, and degrees of freedom (DoFs) as input. The DoF is estimated based on the reported coverage factor. Following a series of hypothesis tests related to homogeneity, symmetry, and normality (Gaussian shape), the NDT recommends the best statistical model for calculating the KCRV and DoE. The original reports generated by NDT are shown in Appendix E.

7.1. NDT calculations

Tables 18a, 19a, 20a, 21a, 22a, 23a and 24a show the decision tree hypothesis test results. Tables 18b, 19b, 20b, 21b, 22b, 23b and 24b list the numeric values of u_i', D_i, $U(D_i)$, $\%D_i$, $\%U(D_i)$ and $D_i/U(D_i)$ for participating NMIs/DIs in CCQM-K155 for arsenic, cadmium, copper, lead, nickel, zinc and tributyltin, as calculated by NDT. In these tables, the symbol * denotes that the measured value reported by the participant (x_i), was excluded from the KCRV calculation. In the u_i' column, all values are standard uncertainty reported by the participants $u(x_i)$, unless accompanied by a hash (#). Those values accompanied by a hash (#) are the reported standard uncertainty and dark uncertainty (*tau)* summed in quadrature, i.e. ($\sqrt{\tau^2 + u^2(x_i)}$). For these participants, $U(D_i)$ values recognizing *(tau)* are used.

7.1.1. NDT calculations for arsenic

Table 18a. NDT decision for arsenic.

Decision Tree Hypothesis test results: As	**Decision Tree recommends**
Cochran's test for Homogeneity: p-value: 0.061 Q = 17.66 (Reference Distribution: Chi-Square with 10 Degrees of Freedom) tau est. = 0.1016 tau/median(x) = 0.02659 tau/median(u) = 0.7812 Shapiro-Wilk test for Normality: p = 0.1554 Miao-Gel-Gastwirth test of Symmetry: p = 0.1096 Assume Homogeneity? Yes (p-value > 0.05) Assume Normality? Yes (p-value > 0.05) Assume Symmetry? Yes (p-value > 0.01)	Selected Procedure: **Adaptive Weighted Average (AWA)** Consensus estimate: 3.832 Standard uncertainty: 0.04927 Standard uncertainty (using parametric bootstrap): 0.05 95% coverage interval: (3.736, 3.929) 95% coverage interval (using parametric bootstrap): (3.733, 3.932) Dark uncertainty (tau): 0.1016

KCRV(As) = 3.832 ng/g
u(KCRV) = 0.050 ng/g

Table 18b. Degrees of equivalence for arsenic.

Institute	x_i **(ng/g)**	u_i' **(ng/g)**	D_i **(ng/g)**	$U(D_i)$ **(ng/g)**	$\%D_i$	$\%U(D_i)$	$D_i/U(D_i)$
FTMC*	2.65	0.5004[#]	-1.1820	0.9857	-30.85	25.72	-1.20
UME	3.59	0.1357[#]	-0.2424	0.2481	-6.33	6.47	-0.98
HSA	3.77	0.10	-0.0624	0.1854	-1.63	4.84	-0.34
NIMT	3.79	0.10	-0.0424	0.1827	-1.11	4.77	-0.23
NIM	3.798	0.071	-0.0344	0.1320	-0.90	3.44	-0.26
NRC	3.82	0.08	-0.0124	0.1417	-0.32	3.70	-0.09
LNE	3.82	0.24	-0.0124	0.4606	-0.32	12.02	-0.03
ISP	3.88	0.2469	0.0476	0.4781	1.24	12.48	0.10
GUM	3.88	0.19	0.0476	0.3630	1.24	9.47	0.13
GLHK	3.90	0.14	0.0676	0.2620	1.76	6.84	0.26
UNIIM	4.1	0.25	0.2676	0.4868	6.98	12.70	0.55
NMIJ	4.21	0.1650[#]	0.3776	0.3120	9.85	8.14	1.21

7.1.2. Cadmium

Table 19a. NDT decision for cadmium.

Decision Tree Hypothesis test results: Cd	**Decision Tree recommends**
Cochran's test for Homogeneity: p-value: p < 0.001 Q = 66.82 (Reference Distribution: Chi-Square with 7 Degrees of Freedom) tau est. = 0.01507 tau/median(x) = 0.06619 tau/median(u) = 2.741 Shapiro-Wilk test for Normality: p = 0.02118 Miao-Gel-Gastwirth test of Symmetry: p = 0.023 Assume Homogeneity? No (p-value < 0.05) Assume Normality? No (p-value < 0.05) Assume Symmetry? Yes (p-value > 0.01)	Selected Procedure: **Hierarchical Laplace-Gauss (HLG)** Consensus estimate: 0.2283 Standard uncertainty: 0.004409 95% coverage interval: (0.2196, 0.2371) Dark uncertainty (tau): 0.01008 Tau posterior 0.025 and 0.975 quantiles: (0.0003426, 0.03277)

KCRV(Cd) = 0.2283 ng/g
u(KCRV) = 0.0044 ng/g

Table 19b. Degrees of equivalence for cadmium.

Institute	x_i **(ng/g)**	u_i' **(ng/g)**	D_i **(ng/g)**	$U(D_i)$ **(ng/g)**	$\%D_i$	$\%U(D_i)$	$D_i/U(D_i)$
ISP*	0.194	0.0122[#]	-0.0344	0.0345	-15.05	15.11	-1.00
NMIJ	0.219	0.005	-0.0093	0.0133	-4.09	5.84	-0.70
UME	0.2232	0.0028	-0.0051	0.0104	-2.25	4.54	-0.50
NIM	0.225	0.006	-0.0033	0.0148	-1.47	6.49	-0.23
GLHK	0.2254	0.0042	-0.0029	0.0122	-1.29	5.33	-0.24
HSA	0.2301	0.0042	0.0018	0.0121	0.77	5.32	0.14
GUM	0.232	0.014	0.0037	0.0289	1.60	12.65	0.13
NIMT*	0.258	0.0117[#]	0.0297	0.0344	12.99	15.05	0.86
UNIIM	0.26	0.0181[#]	0.0317	0.0431	13.86	18.89	0.73
KRISS	0.28	0.0123[#]	0.0517	0.0505	22.62	22.10	1.02
FTMC*	0.329	0.0384[#]	0.1007	0.0787	44.11	34.48	1.28
VNIIFTRI*	0.535	0.0393[#]	0.3067	0.0805	134.34	35.27	3.81

7.1.3. Copper

Table 20a. NDT decision for copper.

Decision Tree Hypothesis test results: Cu	**Decision Tree recommends**
Cochran's test for Homogeneity: p-value: p < 0.001 Q = 28.06 (Reference Distribution: Chi-Square with 9 Degrees of Freedom) tau est. = 0.05451 tau/median(x) = 0.01763 tau/median(u) = 0.7624 Shapiro-Wilk test for Normality: p = 0.9204 Miao-Gel-Gastwirth test of Symmetry: p = 0.2356 Assume Homogeneity? No (p-value < 0.05) Assume Normality? Yes (p-value > 0.05) Assume Symmetry? Yes (p-value > 0.01)	Selected Procedure: **Hierarchical Gauss-Gauss (HGG)** Consensus estimate: 3.099 Standard uncertainty: 0.03544 95% coverage interval: (3.028, 3.17) Dark uncertainty (tau): 0.06788 Tau posterior 0.025 and 0.975 quantiles: (0.01648, 0.1693)

KCRV(Cu) = 3.099 ng/g
u(KCRV) = 0.035 ng/g

Table 20b. Degrees of equivalence for copper.

Institute	x_i **(ng/g)**	u_i' **(ng/g)**	D_i **(ng/g)**	$U(D_i)$ **(ng/g)**	$\%D_i$	$\%U(D_i)$	$D_i/U(D_i)$
ISP	2.95	0.11	-0.1489	0.2555	-4.80	8.24	-0.58
GUM	3.00	0.16	-0.0989	0.3225	-3.19	10.41	-0.31
UME	3.022	0.022	-0.0769	0.0827	-2.48	2.67	-0.93
NMIJ	3.05	0.04	-0.0489	0.1066	-1.58	3.44	-0.46
GLHK	3.09	0.05	-0.0089	0.1223	-0.29	3.95	-0.07
KRISS	3.093	0.008	-0.0059	0.0722	-0.19	2.33	-0.08
HSA	3.107	0.082	0.0081	0.1779	0.26	5.74	0.05
NIM	3.269	0.0913[#]	0.1701	0.2216	5.49	7.15	0.77
NMIA	3.28	0.14	0.1811	0.2903	5.84	9.37	0.62
FTMC*	3.31	0.31	0.2111	0.6087	6.81	19.64	0.35
UNIIM	4.0	0.4057[#]	0.9011	0.8406	29.08	27.12	1.07
VNIIFTRI*	7.93	0.4947[#]	4.8310	0.9764	155.89	31.51	4.95

7.1.4. Lead

Table 21a. NDT decision for lead.

Decision Tree Hypothesis test results: Pb	**Decision Tree recommends**
Cochran's test for Homogeneity: p-value: 0.011 Q = 21.31 (Reference Distribution: Chi-Square with 9 Degrees of Freedom) tau est. = 0.02621 tau/median(x) = 0.02446 tau/median(u) = 0.9359 Shapiro-Wilk test for Normality: p = 0.6361 Miao-Gel-Gastwirth test of Symmetry: p = 0.8262 Assume Homogeneity? No (p-value < 0.05) Assume Normality? Yes (p-value > 0.05) Assume Symmetry? Yes (p-value > 0.01)	Selected Procedure: **Hierarchical Gauss-Gauss (HGG)** Consensus estimate: 1.067 Standard uncertainty: 0.01212 95% coverage interval: (1.043, 1.092) Dark uncertainty (tau): 0.02143 Tau posterior 0.025 and 0.975 quantiles: (0.001417, 0.06419)

KCRV(Pb) = 1.067 ng/g
u(KCRV) = 0.012 ng/g

Table 21b. Degrees of equivalence for lead.

Institute	x_i **(ng/g)**	u_i' **(ng/g)**	D_i **(ng/g)**	$U(D_i)$ **(ng/g)**	$\%D_i$	$\%U(D_i)$	$D_i/U(D_i)$
ISP*	0.543	0.0280[#]	-0.5241	0.0737	-49.12	6.91	-7.11
INMETRO	0.982	0.041	-0.0851	0.0862	-7.98	8.08	-0.99
RISE	1.006	0.039	-0.0611	0.0813	-5.73	7.61	-0.75
NIMT	1.02	0.023	-0.0471	0.0526	-4.42	4.93	-0.90
UME	1.068	0.008	0.0009	0.0290	0.08	2.72	0.03
NMIJ	1.07	0.03	0.0029	0.0643	0.27	6.03	0.04
HSA	1.073	0.023	0.0059	0.0562	0.55	5.27	0.10
GLHK	1.084	0.035	0.0169	0.0729	1.58	6.84	0.23
NIM	1.088	0.017	0.0209	0.0416	1.96	3.90	0.50
KRISS	1.113	0.026	0.0459	0.0746	4.30	6.99	0.62
UNIIM	1.3	0.1023[#]	0.2329	0.2134	21.83	20.00	1.09
FTMC*	1.36	0.1318[#]	0.2929	0.2618	27.45	24.54	1.12
VNIIFTRI*	1.68	0.1121[#]	0.6129	0.2253	57.44	21.12	2.72

7.1.5. Nickel

Table 22a. NDT decision for nickel.

Decision Tree Hypothesis test results: Ni	**Decision Tree recommends**
Cochran's test for Homogeneity: p-value: 0.011 Q = 19.91 (Reference Distribution: Chi-Square with 8 Degrees of Freedom) tau est. = 0.04475 tau/median(x) = 0.009796 tau/median(u) = 0.6393 Shapiro-Wilk test for Normality: p = 0.8835 Miao-Gel-Gastwirth test of Symmetry: p = 0.8878 Assume Homogeneity? No (p-value < 0.05) Assume Normality? Yes (p-value > 0.05) Assume Symmetry? Yes (p-value > 0.01)	Selected Procedure: **Hierarchical Gauss-Gauss (HGG)** Consensus estimate: 4.549 Standard uncertainty: 0.027 95% coverage interval: (4.493, 4.604) Dark uncertainty (tau): 0.05233 Tau posterior 0.025 and 0.975 quantiles: (0.003282, 0.154)

KCRV(Ni) = 4.549 ng/g
u(KCRV) = 0.027 ng/g

Table 22b. Degrees of equivalence for nickel.

Institute	x_i **(ng/g)**	u_i' **(ng/g)**	D_i **(ng/g)**	$U(D_i)$ **(ng/g)**	$\%D_i$	$\%U(D_i)$	$D_i/U(D_i)$
FTMC*	4.28	0.65	-0.2689	1.2680	-5.91	27.87	-0.21
NIMT	4.32	0.0882[#]	-0.2289	0.2118	-5.03	4.66	-1.08
RISE	4.48	0.15	-0.0689	0.3005	-1.51	6.61	-0.23
NRC	4.522	0.022	-0.0269	0.0700	-0.59	1.54	-0.38
KRISS	4.534	0.020	-0.0149	0.0725	-0.33	1.59	-0.20
UME	4.568	0.019	0.0192	0.0665	0.42	1.46	0.29
NMIA	4.58	0.07	0.0312	0.1504	0.68	3.31	0.21
NMIJ	4.62	0.06	0.0712	0.1312	1.56	2.88	0.54
UNIIM	4.7	0.45	0.1511	0.8835	3.32	19.42	0.17
NIM	4.744	0.1041[#]	0.1951	0.2380	4.29	5.23	0.82
VNIIFTRI*	6.67	0.3836[#]	2.1210	0.7636	46.63	16.79	2.78

7.1.6. Zinc

Table 23a. NDT decision for zinc.

Decision Tree Hypothesis test results: Zn	**Decision Tree recommends**
Cochran's test for Homogeneity: p-value: 0.3 Q = 7.237 (Reference Distribution: Chi-Square with 6 Degrees of Freedom) tau est. = 0.03678 tau/median(x) = 0.004316 tau/median(u) = 0.227 Shapiro-Wilk test for Normality: p = 0.3584 Miao-Gel-Gastwirth test of Symmetry: p = 0.465 Assume Homogeneity? Yes (p-value > 0.05) Assume Normality? Yes (p-value > 0.05) Assume Symmetry? Yes (p-value > 0.01)	Selected Procedure: **Adaptive Weighted Average (AWA)** Consensus estimate: 8.54 Standard uncertainty: 0.03427 Standard uncertainty (using parametric bootstrap): 0.04163 95% coverage interval: (8.473, 8.607) 95% coverage interval (using parametric bootstrap): (8.454, 8.625) Dark uncertainty (tau): 0.03678

KCRV(Zn) = 8.540 ng/g
u(KCRV) = 0.042 ng/g

Table 23b. Degrees of equivalence for zinc.

Institute	x_i **(ng/g)**	u_i' **(ng/g)**	D_i **(ng/g)**	$U(D_i)$ **(ng/g)**	$\%D_i$	$\%U(D_i)$	$D_i/U(D_i)$
RISE	8.10	0.35	-0.4399	0.6768	-5.15	7.93	-0.65
KRISS	8.30	0.45	-0.2399	0.8767	-2.81	10.27	-0.27
NMIJ	8.31	0.15	-0.2299	0.2727	-2.69	3.19	-0.84
UME	8.521	0.038	-0.0189	0.0642	-0.22	0.75	-0.29
NRC	8.572	0.034	0.0321	0.0596	0.38	0.70	0.54
UNIIM	8.6	0.5	0.0601	0.9550	0.70	11.18	0.06
NIM	8.764	0.162	0.2241	0.2979	2.62	3.49	0.75
VNIIFTRI*	13.54	0.9607[#]	5.0000	1.8850	58.55	22.07	2.65

7.1.7. Tributyltin

Table 24a. NDT decision for tributyltin.

Decision Tree Hypothesis test results: TBT	**Decision Tree recommends**
Cochran's test for Homogeneity: p-value: $p < 0.001$ Q = 34.44 (Reference Distribution: Chi-Square with 4 Degrees of Freedom) tau est. = 1.228 tau/median(x) = 0.1573 tau/median(u) = 2.014 Shapiro-Wilk test for Normality: p = 0.03042 Miao-Gel-Gastwirth test of Symmetry: p = 0.0648 Assume Homogeneity? No (p-value < 0.05) Assume Normality? No (p-value < 0.05) Assume Symmetry? Yes (p-value > 0.01)	Selected Procedure: **Hierarchical Laplace-Gauss (HLG)** Consensus estimate: 7.020 Standard uncertainty: 0.5572 95% coverage interval: (5.928, 8.111) Dark uncertainty (tau): 1.318 Tau posterior 0.025 and 0.975 quantiles: (0.5055, 3.735)

KCRV(TBT) = 7.020 ng/kg
u(KCRV) = 0.557 ng/kg

Table 24b. Degrees of equivalence for tributyltin.

Institute	x_i **(ng/kg)**	u_i' **(ng/kg)**	D_i **(ng/kg)**	$U(D_i)$ **(ng/kg)**	$\%D_i$	$\%U(D_i)$	$D_i/U(D_i)$
VNIIM	4.1	1.4930[#]	-2.9200	3.9390	-41.60	56.11	-0.74
JSI	6.285	0.250	-0.7296	1.2070	-10.39	17.19	-0.60
UME	7.81	0.33	0.7904	1.2800	11.26	18.23	0.62
NIM	7.96	0.81	0.9404	1.9470	13.40	27.74	0.48
LNE	8.02	0.61	1.0000	1.6450	14.25	23.43	0.61

7.2. Plots of KCRVs to the reported data

The KCRVs proposed using the recommended choice of estimators from the NDT are graphically presented in Figures 8 to 14. The symbol * denotes that the results were not included in the KCRV calculations. All results are sorted by increasing x_i. In these figures, the candidate KCRV is represented by a solid horizontal green line, while the dashed red lines denote the standard uncertainty of the candidate KCRV, u(KCRV). For each measured value displayed in the graphs, the blue dot represents the measured value x_i, and a thick vertical yellow line segment represents $x_i \pm u_i'$.

7.2.1. Arsenic

Figure 8a. Plots of participants' results relative to the KCRV for arsenic.

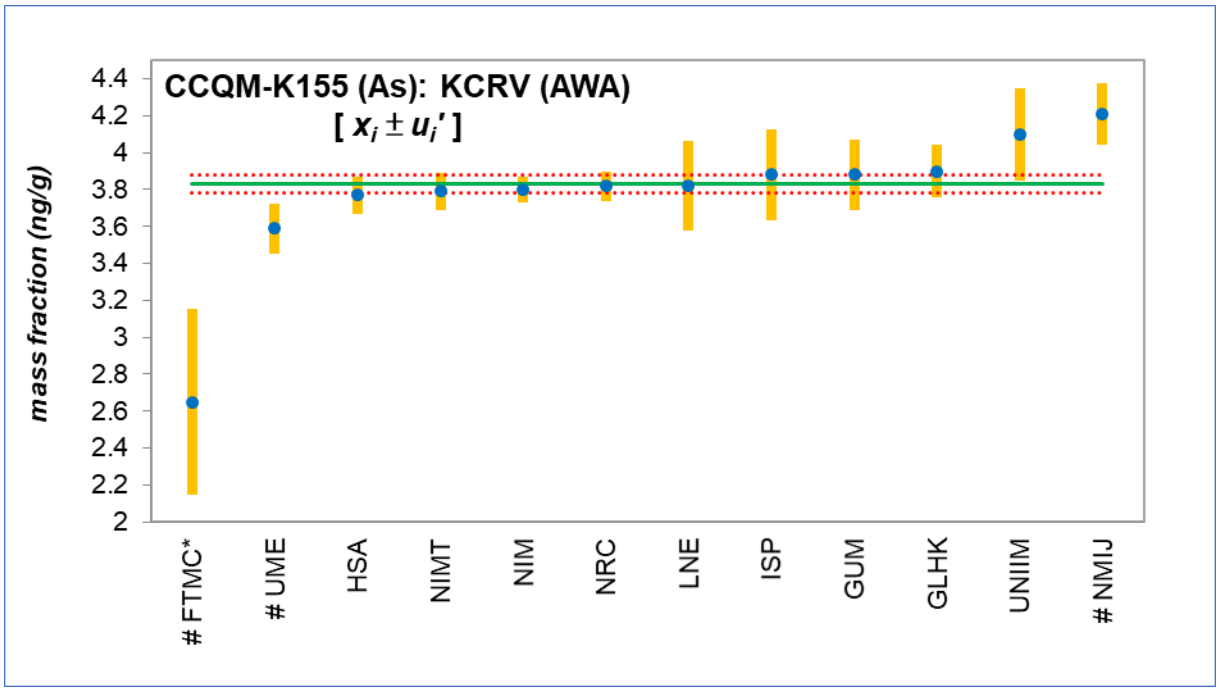
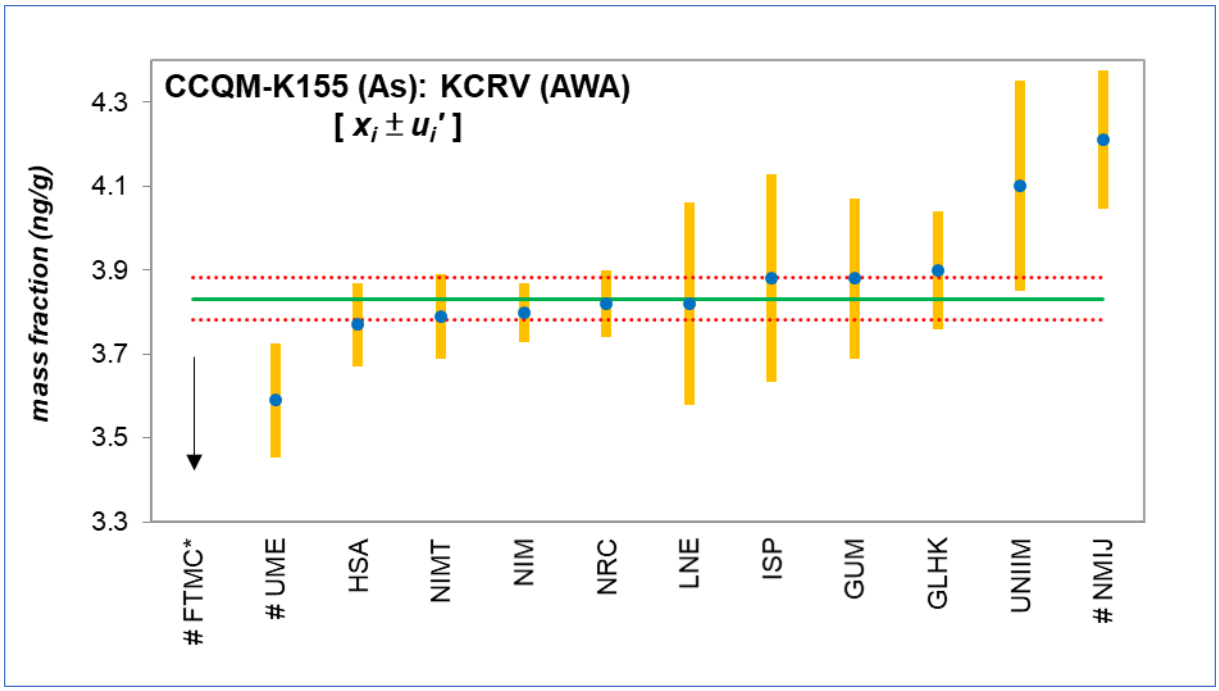


Figure 8b. Plots of participants' results relative to the KCRV for arsenic (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The blue dot represents the measured value x_i, and a thick vertical yellow line segment represents $x_i \pm u_i'$.
3. The participants accompanied by a hash (#) indicates that their u_i' is the reported standard uncertainty and dark uncertainty (tau) summed in quadrature.

7.2.2. Cadmium

Figure 9a. Plots of participants' results relative to the KCRV for cadmium.

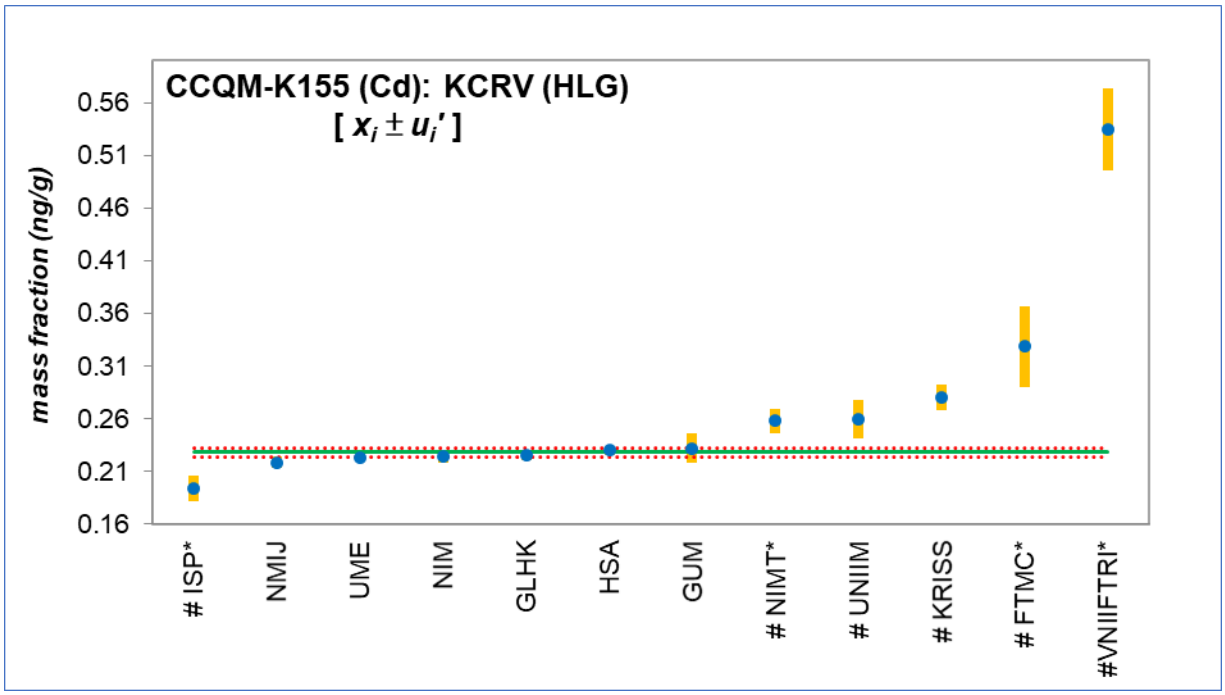
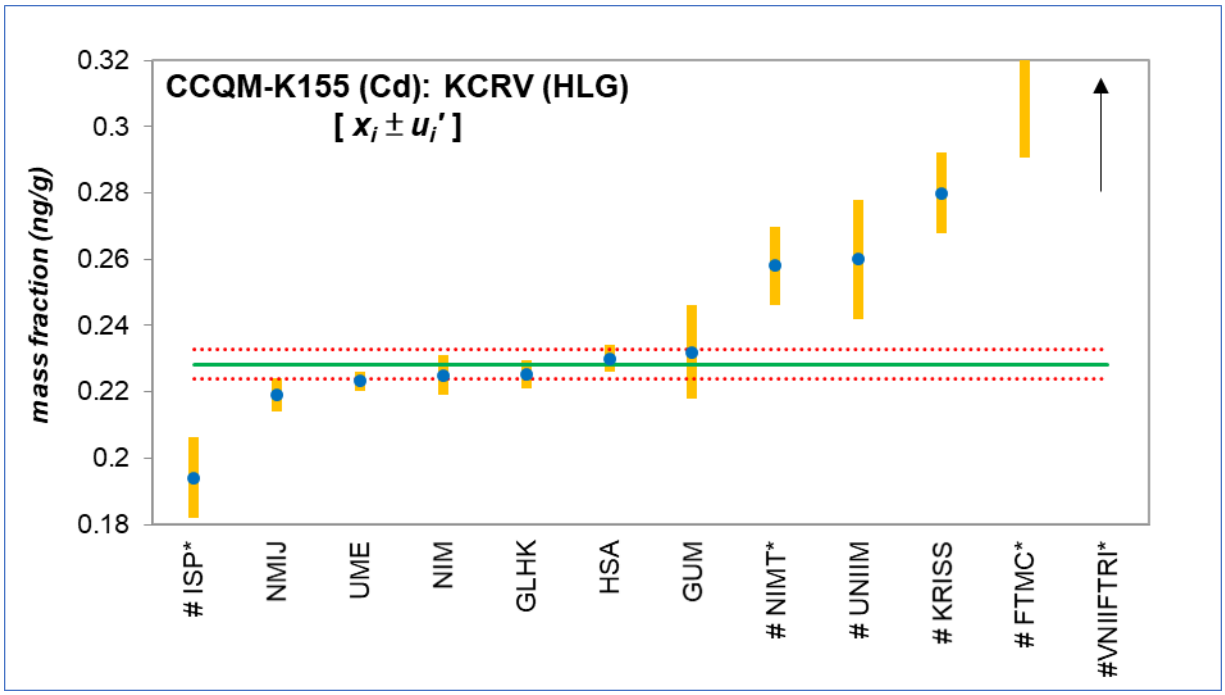


Figure 9b. Plots of participants' results relative to the KCRV for cadmium (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The blue dot represents the measured value x_i, and a thick vertical yellow line segment represents $x_i \pm u_i'$.
3. The participants accompanied by a hash (#) indicates that their u_i' is the reported standard uncertainty and dark uncertainty (tau) summed in quadrature.

7.2.3. Copper

Figure 10a. Plots of participants' results relative to the KCRV for copper.

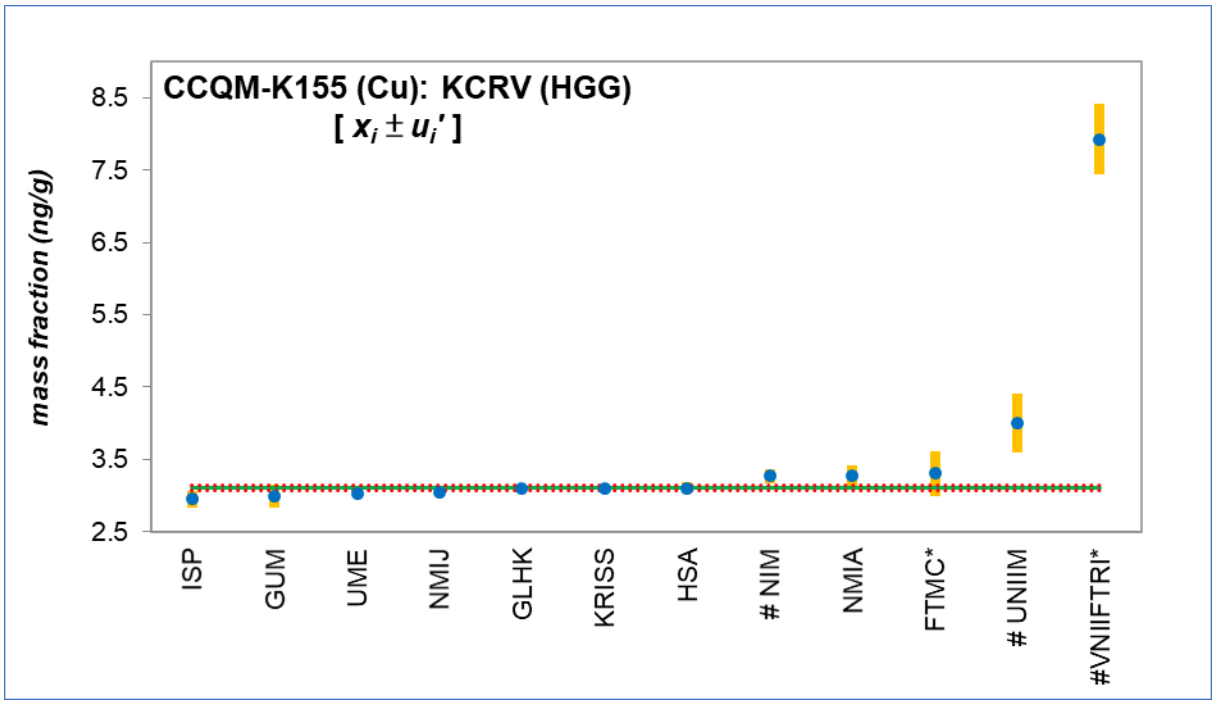
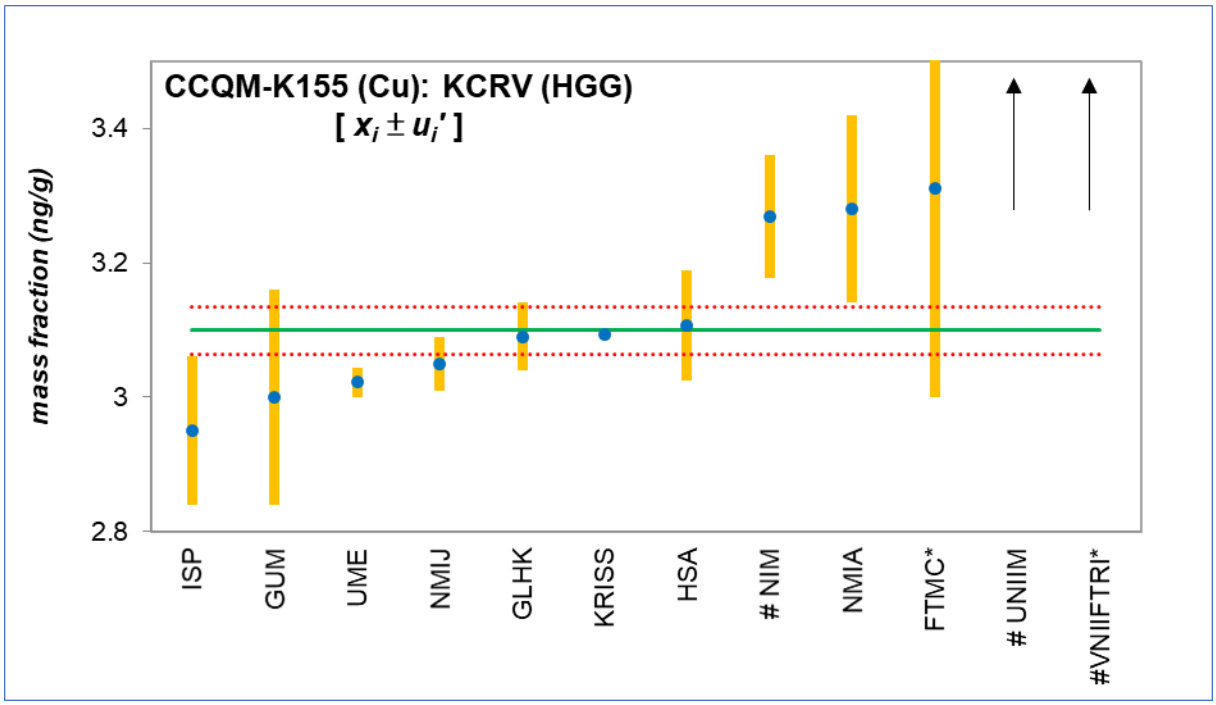


Figure 10b. Plots of participants' results relative to the KCRV for copper (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The blue dot represents the measured value x_i, and a thick vertical yellow line segment represents $x_i \pm u_i'$.
3. The participants accompanied by a hash (#) indicates that their u_i' is the reported standard uncertainty and dark uncertainty (tau) summed in quadrature.

7.2.4. Lead

Figure 11a. Plots of participants' results relative to the KCRV for lead.

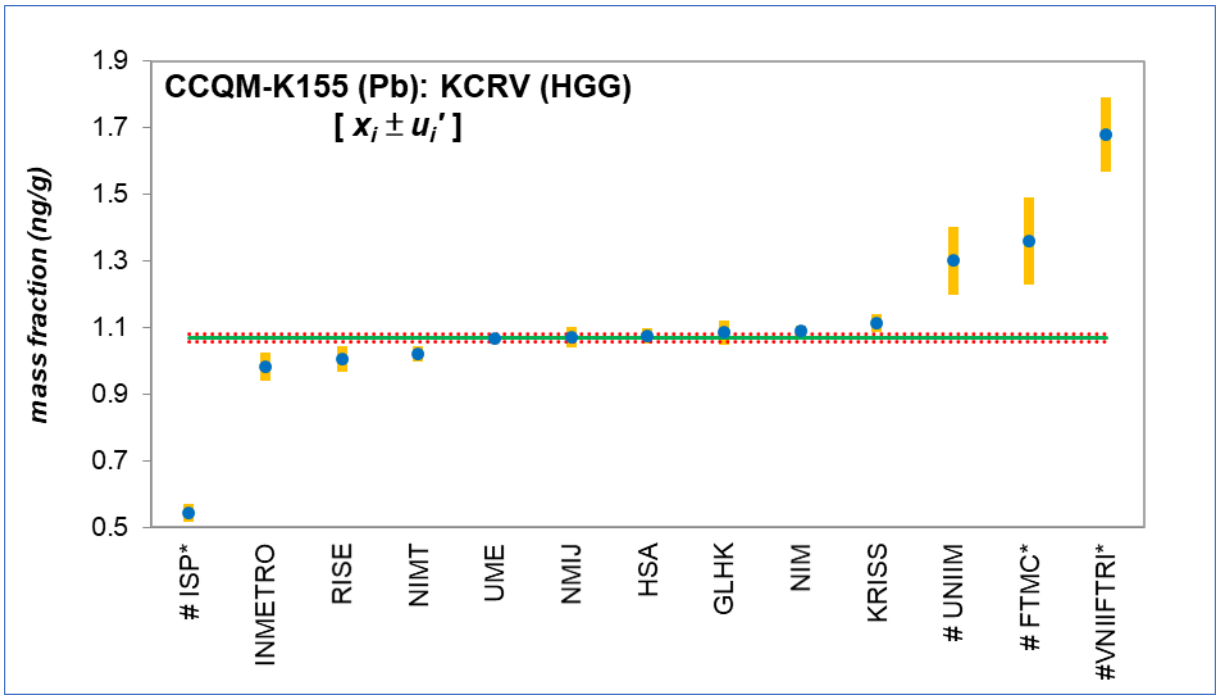
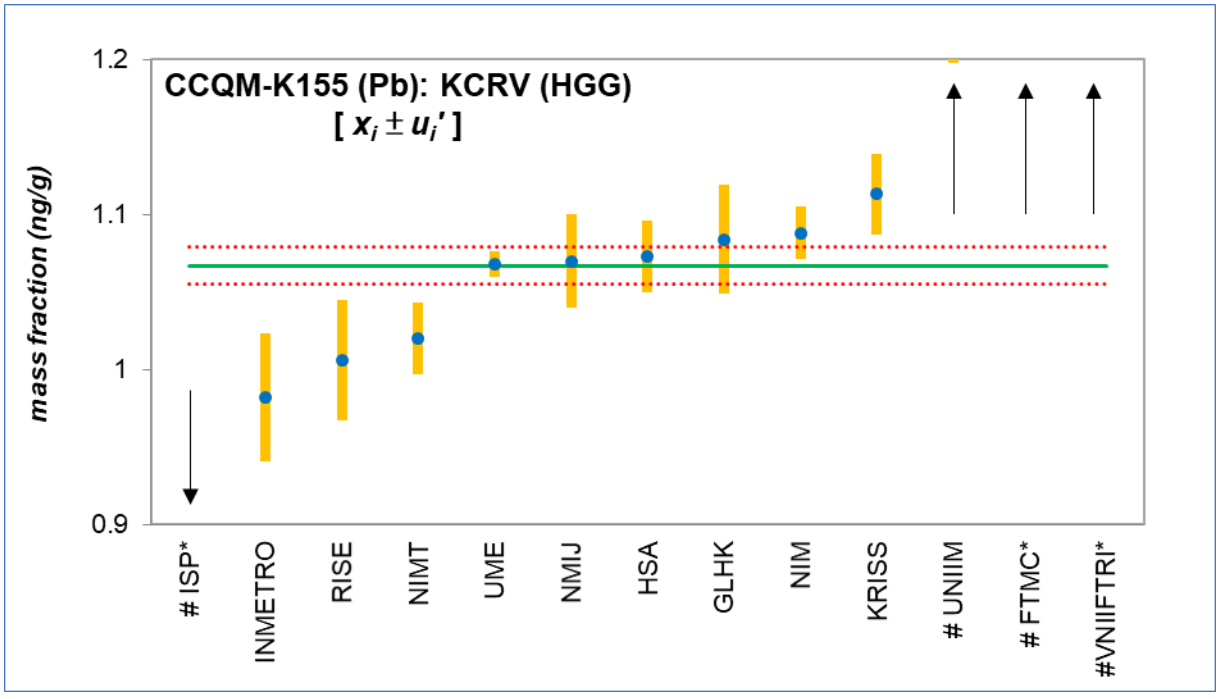


Figure 11b. Plots of participants' results relative to the KCRV for lead (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The blue dot represents the measured value x_i, and a thick vertical yellow line segment represents $x_i \pm u_i'$.
3. The participants accompanied by a hash (#) indicates that their u_i' is the reported standard uncertainty and dark uncertainty (tau) summed in quadrature.

7.2.5. Nickel

Figure 12a. Plots of participants' results relative to the KCRV for nickel.

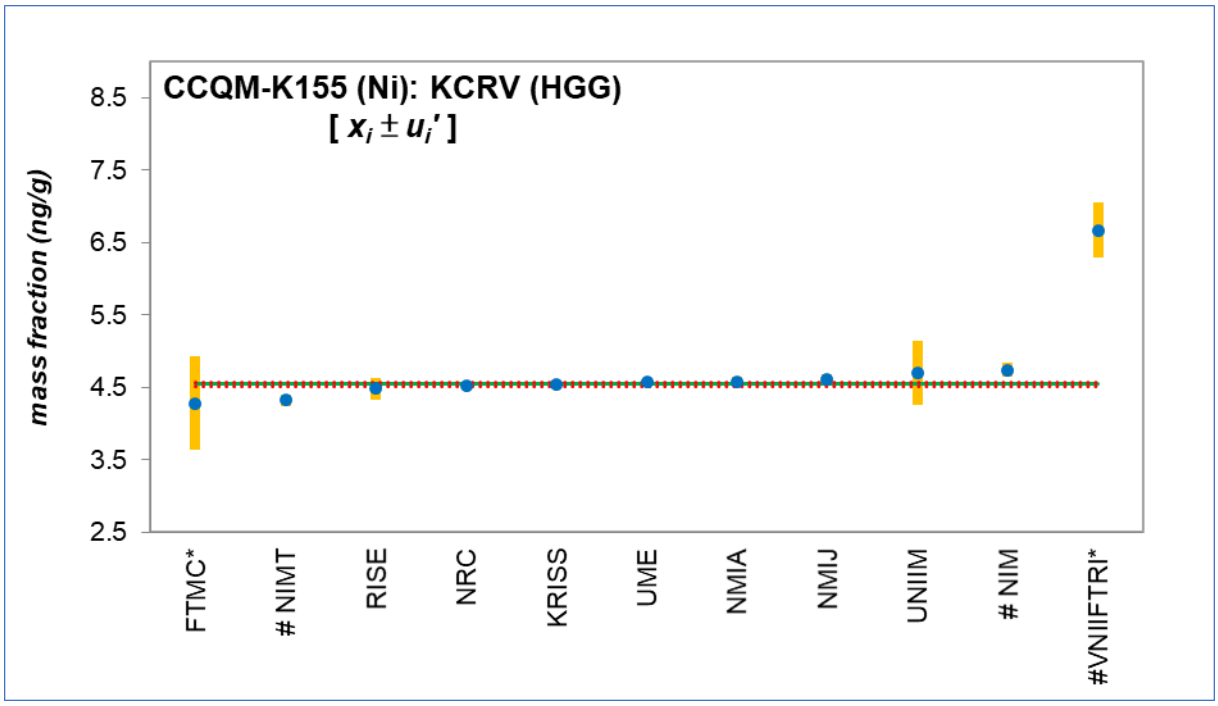
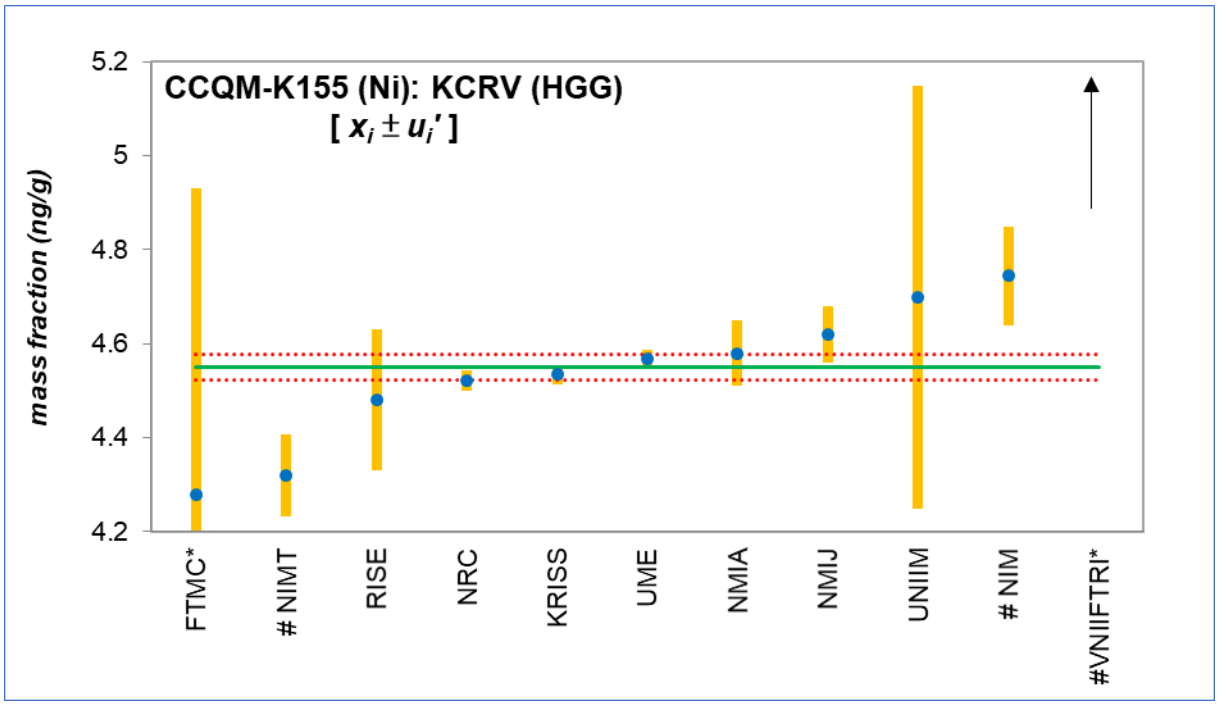


Figure 12b. Plots of participants' results relative to the KCRV for nickel (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The blue dot represents the measured value x_i, and a thick vertical yellow line segment represents $x_i \pm u_i'$.
3. The participants accompanied by a hash (#) indicates that their u_i' is the reported standard uncertainty and dark uncertainty (tau) summed in quadrature.

7.2.6. Zinc

Figure 13a. Plots of participants' results relative to the KCRV for zinc.

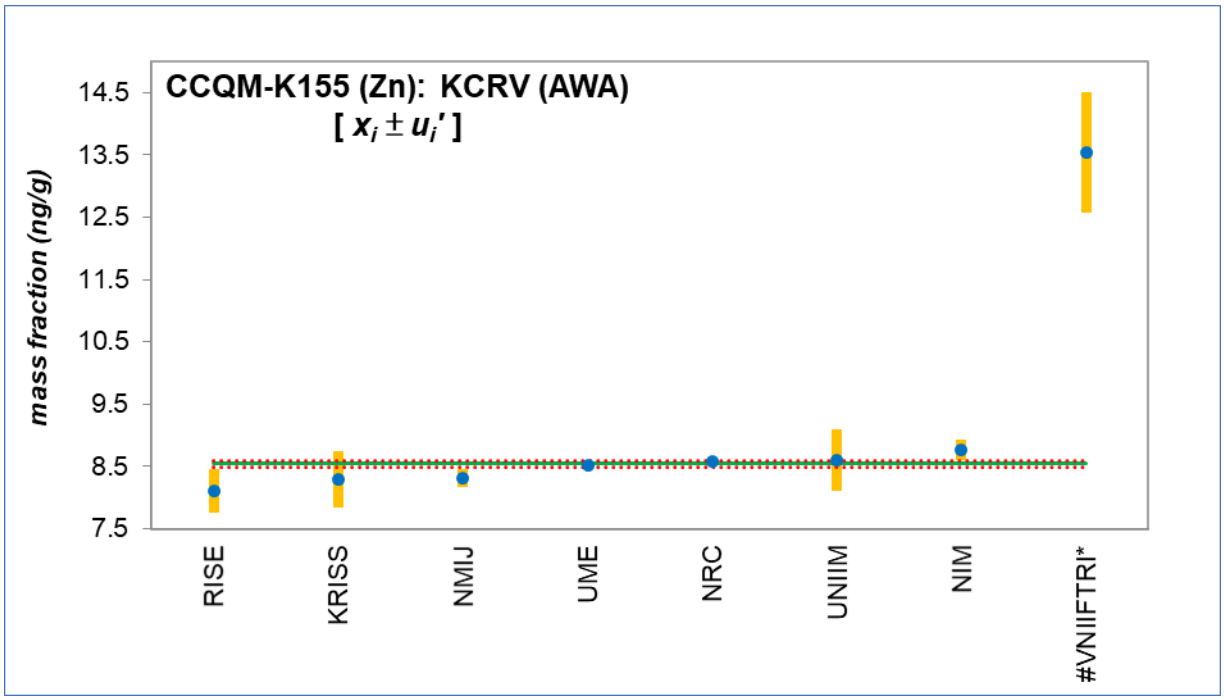
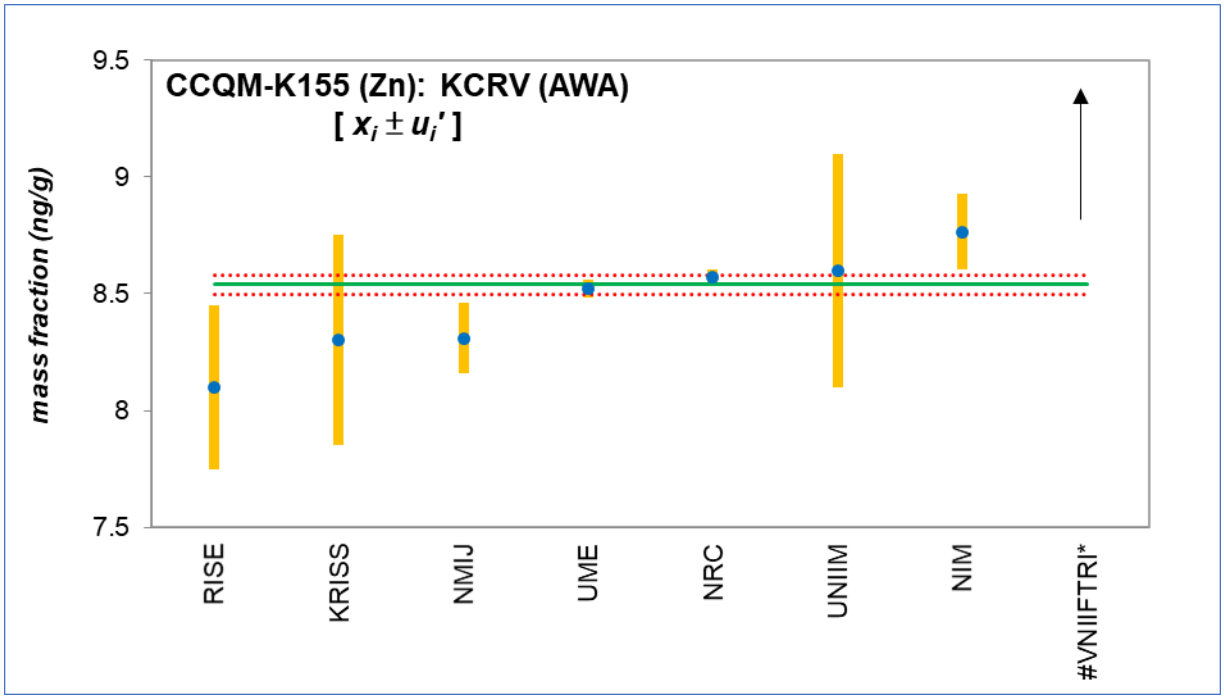


Figure 13b. Plots of participants' results relative to the KCRV for zinc (enlarged).

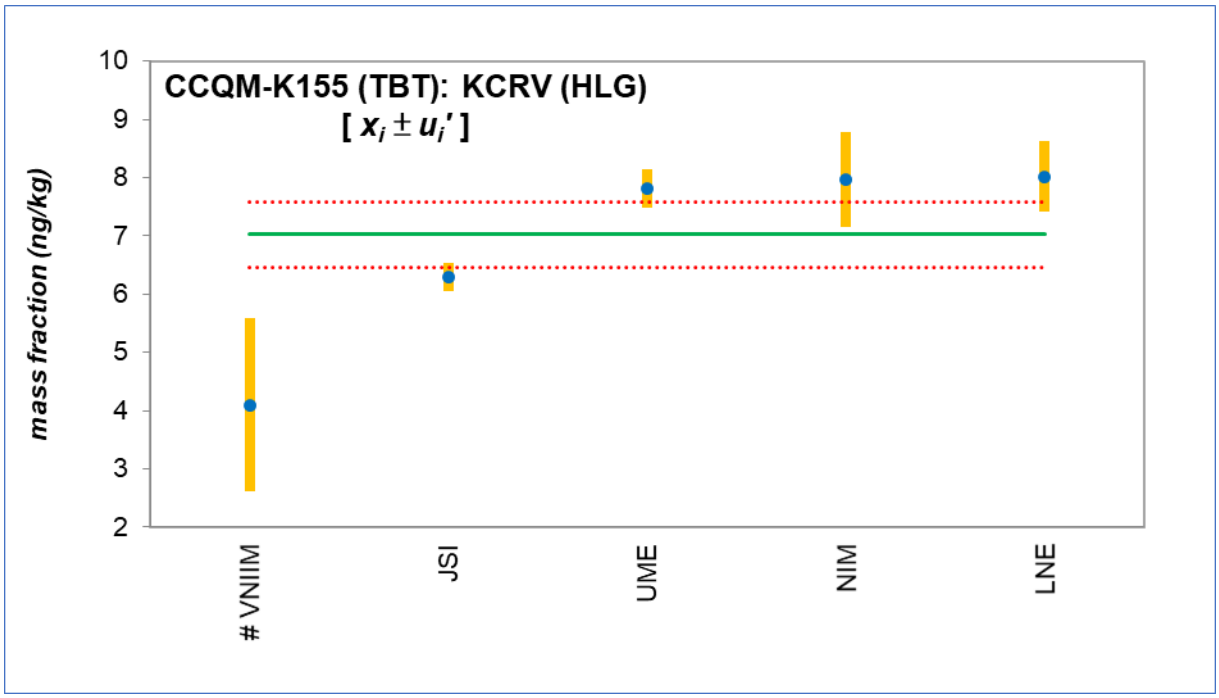


Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The blue dot represents the measured value x_i, and a thick vertical yellow line segment represents $x_i \pm u_i'$.
3. The participants accompanied by a hash (#) indicates that their u_i' is the reported standard uncertainty and dark uncertainty (tau) summed in quadrature.

7.2.7. Tributyltin

Figure 14. Plots of participants' results relative to the KCRV for tributyltin.



Notes:

1. The blue dot represents the measured value x_i, and a thick vertical yellow line segment represents $x_i \pm u_i'$.
2. The participant accompanied by a hash (#) indicates that their u_i' is the reported standard uncertainty and dark uncertainty (tau) summed in quadrature.

7.3. Plots of absolute DoE and relative DoE

Figures 15 to 28 below graphically illustrate both the absolute and relative DoEs for arsenic, cadmium, copper, lead, nickel, zinc and tributyltin using the KCRVs calculated by NDT. All results are sorted by increasing x. For the plot of absolute DoE, the y-axis of each graph displays the absolute DoE, D_i, in ng/kg for tributyltin, and ng/g for others. Red dots represent the D_i. For the NDT procedures used to estimate each of 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, $U(D_i)$. The horizontal line denotes perfect agreement with the KCRV. For the plot of relative DoE in %, the y-axis of each graph displays the DoE relative to the KCRV as percent, $\%D_i$ (i.e. $100 \cdot D_i$/KCRV). The error bars represent the $U(D_i)$ relative to the KCRV as percent, $\%U(D_i)$ (i.e. $100 \cdot U(D_i)$/KCRV).

7.3.1. DoE of arsenic

Figure 15a. Plot of absolute degrees of equivalence for arsenic.

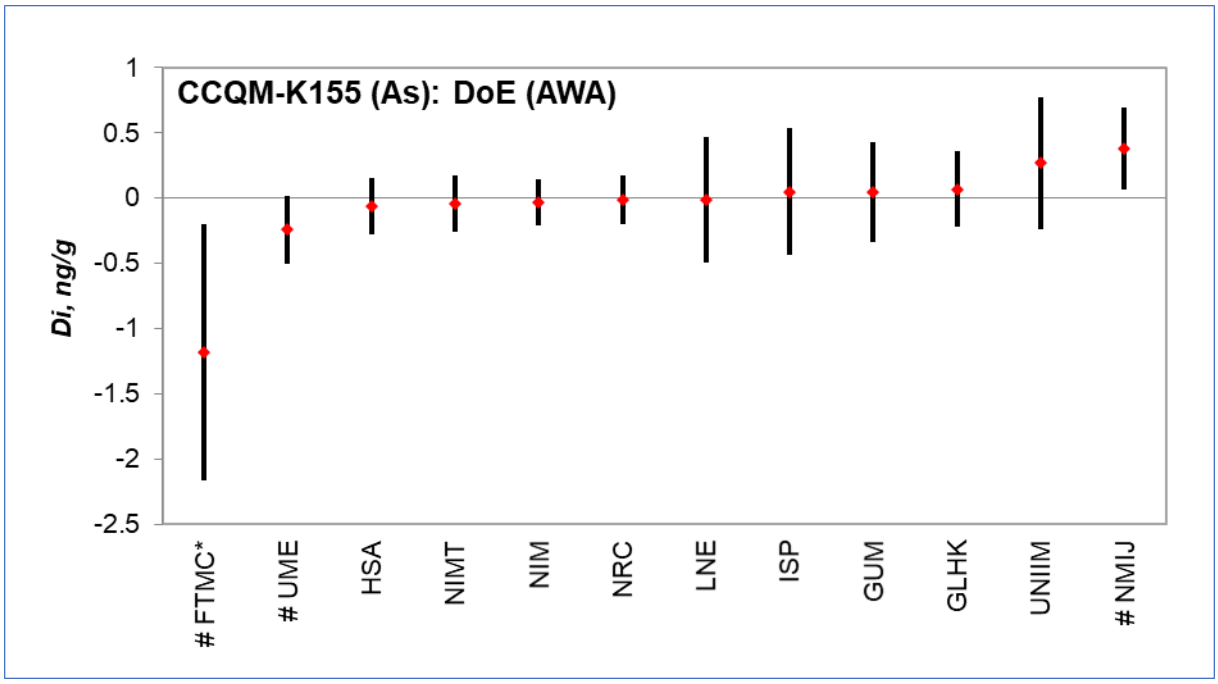
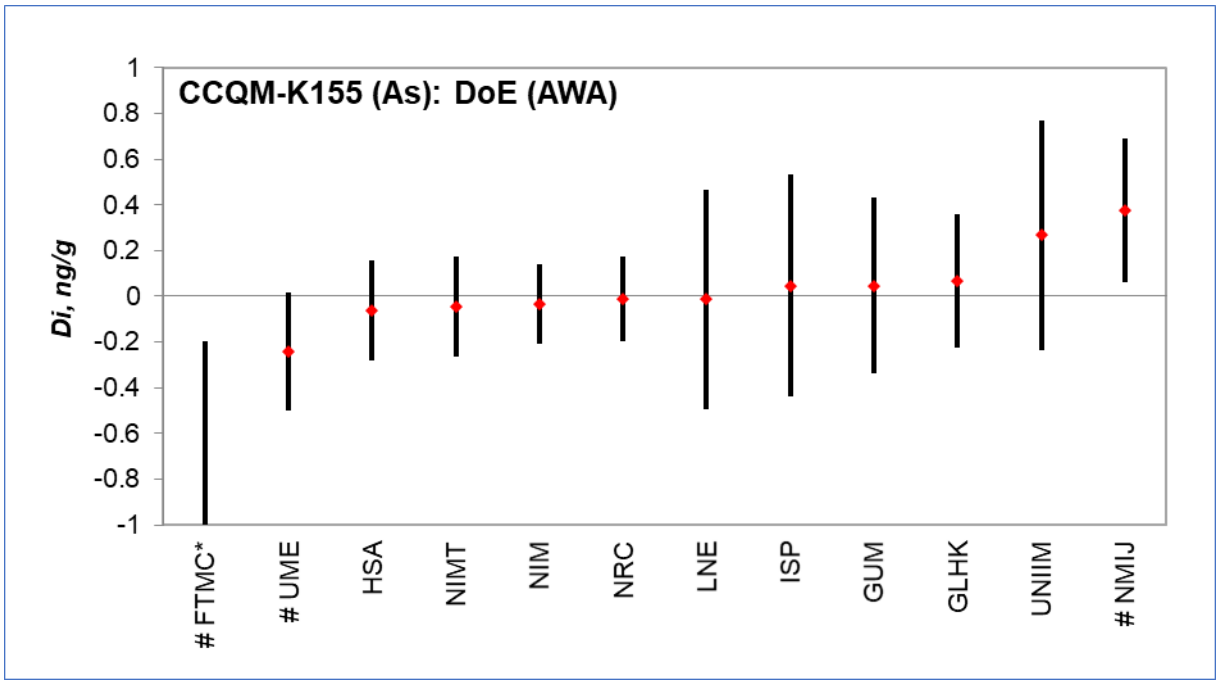


Figure 15b. Plot of absolute degrees of equivalence for arsenic (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE, D_i, and a vertical black line segment represents the expanded uncertainty of D_i at 95 % confidence level, $U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

Figure 16a. Plot of relative degrees of equivalence in % for arsenic.

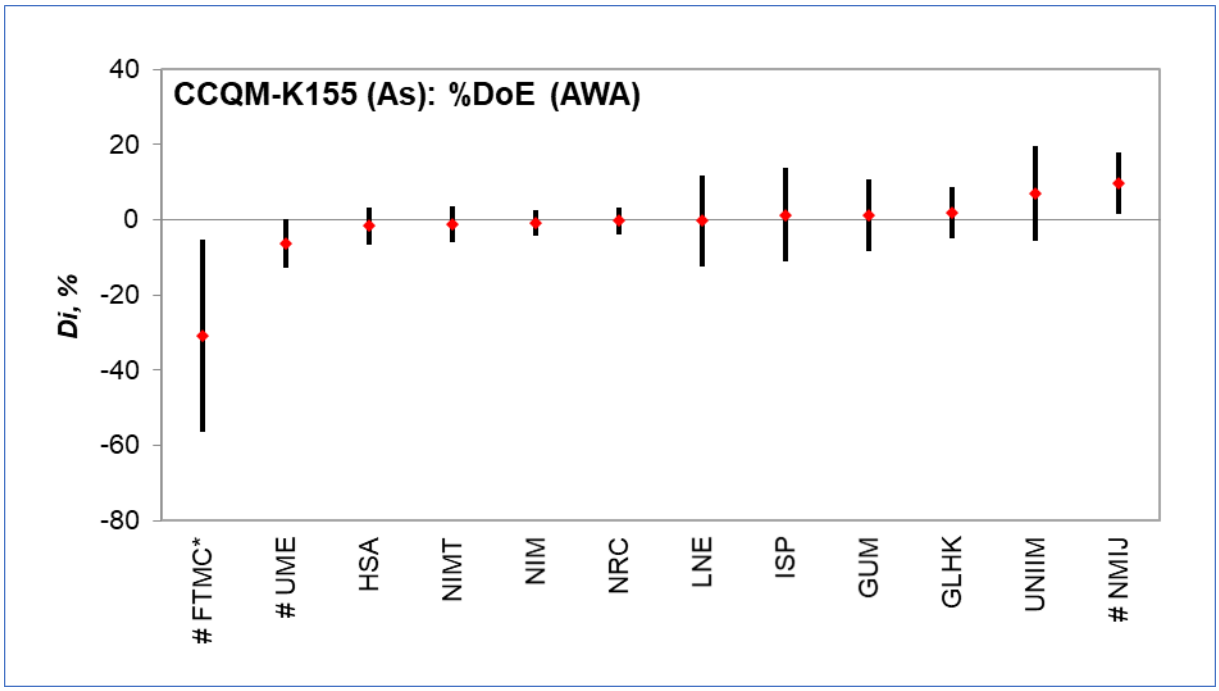
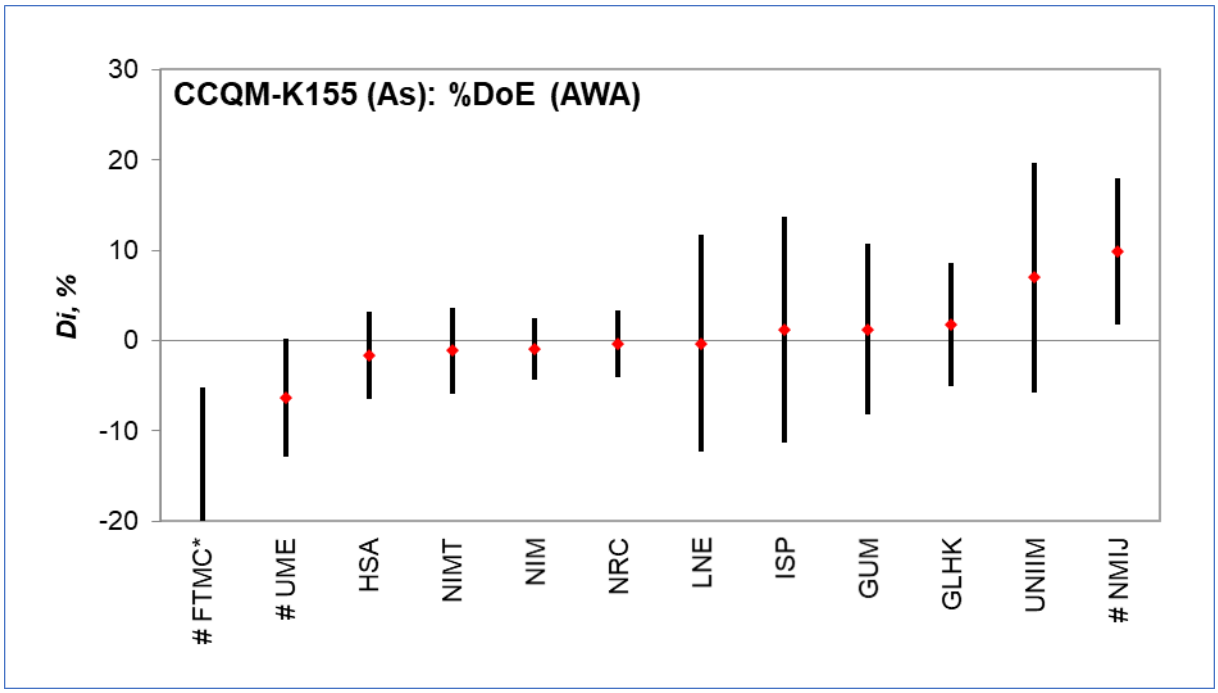


Figure 16b. Plot of relative degrees of equivalence in % for arsenic (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE relative to the KCRV as percent, $\%D_i$, and a vertical black line segment represents the $U(D_i)$ relative to the KCRV as percent, $\%U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

7.3.2. DoE of cadmium

Figure 17a. Plot of absolute degrees of equivalence for cadmium.

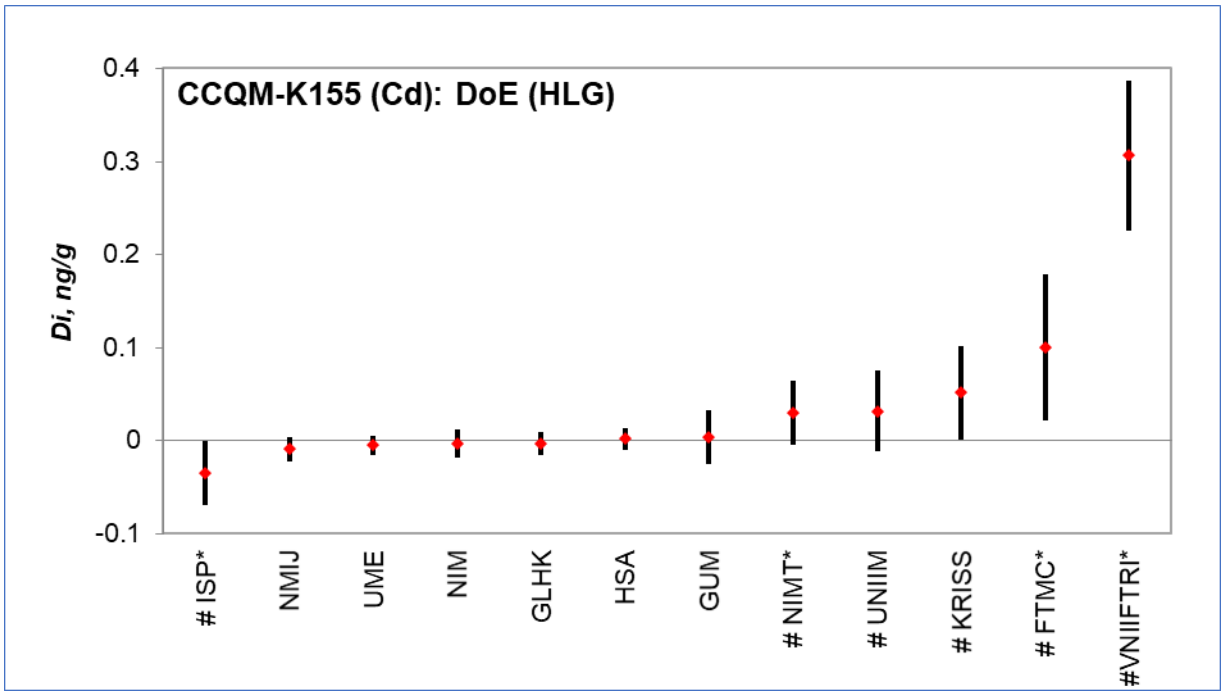
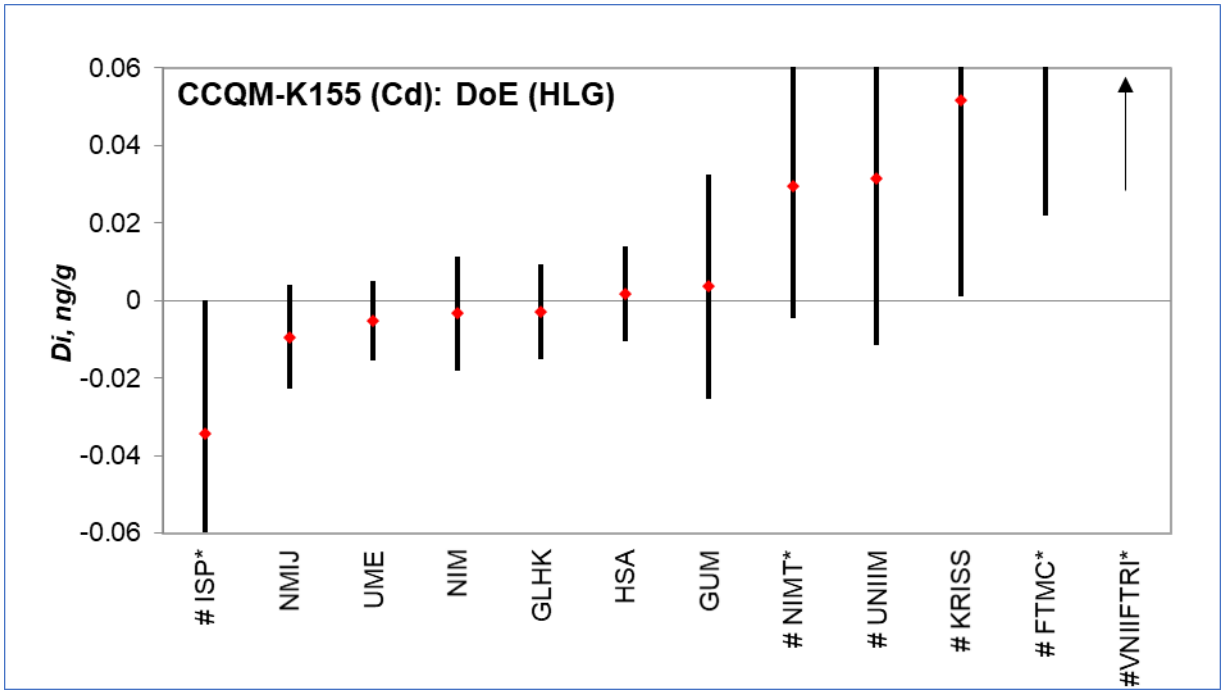


Figure 17b. Plot of absolute degrees of equivalence for cadmium (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE, D_i, and a vertical black line segment represents the expanded uncertainty of D_i at 95 % confidence level, $U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

Figure 18a. Plot of relative degrees of equivalence in % for cadmium.

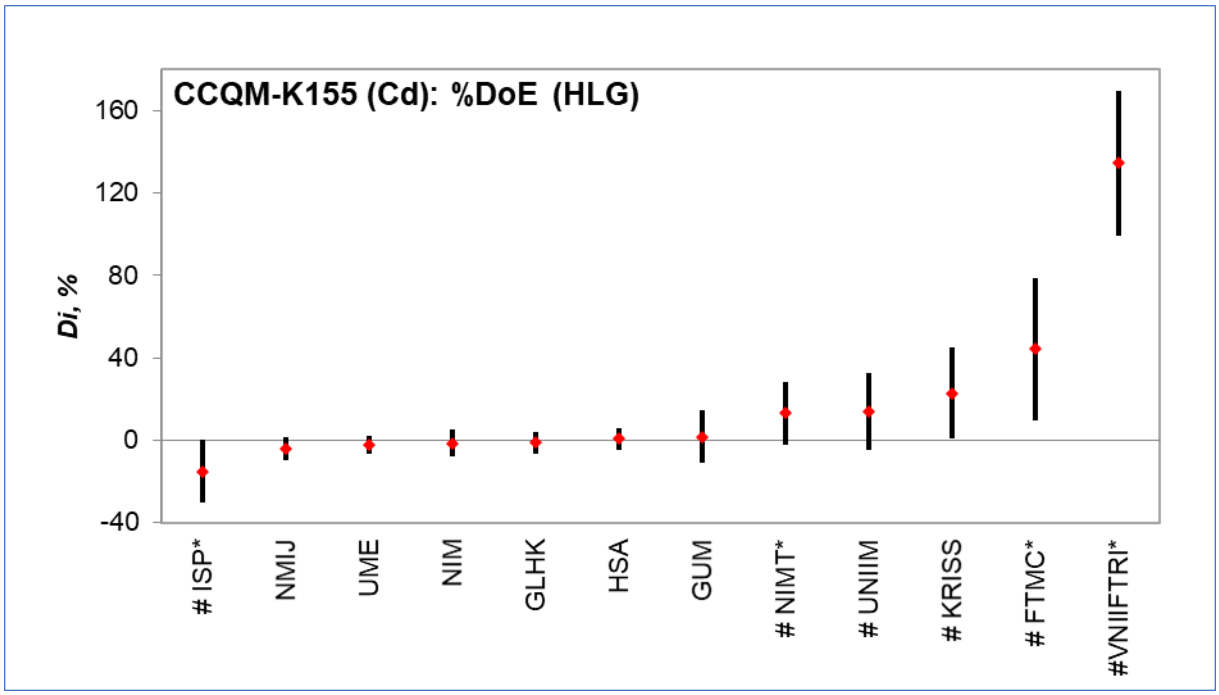
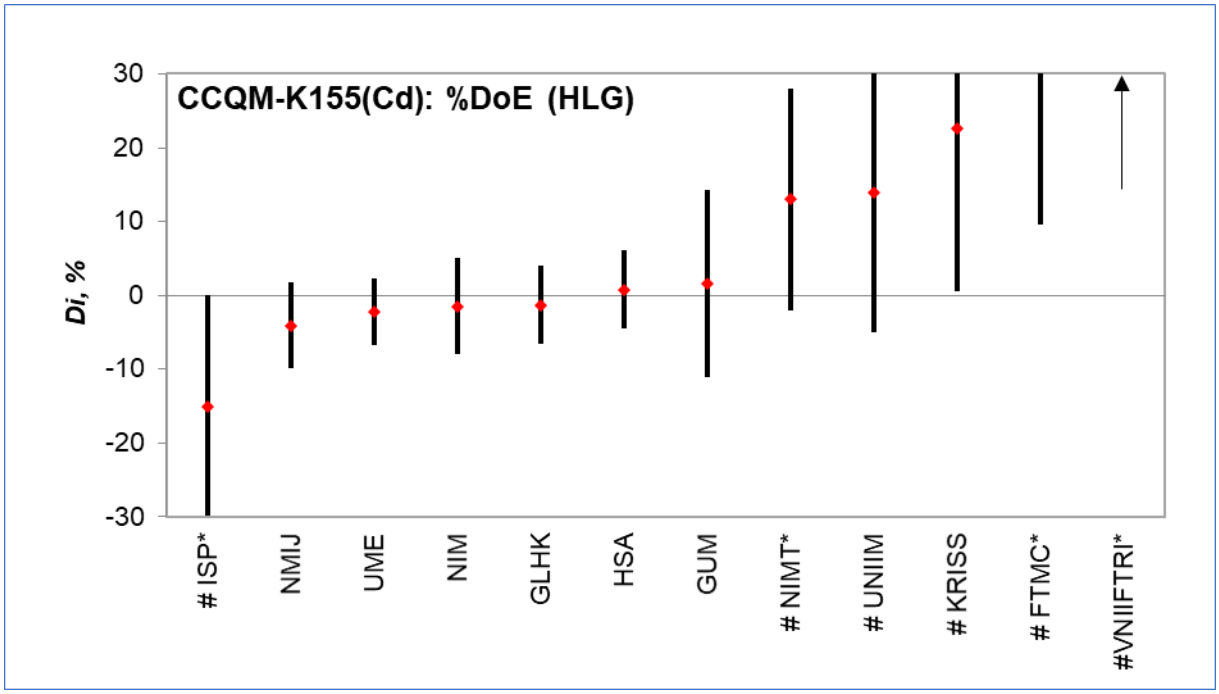


Figure 18b. Plot of relative degrees of equivalence in % for cadmium (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE relative to the KCRV as percent, $\%D_i$, and a vertical black line segment represents the $U(D_i)$ relative to the KCRV as percent, $\%U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

7.3.3. DoE of copper

Figure 19a. Plot of absolute degrees of equivalence for copper.

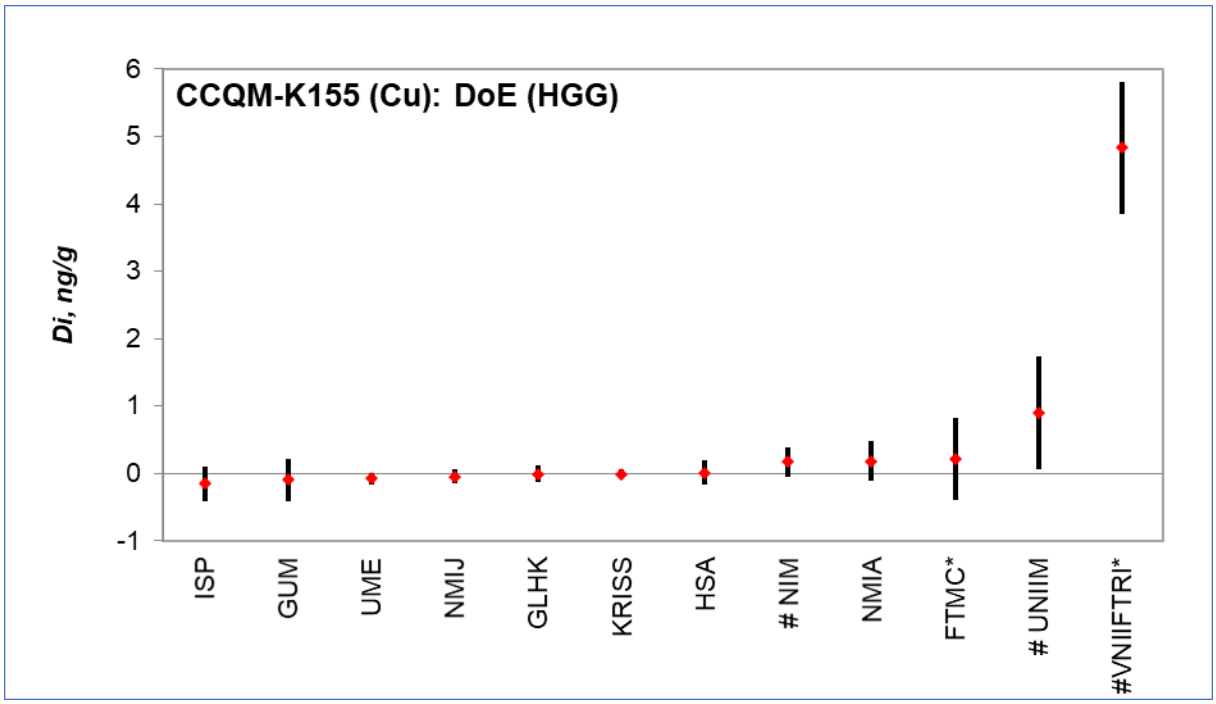
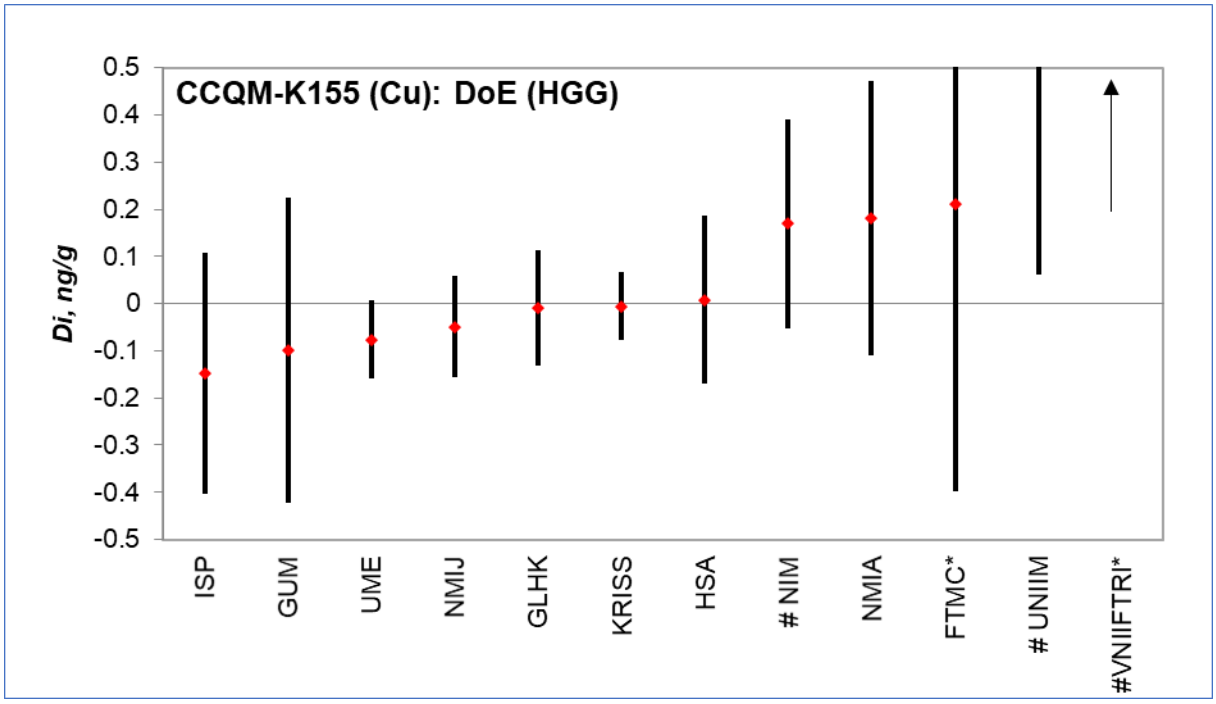


Figure 19b. Plot of absolute degrees of equivalence for copper (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE, D_i, and a vertical black line segment represents the expanded uncertainty of D_i at 95 % confidence level, $U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

Figure 20a. Plot of relative degrees of equivalence in % for copper.

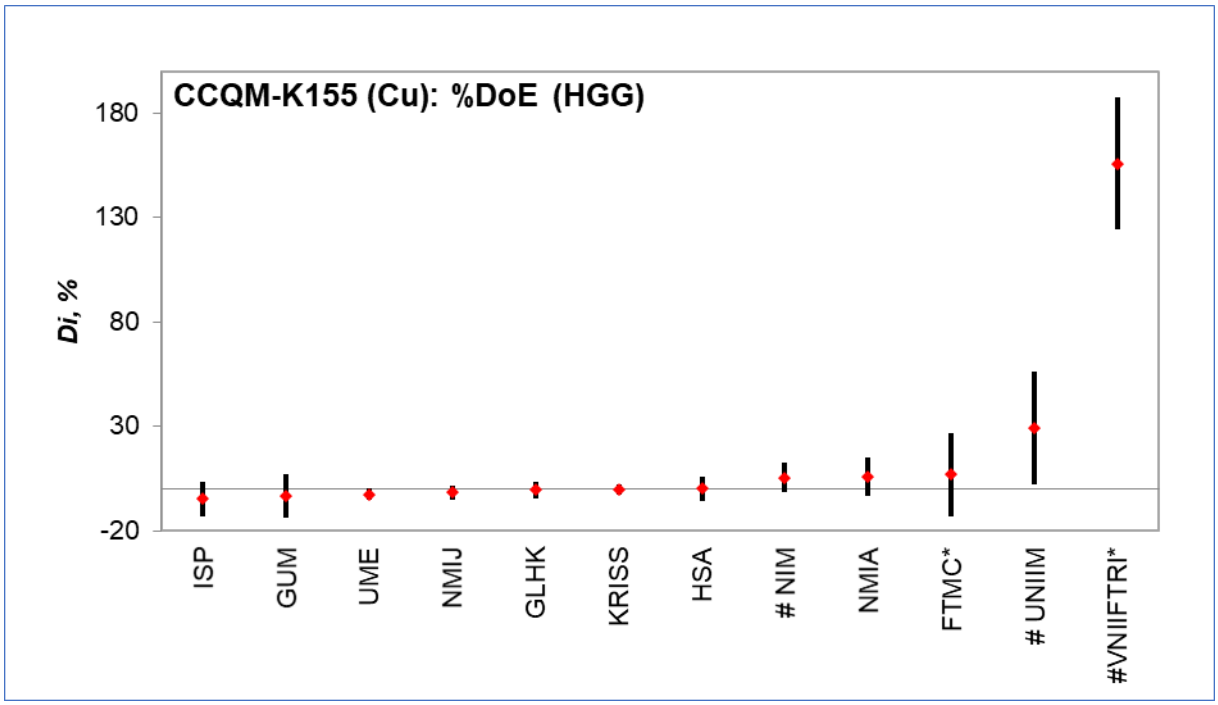
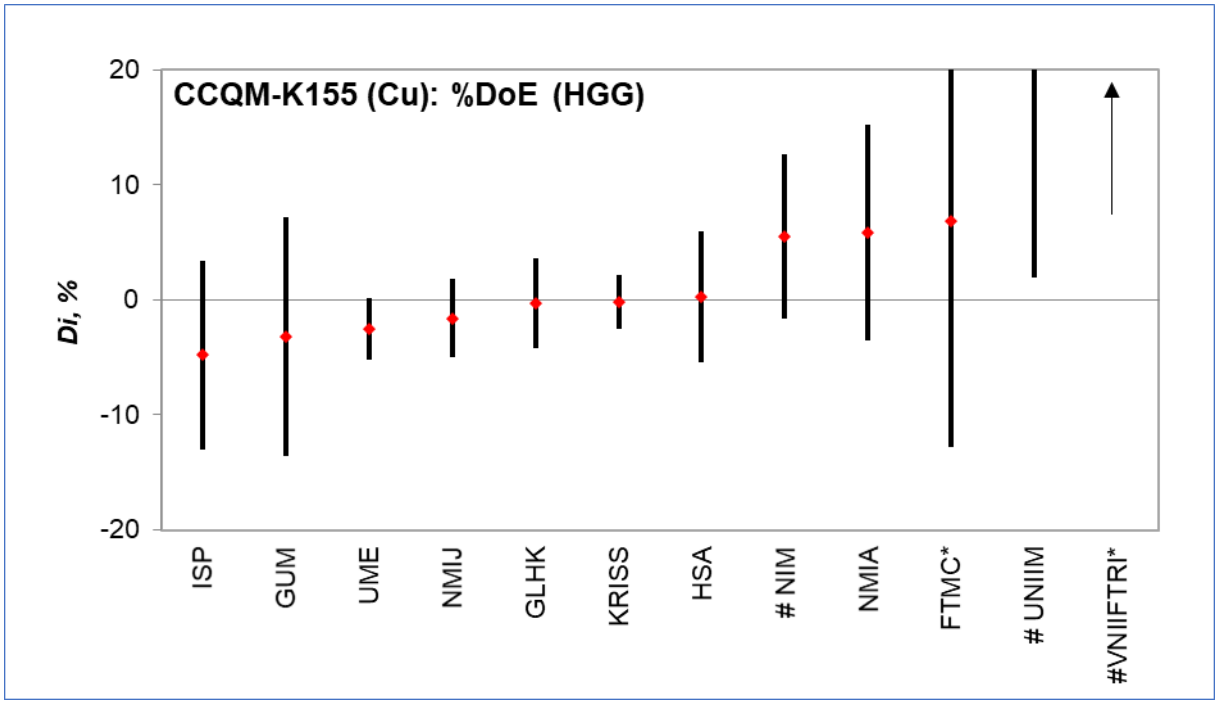


Figure 20b. Plot of relative degrees of equivalence in % for copper (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE relative to the KCRV as percent, $\%D_i$, and a vertical black line segment represents the $U(D_i)$ relative to the KCRV as percent, $\%U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

7.3.4. DoE of lead

Figure 21a. Plot of absolute degrees of equivalence for lead.

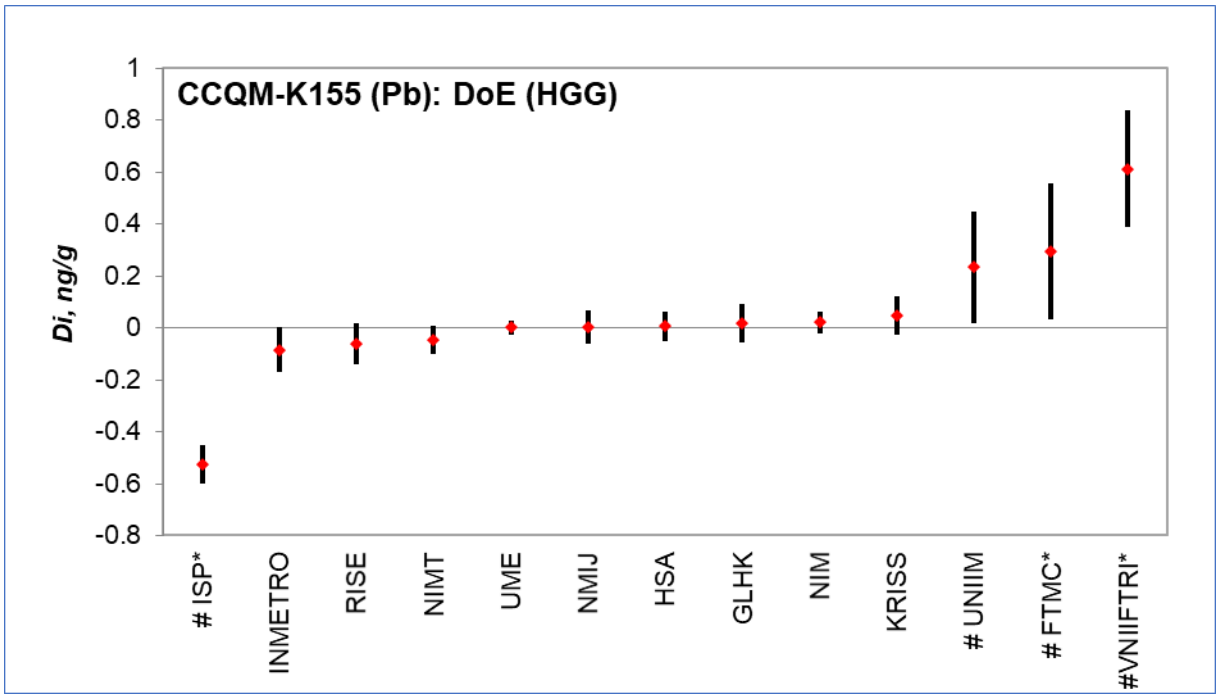
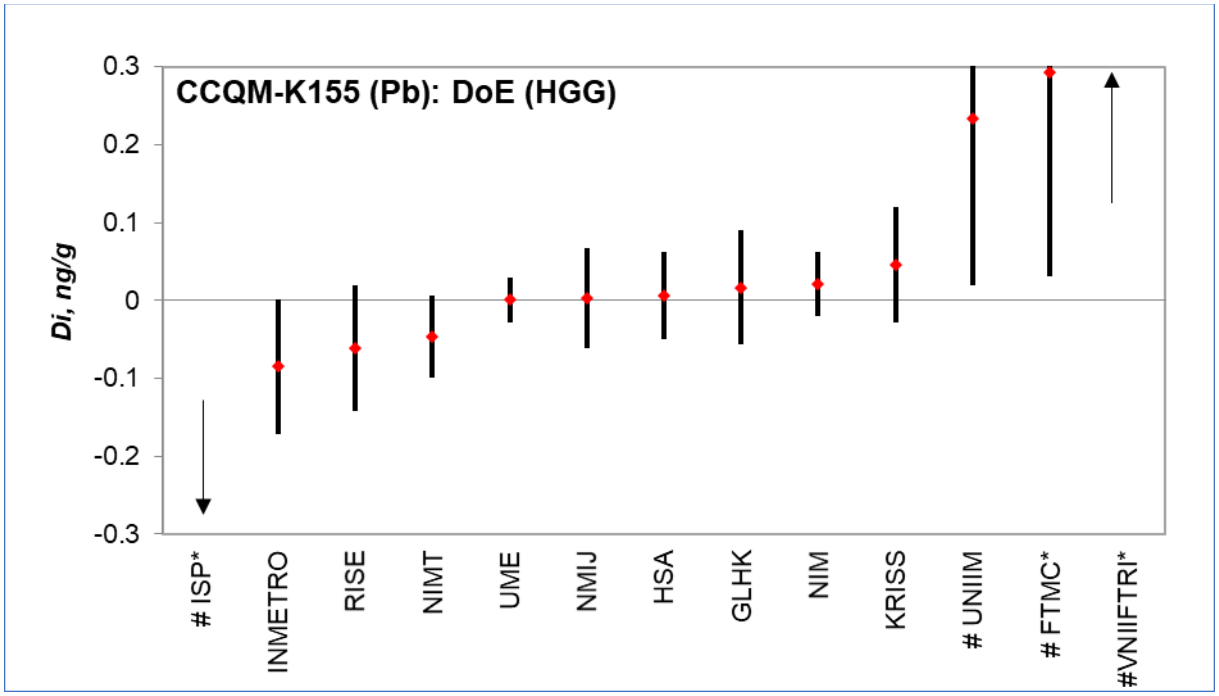


Figure 21b. Plot of absolute degrees of equivalence for lead (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE, D_i, and a vertical black line segment represents the expanded uncertainty of D_i at 95 % confidence level, $U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

Figure 22a. Plot of relative degrees of equivalence in % for lead.

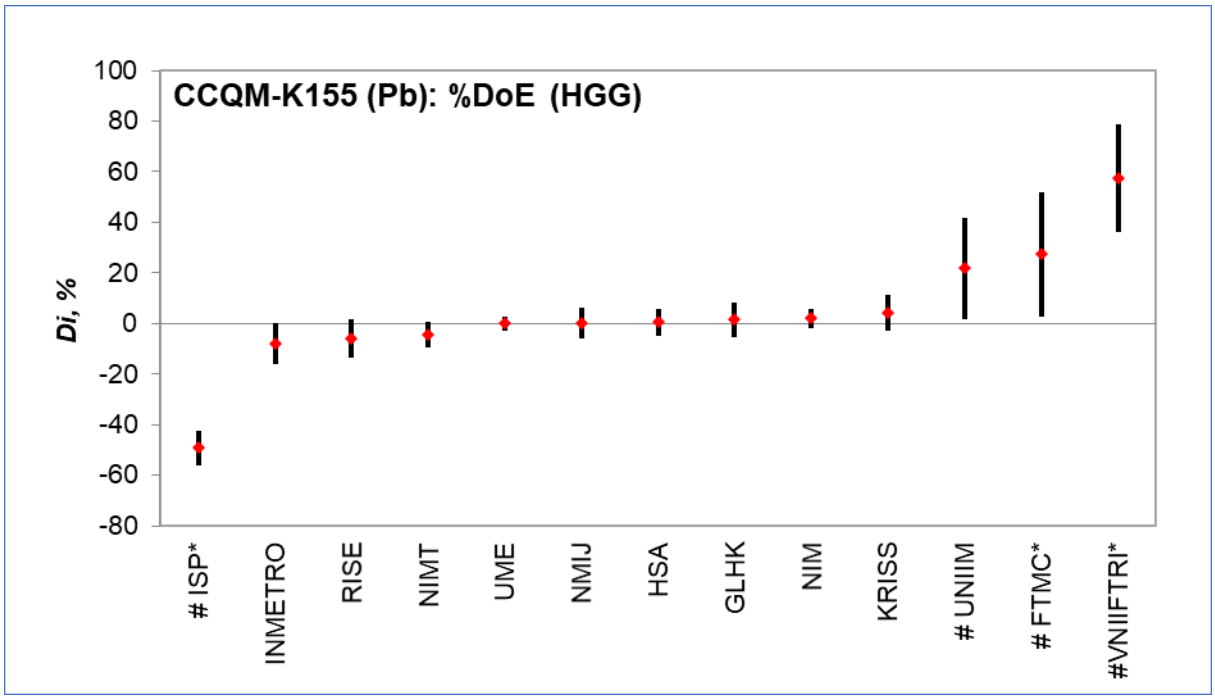
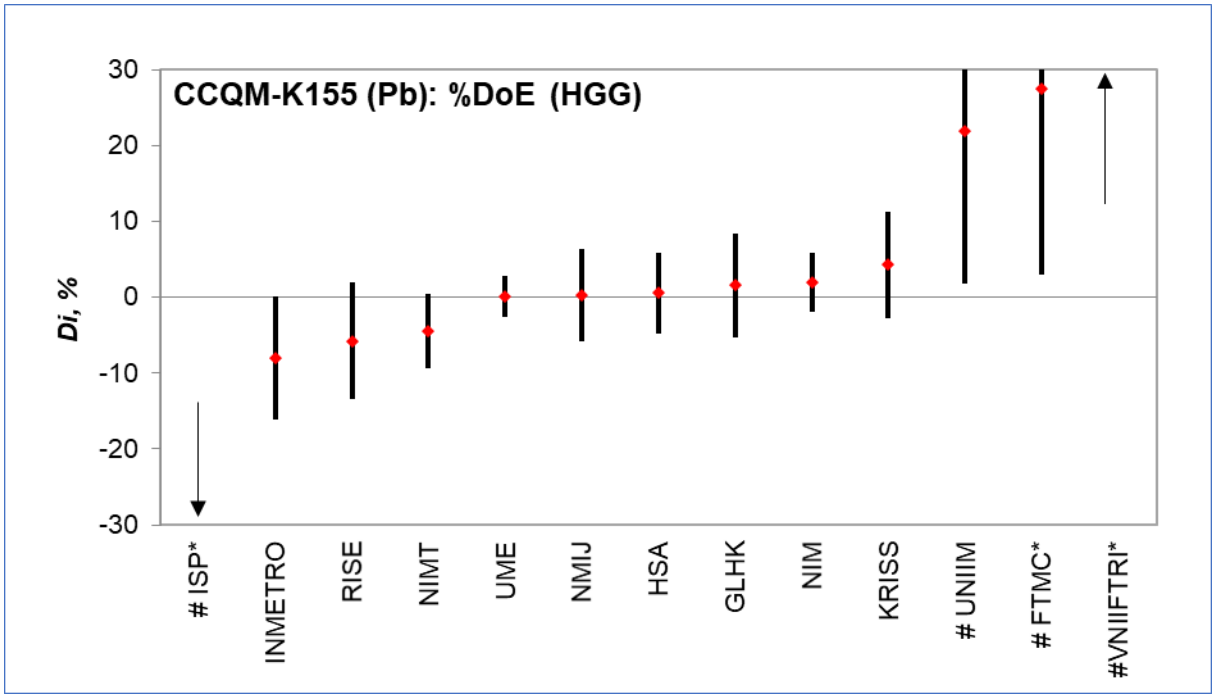


Figure 22b. Plot of relative degrees of equivalence in % for lead (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE relative to the KCRV as percent, $\%D_i$, and a vertical black line segment represents the $U(D_i)$ relative to the KCRV as percent, $\%U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

7.3.5. DoE of nickel

Figure 23a. Plot of absolute degrees of equivalence for nickel.

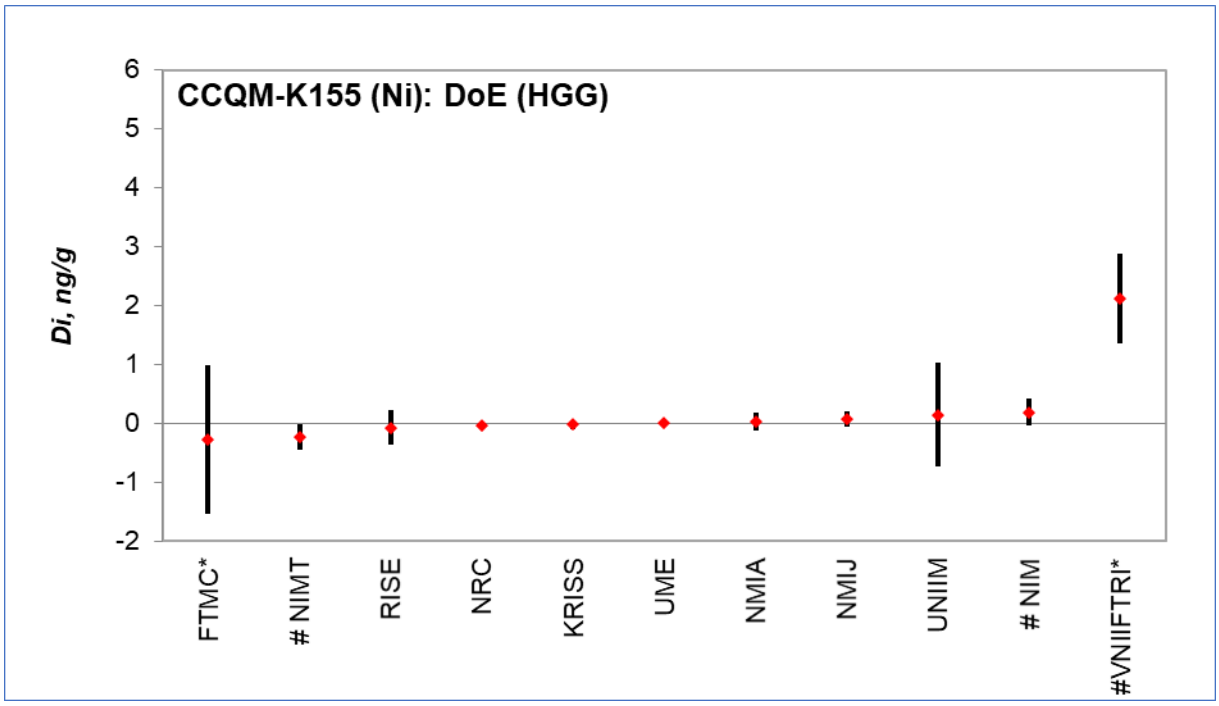
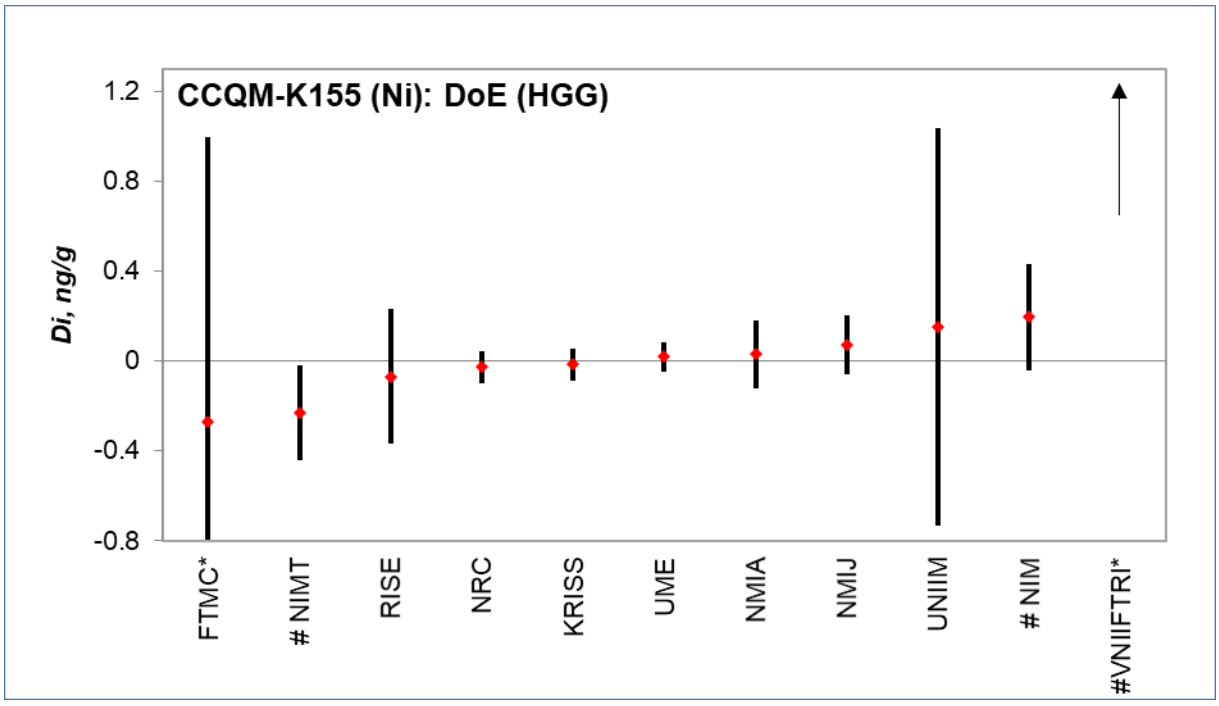


Figure 23b. Plot of absolute degrees of equivalence for nickel (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE, D_i, and a vertical black line segment represents the expanded uncertainty of D_i at 95 % confidence level, $U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

Figure 24a. Plot of relative degrees of equivalence in % for nickel.

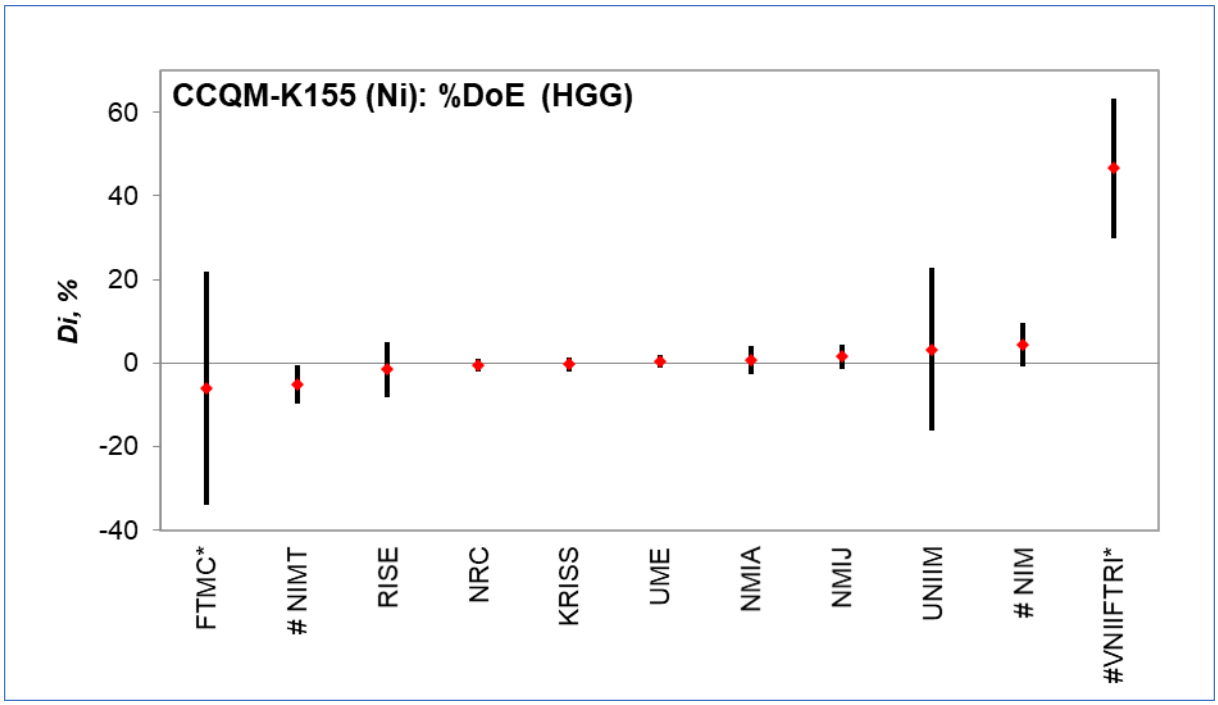
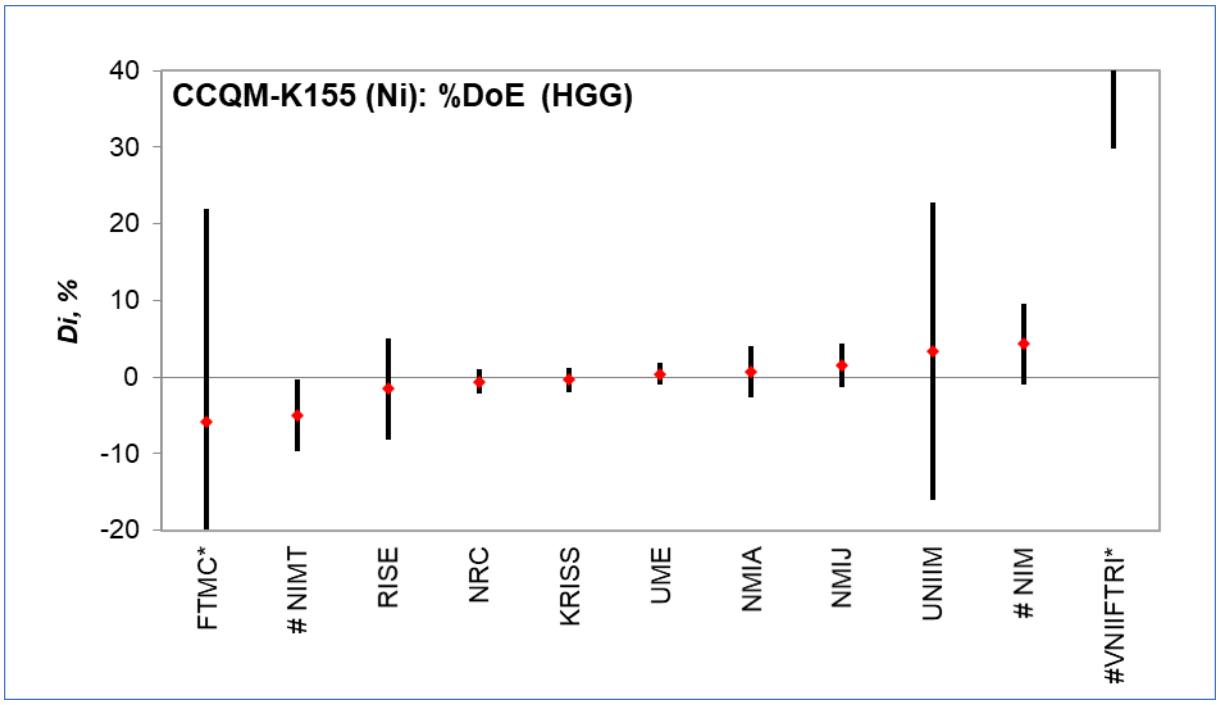


Figure 24b. Plot of relative degrees of equivalence in % for nickel (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE relative to the KCRV as percent, $\%D_i$, and a vertical black line segment represents the $U(D_i)$ relative to the KCRV as percent, $\%U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

7.3.6. DoE of zinc

Figure 25a. Plot of absolute degrees of equivalence for zinc.

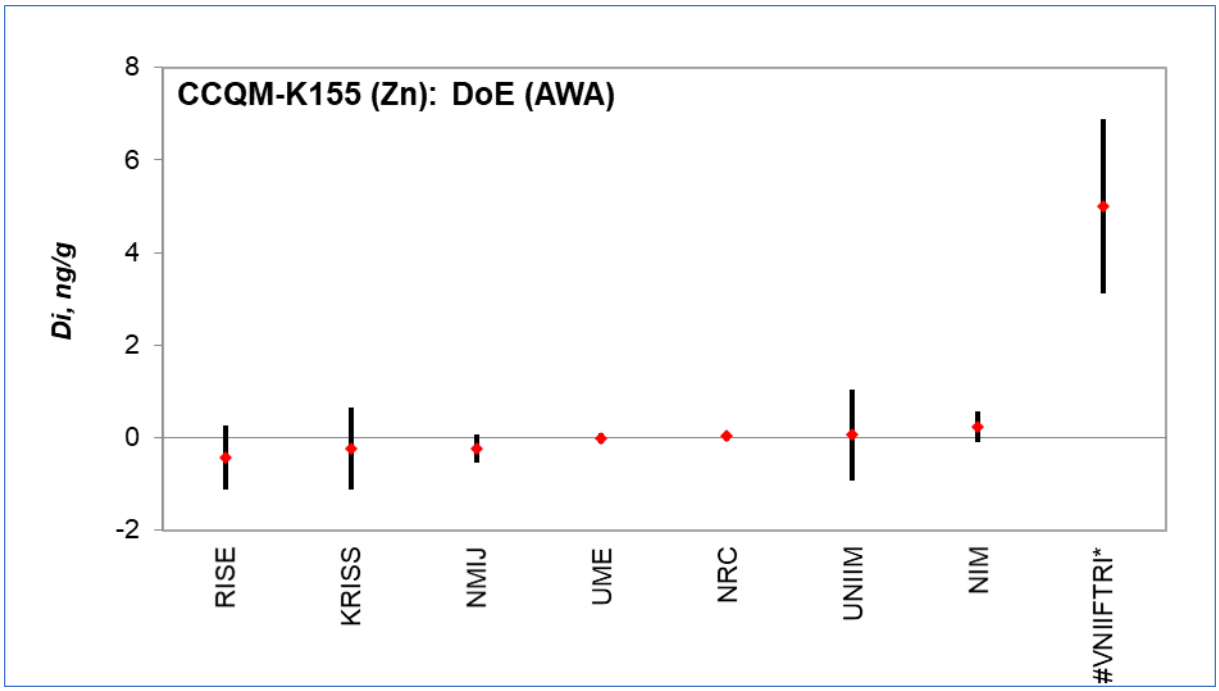
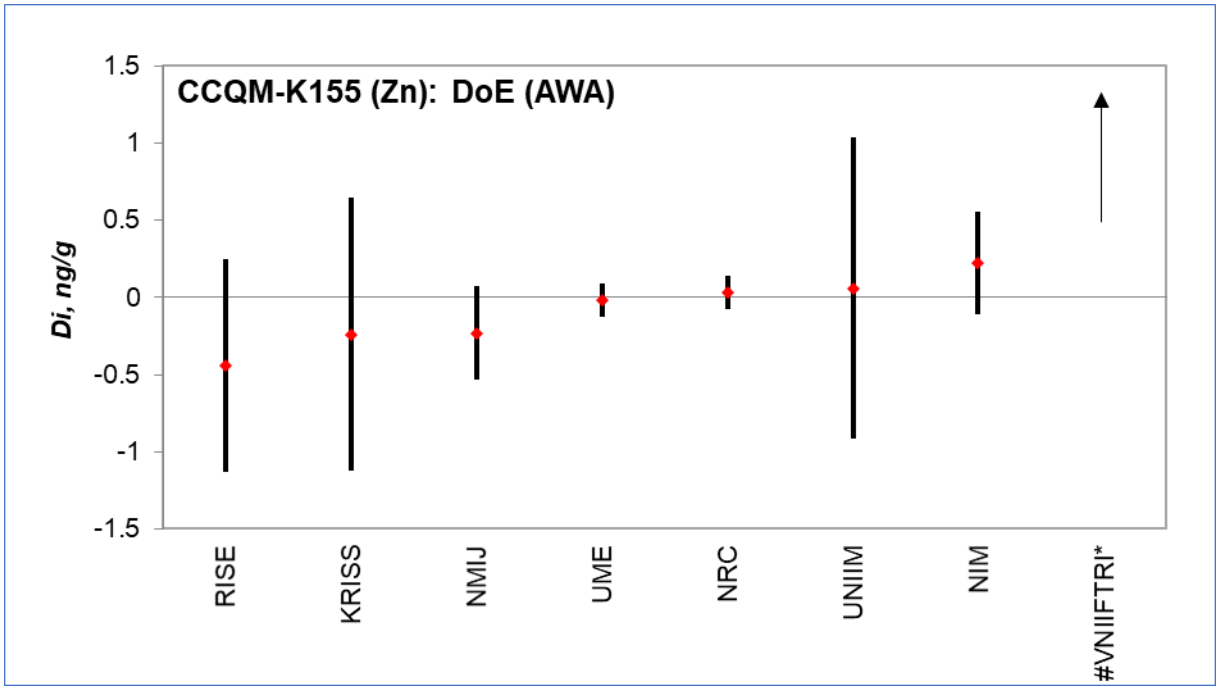


Figure 25b. Plot of absolute degrees of equivalence for zinc (enlarged).



Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE, D_i, and a vertical black line segment represents the expanded uncertainty of D_i at 95 % confidence level, $U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

Figure 26a. Plot of relative degrees of equivalence in % for zinc.

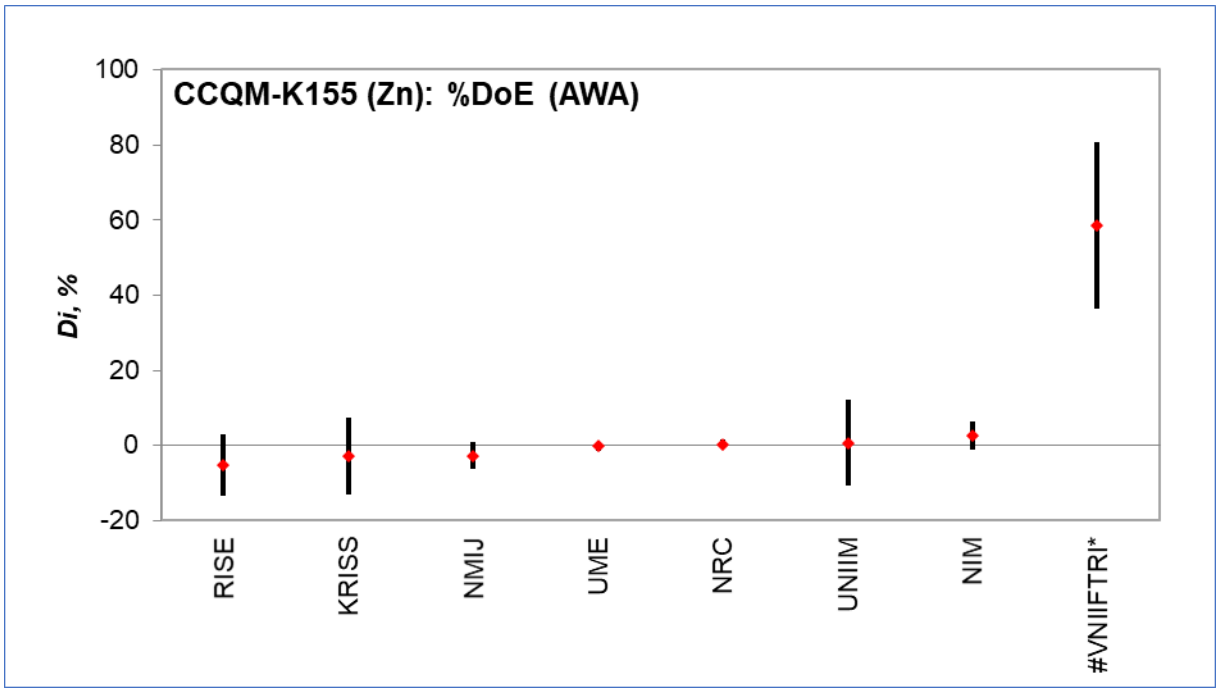
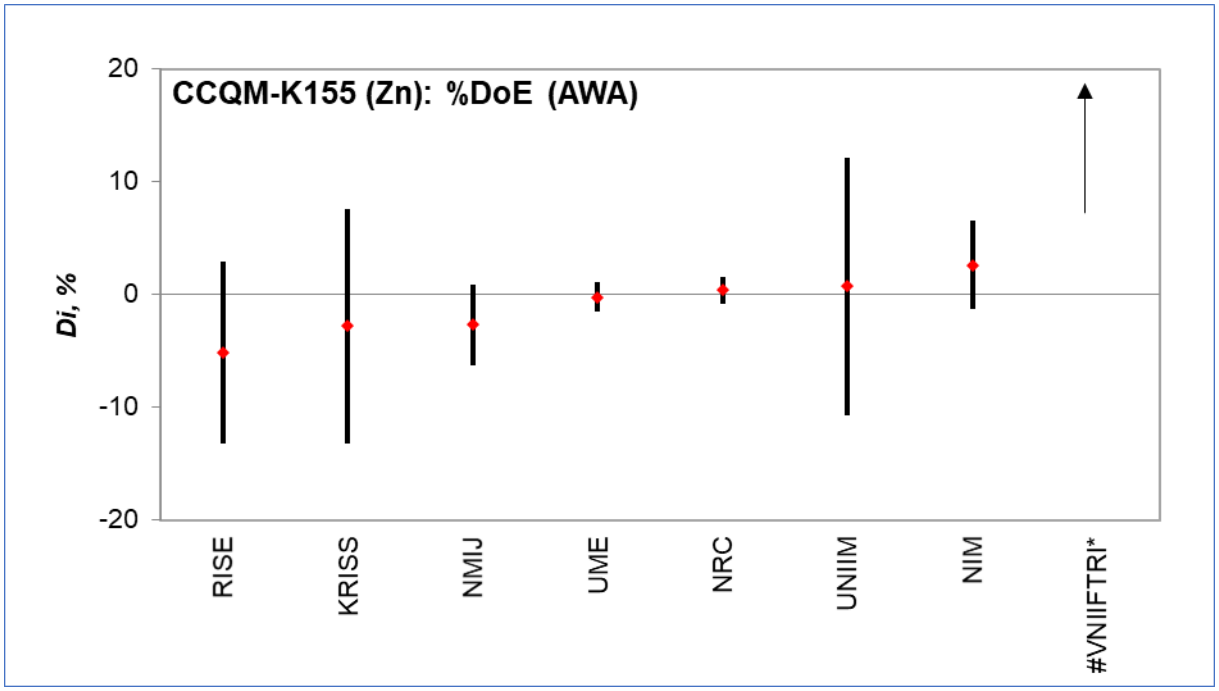


Figure 26b. Plot of relative degrees of equivalence in % for zinc (enlarged).

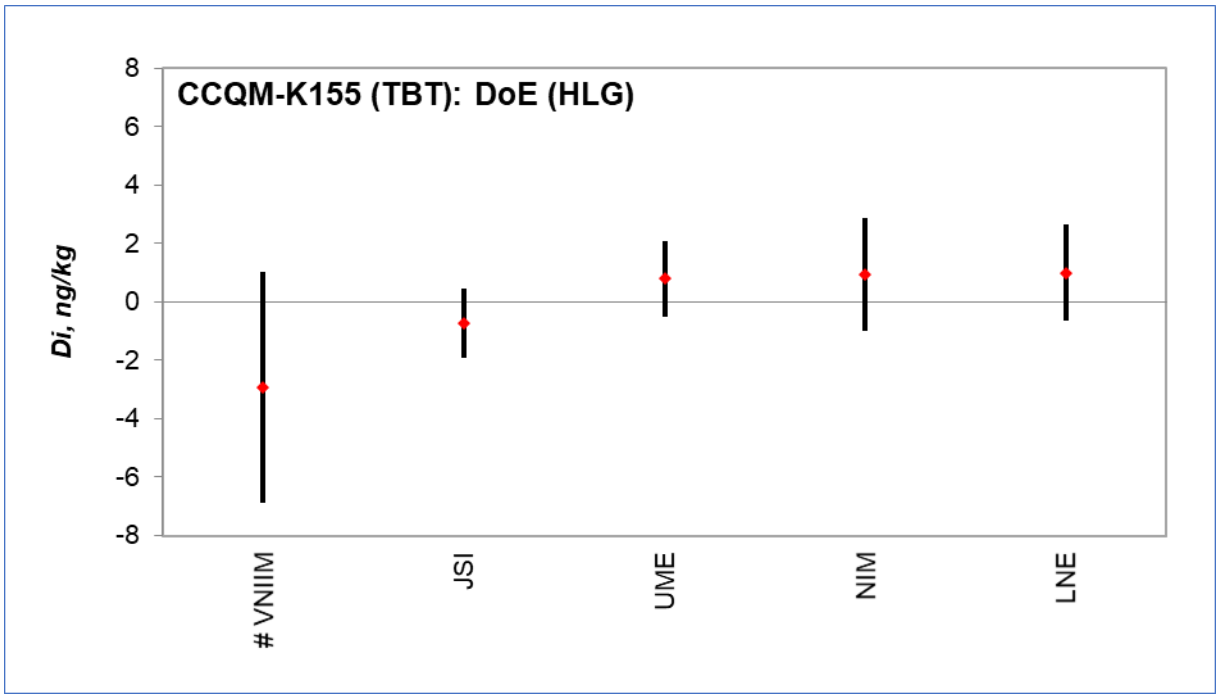


Notes:

1. The symbol * denotes that the measured value (x_i) is excluded from the KCRV calculation.
2. The red dot represents the DoE relative to the KCRV as percent, $\%D_i$, and a vertical black line segment represents the $U(D_i)$ relative to the KCRV as percent, $\%U(D_i)$.
3. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

7.3.7. DoE of tributyltin

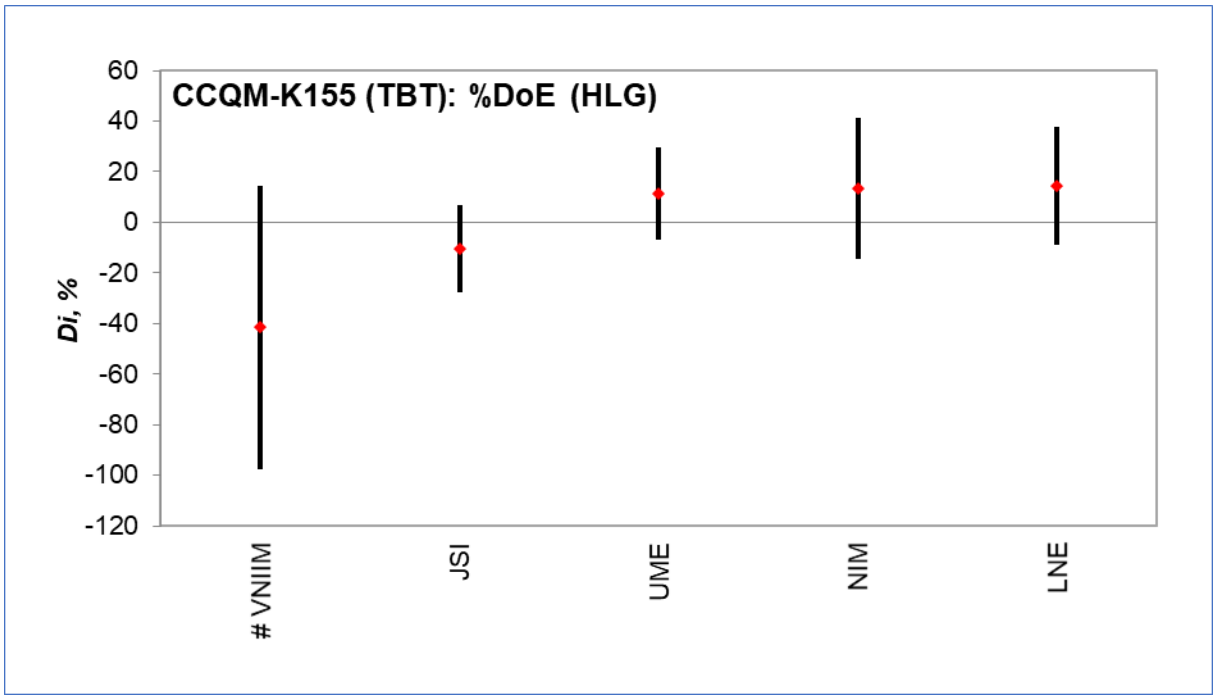
Figure 27. Plot of absolute degrees of equivalence for tributyltin.



Notes:

1. The red dot represents the DoE, D_i, and a vertical black line segment represents the expanded uncertainty of D_i at 95 % confidence level, $U(D_i)$.
2. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

Figure 28. Plot of relative degrees of equivalence in % for tributyltin



Notes:

1. The red dot represents the DoE relative to the KCRV as percent, $\%D_i$, and a vertical black line segment represents the $U(D_i)$ relative to the KCRV as percent, $\%U(D_i)$.
2. The participants accompanied by a hash (#) indicates that $U(D_i)$ recognizing dark uncertainty are used.

8. USE OF CCQM-K155 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

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

Successful participation in CCQM-K155 demonstrates measurement capabilities for determining mass fraction of transition elements (excluding mercury) and metalloids/semi-metals, with mass fractions ranging from 0.1 ng/g to 50 ng/g. Additionally, it covers small organo-tin and organo-mercury compounds with mass fractions from 1 ng/kg to 50 ng/g in a high-salt content matrix (seawater). Table 25 shows the Core Capability Table.

Core Capability Table

Table 25. Core Capability Table

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

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

9. CONCLUSIONS

Most participating NMIs/DIs employed dilution or co-precipitation for sample treatment and analyzed the samples using IDMS or standard addition method with ICP-MS, applying various interference removing techniques for the measurement of arsenic, cadmium, copper, lead, nickel and zinc. For tributyltin, most participants utilized derivatization followed by liquid-liquid extraction, with analysis conducted using isotope dilution GC-ICP-MS.

The proposed KCRVs (along with corresponding expanded uncertainties) and degrees of equivalence were calculated using the NIST Decision Tree. The majority of results from participating NMIs/DIs in CCQM-K155 aligned with the KCRV within their expanded uncertainties, demonstrating their capability to determine elements and tributyltin in seawater.

10. ACKNOWLEDGEMENTS

UME and GLHK would like to express their gratitude to the participating NMIs/DIs for their support and for providing the information requested for this study. We also extend our thanks to Dr. Michael Winchester and Dr. Antonio Possolo for their valuable comments and recommendations.

11. REFERENCES

1. Directive 2000/60/EC of the European Parliament and of the Council.

2. Directive 2013/39/EU of the European Parliament and of the Council.

3. U.S. Federal Water Pollution Control Act [Clean Water Act (CWA)]. (https://www.epa.gov/sites/production/files/2017-08/documents/federal-water-pollution-control-act-508full.pdf)

4. U.S.EPA Water Quality Criteria. (https://www.epa.gov/wqc)

5. ISO 17034:2016 “General requirements for the competence of reference material producers”, 2016, Geneva, Switzerland.

6. ISO Guide 35:2017 “Reference materials – Guidance for characterization and assessment of homogeneity and stability”, 2017, Geneva, Switzerland.

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

8. CIPM MRA-G-13 “Calibration and measurement capabilities in the context of the CIPM MRA, Guidelines for their review, acceptance and maintenance”, Version 1.2, 20/07/2022.

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

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

APPENDIX A: Technical Protocol

CCQM-K155/-P196
Elements and Tributyltin in Seawater

CCQM-K155/-P196
Elements and Tributyltin in Seawater

Technical Protocol

1. Introduction

Monitoring of trace elements and tributyltin in seawater is essential to determine baselines, measure change and assess overall ecosystem, which can improve the management and protection of marine resources, and can also protect human health. Regards to this, European Union (EU) implemented the Directive 2000/60/EC (Water Framework Directive (WFD) [14.1], which aims at achieving a long-term high level protection from chemical pollution of the aquatic environment, covering lakes, ground water and coastal waters. The WFD establishes a list of priority substances. The daughter Directive 2013/39/EU [14.2] lays down the environmental quality standards (EQS) for priority substances and other pollutants with the aim of achieving good surface water chemical status. For example, the maximum allowable concentrations of cadmium in seawater are set from 0.45 µg/L to 1.5 µg/L (depending on water hardness classes). In United States, the Clean Water Act (CWA) [14.3] establishes the basic structure for regulating discharges of pollutants into the waters (include seawater) and regulating the quality standards. United States Environmental Protection Agency (USEPA) develop Water Quality Criteria for ambient water quality (freshwater and saltwater) that accurately reflect the latest scientific knowledge on the impacts of pollutants on human health and the environment. Arsenic, Cadmium, Chromium (VI), Copper, Lead, Mercury, Nickel, Selenium, Silver and Zinc are recommended pollutants which are listed in the table for saltwater. [14.4] The use of reliable methods for measurement of trace elements in seawater is important in safeguarding the ecosystem and the public health.

According to the IAWG's five-year plan, it is recommended to have a key comparison under the measurement service category of high salts content for the year 2019. In this regards, TÜBITAK UME and GLHK proposed to coordinate a new key comparison and a parallel-run pilot study (CCQM-K155 and CCQM-P196) for the determination of trace elements and tributyltin in seawater at the CCQM IAWG Meeting in September 2017. The proposed key comparison was further discussed at the CCQM IAWG Meeting in April 2018. Lead, Mercury, Nickel, Zinc and Tributyltin have been selected as the analytes for examination in TÜBITAK UME samples, whereas Arsenic, Cadmium and Copper have been selected as the analytes for examination in GLHK sample.

2. Objectives

The study is based on the analysis of Arsenic, Cadmium, Copper, Lead, Mercury, Nickel, Zinc and Tributyltin in seawater. Its aim is to demonstrate the capability of participating national metrology institutes (NMIs) and designated institutes (DIs) in measuring the mass fractions of the analytes at µg/kg levels in a test sample of seawater by various analytical techniques. The mass fractions of the analytes reported will be used for comparability purposes.

This key comparison facilitates claims by participants on the Calibration and Measurement Capabilities (CMCs) as listed in Appendix C of the Key Comparison Database (KCDB) under the Mutual Recognition Arrangement of the International Committee for Weights and Measures (CIPM MRA).

3. Co-ordinating laboratories

The CCQM-K155 & -P196 are co-ordinated by the TÜBITAK UME and GLHK. TUBITAK UME takes responsibility for preparation, homogeneity and stability studies and distribution of the examination sample contained Lead, Mercury, Nickel and Zinc for the Sample A, Tributyltin for the Sample C, and GLHK takes responsibility for preparation, homogeneity and stability studies and distribution of the examination sample contained Arsenic, Cadmium and Copper for the Sample B. TÜBITAK UME and GLHK both take responsibility for data analysis and evaluation of results, preparation of reports, and communication with participants.

4. Test material

Sample A (Lead, Mercury, Nickel and Zinc)

The sampling of seawater (Sample A) was performed from the Marmara Sea (40 31,423 N; 027 11, 333 E) by TÜBITAK Marmara Research Vessel of Environment and Cleaner Production Institute. About 100 L of seawater was acidified by subboiled HNO_3 to adjust the pH to 1.6. The salinity and total dissolved solid (TDS) of the water is 27 psu and 1.7 %, respectively. Whole processing of reference materials including cleaning of bottles and processing equipment, spiking, homogenization and filling had been taken in ISO 6 Clean Chemical Laboratory. Approximately 100 L raw material was transferred into pre-cleaned 114 L HDPE drum, and was homogenized for 4 hours after spiking. The whole batch was filtered from one drum to another via 0.8/0.2 µm (Pall Corp, Supor® Membrane, AcroPackTM 1000, PN 12992) which also used for removing bacterial retention. Materials were filled into 250 mL low density polyethylene bottles manually in ISO 6 clean laboratory. Bottles was irradiated using a

gamma source at a dose of about 25 kGy. All the bottles were placed into aluminised PET sachets after gamma irradiation, and placed at 4 °C temperature room.

All the requirements of ISO 17034:2016 [14.5] and ISO Guide 35:2017 [14.6] were fulfilled for establishing the homogeneity and stability of seawater and bottles used for these studied were selected using random stratified sampling scheme covering the whole batch.

The homogeneity study was performed using 10 bottles. Three independent subsamples were taken from each unit using 5.0 of sample. As co-precipitation was applied with isotope dilution mass spectrometry technique (IDMS) for determination of Pb, Ni and Zn, Cold vapour IDMS was applied for the measurements of Hg determination.

Trend analysis were performed for both filling sequence and analytical sequence order. Assessment of homogeneity data was performed by one way ANOVA, and results are given in Table 1.

Table 1. Homogeneity assessment of data for Sample A.

Analyte	ANOVA test		Relative standard uncertainty due to between-bottle (in) homogeneity, u_{bb} (%)
	F-statistics	Critical value	
Lead	0.96	2.39	0.08
Mercury	0.68	2.42	1.52
Nickel	1.67	2.39	0.11
Zinc	0.07	2.42	1.62

Based on the results, it is concluded that the bottles were sufficiently homogeneous, and no trend for filling sequence were observed at 95 % confidence level.

Stability studies will be carried out using an isochronous design. For the short term stability study, (18 ± 2) °C and (60 ± 2) °C were be tested for periods of 1, 2 and 4 weeks. For each of time point at two temperatures, two units were placed related test cabinets and 2 units for reference point was stored in reference temperature (4 °C) for 4 weeks. As mercury was a critical parameter and showed a degradation at 60 °C, it has been decided that the dispatch of the samples will be performed at 4 - 8 °C conditions to prevent any possible degradation. Long-term stability will be established at 18 °C covering the whole inter-laboratory comparison period. All the bottles will be analysed in triplicate to monitor the stability of the samples.

Sample B (Arsenic, Cadmium and Copper)

About 12 L of seawater was collected from the Victoria Harbour in Hong Kong. The material has a salinity of about 28. It was filtered through 0.45 µm PES filters (HPWP, Millipore) and 0.22 µm PES filters (GPWP, Millipore) into a pre-cleaned 15 L polypropylene carboy. The seawater was acidified to about pH 1.5 with ultrapure nitric acid. The material was spiked and confirmed to contain quantities of Arsenic, Cadmium

and Copper. It was subjected to mix thoroughly by a mechanical stirrer for one week for homogenization. The material was irradiated using a gamma source at a dose of about 10 kGy for disinfection. The irradiated material was packed into pre-cleaned and nitrogen-flushed 125 mL high density polyethylene bottles, each of about 100 mL. About 110 bottles of sample were prepared. Finally, each bottle of sample was vacuum-sealed in a polypropylene bag. All prepared bottles of sample are stored at 4°C refrigerator prior to distribution or use.

The homogeneity study was conducted after the testing material was bottled and irradiated. 10 bottles of the test material (stored at 4 °C refrigerator) were randomly selected from the whole lot of bottles prepared. Two test portions of 10 g were taken from each bottle for analysis. Following validated procedures, the samples were analysed using gravimetric standard additions with ICP-MS for Arsenic and Copper and co-precipitation with double isotope dilution ICP-MS for Cadmium. ANOVA technique was applied to assess the between-unit (in) homogeneity in accordance with ISO Guide 35:2017 [14.6]. The results are summarised in Table 2.

Table 2. Homogeneity assessment of data for Sample B.

Analyte	ANOVA test		Relative standard uncertainty due to between-bottle (in) homogeneity, u_{bb} (%)
	F-statistics	Critical value	
Arsenic	1.16	3.02	1.11
Cadmium	1.59	3.02	0.73
Copper	0.51	3.02	1.04

The homogeneity study results indicated that no significant (in) homogeneity was observed in the test material. The test material was considered fit for the purpose of the key comparison.

For the short-term stability (i.e. stability of the test material under "transport conditions"), the study will be conducted on the isochronous approach over a period of 4 weeks at a simulated transport temperature (conditioned at 40 ± 5 °C) against the reference temperature at about 4 °C using the same analytical procedures as for the homogeneity study. Two bottles of sample will be randomly taken from the reference temperature to the simulated transport temperature on three occasions (1, 2 and 4 weeks) over the study period. Each bottle of sample will be analysed in duplicate for monitoring the sample (in)stability. The trend-analysis technique proposed by ISO Guide 35:2017 [14.6] will be applied to assess the stability of the test material at 40 °C.

For the long-term stability (i.e. stability of the test material under "storage conditions"), the study will be conducted on the classical approach covering the period from "the planned date of distribution of the test samples to participants" to "the deadline for submission of results" at the storage temperature (conditioned at about 4 °C).

CCQM-K155/-P196
Elements and Tributyltin in Seawater

Sample C (Tributyltin)
Due to the limited stability of tributyltin in sea water (up to 4 months), inter-comparison samples will be prepared shortly before the distribution. The sampling will be performed from the coast of TÜBITAK in Marmara Sea. The samples will be filtered through 0.2 µm filters (ISOLAB) into a pre-cleaned 20 L glass bottle. After homogenization, sea water will be filled into 1 L amber glass bottles with PTFE septum caps. All the bottles will be stored at 4 °C refrigerator prior to distribution. Homogeneity measurements will be performed before the sample shipment.

Based on the previous feasibility studies, the samples has proven to be stable over a period of four weeks when tested at 23 °C and 45 °C dispatch conditions. The long-term stability of the samples will be monitored at 4 °C throughout the measurement period to check any degradation in the samples.

5. Measurands

Sample A: Lead, Mercury, Nickel and Zinc
Participating laboratories will be provided with one bottle containing about 250 mL of seawater. All the four analytes and their expected mass fractions are listed in Table 3.

Table 3. Measurand ranges in Sample A

Analyte	Expected mass fraction (µg/kg)
Lead	0.5 – 10
Mercury	0.1 – 2
Nickel	1 – 20
Zinc	1 – 20

Sample B: Arsenic, Cadmium and Copper
Participating laboratories will be provided with one bottle containing about 100 mL of seawater. All the three analytes and their expected mass fractions as determined by inductively coupled plasma mass spectrometry are listed in Table 4.

Table 4. Measurand ranges in Sample B

Analyte	Expected mass fraction (µg/kg)
Arsenic	1 – 20
Cadmium	0.1 – 2
Copper	1 – 20

Sample C: Tributyltin

Participants will be provided with one bottle containing about 1 L of seawater. Tributyltin expected mass fraction is listed in Table 5.

Table 5. Tributyltin range in Sample C

Analyte	Expected mass fraction (ng/kg)
Tributyltin	1 – 20

6. Methods/procedures

Participants are welcome to carry out the analysis of the eight analytes (i.e. Arsenic, Cadmium, Copper, Lead, Mercury, Nickel, Zinc and Tributyltin) and submit the analytical results accordingly.

Participants shall use any analytical methods of their choice. Upon receipt, the samples shall be stored at refrigerator (about 4 °C) prior to analysis. The sample shall be mixed thoroughly for about 30 seconds by hand-shaking and allowed the contents to settle for one minute prior to opening. For all samples, participants shall perform at least three independent measurements on three separate portions of the sample and determine the mass fractions of the analytes.

7. Reporting and submission of results

A reporting form will be provided to participants after test materials are distributed. Each participant will be expected to report individual results, detailed uncertainty budget, details about the method used, etc. At least three independent measurements will be expected for each measurand. All analytical calibrations should be performed using metrologically traceable standards.

Key Comparison Reference Value (KCRV) for each measurand will be either the mean or the median of the submitted key comparison data. If any participant submits results by multiple methods, the result with the smallest uncertainty will be chosen for the calculation of the reference value. Results from participants of pilot study will not be used for KCRV determination.

- For each analyte, the mean value of at least three independent measurements on three separate portions of the sample and its associated measurement uncertainty shall be reported;
- Report the mass fractions of the analytes and the associated uncertainties in µg/kg;
- Participants shall provide (i) description of analytical methods (including sample preparation methods, calibration methods and analytical instruments used) and (ii)

details of the uncertainty estimation (including complete specification of the measurement equations and description of all uncertainty sources and their typical values); and

- Sources, purity and traceability of reference materials used for calibration purpose shall be provided.

The Report Form for Samples A and B shall be submitted to TÜBITAK UME (E-mail: betul.ari@tubitak.gov.tr) and GLHK (E-mail: yttsoi@govtlab.gov.hk) before the scheduled deadline.
The Report Form for Sample C shall be submitted to TÜBITAK UME (E-mail: betul.ari@tubitak.gov.tr) before the scheduled deadline.

8. Measurement uncertainty

Measurement uncertainty is best estimated within the individual laboratory environment. An estimate of uncertainty of measurement is normally based on the combination of a number of influencing parameters (components of uncertainty) such as errors in reference values, instrument errors, repeatability, thermal effects, weighing errors, (in)homogeneity etc. As stipulated in ISO Guide to the Expression of Uncertainty in Measurement [14.7], the influence of each component of uncertainty on the measurement result shall be quantified and expressed numerically as a standard deviation. These values are then combined according to the rules of the propagation of uncertainty to produce a combined standard deviation (combined standard uncertainty) and the combined standard uncertainty is multiplied by a coverage factor to produce an expanded uncertainty at the required level of confidence.

To facilitate in-depth performance evaluation, participants shall clearly identify and quantify those factors that are considered to contribute to the measurement uncertainty of the analysis.

9. Programme schedule

The time schedule for the various phases of the comparison is as follows:

Time schedule	Phase
September 2017	Presentation of the proposed comparison at the CCQM IAWG Meeting
April 2018	Discussion and update on progress for the comparison at the CCQM IAWG Meeting
October 2018 and April 2019	Presentation of the results of the homogeneity and stability studies for the comparison at the CCQM IAWG Meeting
February 2019	Call for participation
31 August 2019	Deadline for registration
October 2019	Distribution of samples
31 January 2020	Deadline for submission of results (Sample C)
29 February 2020	Deadline for submission of results (Sample A & B)
April 2020	Presentation of participants' results at the CCQM IAWG Meeting

10. Requirements for participation

NMIs and DIs

Participation in key comparisons organised by the CCQM is only open to laboratories that meet the requirements of Section 6 of the CIPM-MRA, and are listed in Appendix A of the CIPM-MRA, and the BIPM.

Participation is open to all interested NMIs or officially DIs that can perform the determination.

Guest laboratories: Participation in CCQM pilot studies

Other expert institutes, from countries that are members of the Metre Convention, may also participate in the pilot study provided that their contribution has added value or where they may qualify later as a designated institute in the field under study, according to Section 6 of the CIPM-MRA. This participation should first be agreed with the NMI of their country and if necessary the NMI should contact the study coordinator for further information. Please see the Request Form for Guest Laboratories for details: http://www.bipm.org/utils/en/pdf/guest_laboratories_request_form.pdf.

11. Registration

Please complete and return the Registration Forms to TÜBITAK UME (E-mail: betul.ari@tubitak.gov.tr) for the participation of Sample A and Sample C and to GLHK (E-mail: whfung@govtlab.gov.hk) for the participation of Sample B of CCQM-K155/-P196 on or before the deadline for registration. Successful registration will be notified by e-mail.

12. Confidentiality

The participating laboratories will receive the reports giving all results for assessment/comments. They will be identified in the reports. The key comparison/pilot study is conducted in the belief that participants will perform the analysis and report results with scientific rigour. Collusion between participants or falsification of results is clearly against the spirit of this study.

13. Contact

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

Sample A & C (TÜBITAK Ulusal Metroloji Enstitüsü, TÜBITAK UME)
Betul Ari
E-mail: betul.ari@tubitak.gov.tr
Tel.: +90 262 679 5000 Ext. 6205

and

Murat Tunc
E-mail: tunc.murat@tubitak.gov.tr
Tel.: +90 262 679 5000 Ext. 6208

Sample B (Government Laboratory, Hong Kong SAR, China, GLHK)
Dr. Wai-hong FUNG
E-mail: whfung@govtlab.gov.hk
Tel.: +852 2762 3853

and

Dr. Yuk-tai TSOI
E-mail: yttsoi@govtlab.gov.hk
Tel.: +852 2762 3862

14. References

14.1. Directive 2000/60/EC of the European Parliament and of the Council.

14.2. Directive 2013/39/EU of the European Parliament and of the Council.

14.3. U.S. Federal Water Pollution Control Act [Clean Water Act (CWA)]. (https://www.epa.gov/sites/production/files/2017-08/documents/federal-water-pollution-control-act-508full.pdf)

14.4. U.S.EPA Water Quality Criteria. (https://www.epa.gov/wqc)

14.5. ISO 17034:2016 "General Requirements for competence of reference material procedures"

14.6 ISO Guide 35:2017 "Reference materials – Guidance for characterization and assessment of homogeneity and stability", 2017, Geneva, Switzerland.

14.7. ISO/IEC Guide 98-3:2008 "Uncertainty of measurement -- Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)", 2008, Geneva, Switzerland.

-End-

APPENDIX B: Registration Form

CCQM-K155/-P196
Elements and Tributyltin in Seawater

TÜBİTAK UME

Registration Form

Institute/ Laboratory: _____

NMI/DI: National Metrology Institute (NMI) or Designated Institute (DI)*

Postal address: _____

_____

Zip/Postal code: _____

Authorised person: _____ _____ _____

Title Given name Surname

E-mail: _____

Telephone no.: _____

Alternative contact person and telephone no.: _____

Date: _____

Any particular local customs / quarantine requirements / special permits for samples sent into your country are needed? Yes / No*

(* *Please delete where appropriate.*)

CCQM-K155/-P196
Elements and Tributyltin in Seawater

Confirmation of Participation

I, on behalf of my institute/laboratory, would like to participate in CCQM-K155/-P196. Please send the test material to the postal address.

Please indicate the analyte(s) that you would like to determine by indicating "Yes" under the column heading of CCQM-K155/-P196 as follows:

Sample	Analyte	CCQM-K155	CCQM-P196
Sample A	Lead		
	Mercury		
	Nickel		
	Zinc		
Sample B	Arsenic		
	Cadmium		
	Copper		
Sample C	Tributyltin		

Notes: (i) Participation in CCQM-K155 is restricted to national metrology institutes and designated institutes. Please complete this form and return it to **TÜBITAK UME (E-mail: betul.ari@tubitak.gov.tr)** and **GLHK (E-mail: yttsoi@govtlab.gov.hk)** on or before the deadline (31 August 2019) for registration.

(ii) Please note that TÜBITAK UME and GLHK will NOT be responsible for any import taxes or charges due to the test samples.

APPENDIX C: Reporting Form

CCQM-K155/-P196
Elements and Tributyltin in Seawater

TÜBİTAK UME

Report Form (Samples A and B)

Institute/ Laboratory: _____

NMI/DI: National Metrology Institute (NMI) or Designated Institute (DI)*

Postal address: _____

_____

Authorised person: _____ _____ _____
Title Given name Surname

E-mail: _____

Telephone: _____

Date: _____

(* Please delete where appropriate.)

I. Analytical results and measurement uncertainties

Analyte	Mean value (µg/kg)	Combined standard uncertainty (µg/kg)	Coverage factor *k*	Expanded uncertainty (µg/kg)
e.g. Arsenic	5	0.2	2	0.4
Arsenic				
Cadmium				
Copper				
Lead				
Mercury				
Nickel				
Zinc				

Please note that the study is conducted in the belief that participants will perform the analysis and report results with scientific rigour. Collusion and falsification of results are clearly against the spirit of this study.

CCQM-K155/-P196
Elements and Tributyltin in Seawater

II. Methods of measurement

Analyte	Sample treatment	Calibration method	Analytical instrument	Reference material used for calibration (Traceability)
e.g. Cadmium	Co-precipitation by NH_4OH and TMAH	IDMS	ICP-MS	NIST SRM 3108 Cadmium standard solution
Arsenic				
Cadmium				
Copper				
Lead				
Mercury				
Nickel				
Zinc				

CCQM-K155/-P196
Elements and Tributyltin in Seawater

III. Questionnaire

1. Analytical methods used
2. Description of the analytical methods including sample treatment, calibration methods and analytical instruments used
3. Amount and number of sample aliquots taken for elemental analysis
4. Reference materials used for calibration purposes
5. For IDMS, indicate reference and spiked isotopes used
6. Detail of the uncertainty estimation
   - Complete specification of the measurement equations
   - Description of all uncertainty sources and their typical values

Note: Please complete this form and return it to TÜBITAK UME (E-mail: betul.ari@tubitak.gov.tr) and GLHK (E-mail: yttsoi@govtlab.gov.hk) on or before the deadline (29 February 2020) for submission of results.

CCQM-K155/-P196
Elements and Tributyltin in Seawater

Report Form (Sample C)

Institute/ Laboratory: _____

NMI/DI: National Metrology Institute (NMI) or Designated Institute (DI)*

Postal address: _____

_____

Authorised person: _____ _____ _____

Title Given name Surname

E-mail: _____

Telephone: _____

Date: _____

(* Please delete where appropriate.)

I. Analytical results and measurement uncertainties

Analyte	Mean value (ng/kg)	Combined standard uncertainty (ng/kg)	Coverage factor *k*	Expanded uncertainty (ng/kg)
Tributyltin				

Please note that the study is conducted in the belief that participants will perform the analysis and report results with scientific rigour. Collusion and falsification of results are clearly against the spirit of this study.

II. Methods of measurement

Analyte	Sample treatment	Calibration method	Analytical instrument	Reference material used for calibration (Traceability)
Tributyltin				

CCQM-K155/-P196
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III. Questionnaire

1. Analytical methods used
2. Description of the analytical methods including sample treatment, calibration methods and analytical instruments used
3. Amount and number of sample aliquots taken for elemental analysis
4. Reference materials used for calibration purposes
5. For IDMS, indicate reference and spiked isotopes used
6. Detail of the uncertainty estimation
   - Complete specification of the measurement equations
   - Description of all uncertainty sources and their typical values

Note: Please complete this form and return it to TÜBITAK UME (E-mail: betul.ari@tubitak.gov.tr) on or before the deadline (31 January 2020) for submission of results.

APPENDIX D: Summary of Participants' Uncertainty Estimation Approaches

The following are text excerpts and/or pictures of the uncertainty-related information provided by the participants in the reporting form. Information is grouped by participant and presented in alphabetized acronym order.

Uncertainty Information from FTMC

6. Detail of the uncertainty estimation
   - Complete specification of the measurement equations
   - Description of all uncertainty sources and their typical values

$$U = k \times u_c$$

$$u_c = c_x \times \sqrt{u_1^2 + u_2^2}$$

$$u_1 = \frac{U_{CRM}}{k_{CRM} \times c_{CRM}}$$

$$u_2 = \frac{STDEV}{c_X}$$

where
U – expanded uncertainty, µg/kg
k – coverage factor assuming t-distribution (95 % confidence level)
u_c – combined standard uncertainty
c_x – mean value of the measured concentration of the element in a sample, µg/kg
c_{CRM} – certified concentration of the element in SRM 1643f or NMIA MX014, µg/kg
U_{CRM} – expanded uncertainty of the certified concentration of the element in SRM 1643f or NMIA MX014, µg/kg
k_{CRM} – coverage factors (for each element expanded uncertainty) from the certificate of the certified reference material (SRM 1643f or NMIA MX014)
$STDEV$ – reproducibility standard deviation of the measurement results, µg/kg

Uncertainty Information from GLHK

6. Detail of the uncertainty estimation

- Complete specification of the measurement equations

IDMS

The mass fraction of Cd and Cu in the analytical sample was calculated according to equation (1):

$$c_x = D \cdot \left[\left(c_z \cdot \frac{m_y \cdot m_z}{m'_y} \cdot \frac{K_y \cdot R_y - K_b \cdot R_b}{K_b \cdot R_b - K_x \cdot R_x} \cdot \frac{K'_b \cdot R'_b - K_z \cdot R_z}{K_y \cdot R_y - K'_b \cdot R'_b} \cdot \frac{\sum (K_{xi} \cdot R_{xi})}{\sum (K_{zi} \cdot R_{zi})} - B \right) \cdot m_x^{-1} \cdot w^{-1} \right] \quad (1)$$

where:

c_x	is the amount content in the sample, in nmol.g^{-1};
c_z	is the amount content in the primary assay standard solution, in nmol.g^{-1};
m_y	is the mass of the spike in the sample-spike blend, in g;
m_x	is the mass of the sample in the sample-spike blend, in g;
m'_y	is the mass of the spike in the primary assay standard-spike blend, in g;
m_z	is the mass of the primary assay standard solution in the primary assay standard-spike blend, in g;
K_y	is the mass bias correction factor for the isotope ratio in the spike;
R_y	is the isotope ratio in the spike;
K_b	is the mass bias correction factor for the measured isotope ratio in the sample-spike blend;
R_b	is the measured isotope ratio in the sample-spike blend;
K_x	is the mass bias correction factor for the isotope ratio in the sample;
R_x	is the isotope ratio in the sample;
K'_b	is the mass bias correction factor for the measured isotope ratio in the primary assay standard-spike blend;
R'_b	is the measured isotope ratio in the primary assay standard-spike blend;
K_z	is the mass bias correction factor for the isotope ratio in the primary assay standard;
R_z	is the isotope ratio in the primary assay standard;
$\sum_i (K_{xi} \cdot R_{xi})$	is the sum of isotope ratios in the sample;
$\sum_i (K_{zi} \cdot R_{zi})$	is the sum of isotope ratios in the primary assay standard;
B	is the method blank, in nmol;
D	is the factor for repeatability (assume D = 1); and

Gravimetric standard additions:

The mass fraction of As and Pb in the analytical sample was calculated according to equation (2):

$$c_x = D \cdot \left(c_z \cdot \frac{m_d \cdot m_z}{m_x \cdot m_a} \cdot \frac{R_{us}}{R_s - R_{us}} \right) \quad (2)$$

where:

c_x	is the mass fraction of analyte in the sample (μg/kg);
c_z	is the mass fraction of analyte in the calibration standard solution (μg/kg);
m_d	is the mass of the digested sample solution (g);
m_x	is the mass of the sample (g);
m_z	is the mass of the calibration standard solution added to the spiked sample solution (g);
m_a	is the mass of the digested sample solution added to the unspiked/spiked sample solution (g);
R_{us}	is the measured ratio (i.e. signal intensity of analyte/signal intensity of internal standard) in the un-spiked sample solution;
R_s	is the measured ratio in the spiked sample solution;
D	is the factor for repeatability (assume D = 1).

- Description of all uncertainty sources and their typical values

Analysis of Arsenic: Please refer to Table 1

Analysis of Cadmium: Please refer to Table 2

Analysis of Copper: Please refer to Table 3

Analysis of Lead: Please refer to Table 4

Table 1. An example of uncertainty budget showing all uncertainty sources and their typical values in one of the replicate measurements of the mass fraction of As in CCQM-K155/P196

Uncertainty budget								
Measured Ratio of	**$^{75}As/^{74}Ge$**							
Sample	**CCQM-K155-59-d6**							
Unspiked sample solution	**206A**							
Spiked sample solution	**206C**							
Symbol	Type	Value x	Standard uncertainty $u(x_i)$	Relative standard uncertainty $u(x_i)/x_i$	Contribution to total u_c (%)	$u(y,x_i) = (dy/dx_i)*u(x_i)$	Sensitivity coefficient $(dy/dx_i) = u(y,x_i)/u(x_i)$
c_z (µg/kg)	B	6.7040	0.0079	0.0012	0.11	4.6324E-03	0.5869
m_x (g)	B	10.2636	0.0005	0.0000	0.00	-1.9168E-04	-0.3834
m_d (g)	B	50.0517	0.0005	0.0000	0.00	3.9308E-05	0.0786
m_z (g)	B	15.2595	0.0005	0.0000	0.00	-1.2893E-04	-0.2579
m_y (g)	B	2.0253	0.0005	0.0002	0.00	9.7143E-04	1.9429
R_{ss}	A	0.1535	0.0022	0.0140	56.20	1.0667E-01	49.5010
R_s	A	0.3228	0.0022	0.0067	12.03	-4.9344E-02	-22.9502
D	A	1	0.0203	0.0203	31.66	8.0068E-02	3.9349
				$\Sigma A_{contrib}$	99.89		
$c_{x,i}$ (µg/kg)		3.9349		$\Sigma B_{contrib}$	0.11		
				Total	100.00		
$c_{x,i}$		3.9349 µg/kg					
$u_c(c_{x,i})$		0.142292 µg/kg					
U (k=2)		0.284584 µg/kg					
Relative standard uncertainty		3.62 %					
Relative expanded uncertainty (k = 2)		7.23 %					
Range		3.6503 µg/kg		4.2195 µg/kg			

Table 2. An example of uncertainty budget showing all uncertainty sources and their typical values in one of the replicate measurements of the mass fraction of Cd in CCQM-K155/P196.

Uncertainty budget								
Measured isotope ratio of	$^{114}Cd/^{111}Cd$							
Sample	CCQM-K155-31							
Sample-spike blend code	201							
Standard-spike blend code	221							
Symbol	Value x	Standard uncertainty $u(x_i)$	Relative standard uncertainty $u(x_i)/x_i$	Contribution to total u_c (%)	$u(y,x_i) = (dy/dx_i)^*u(x_i)$	Sensitivity coefficient $(dy/dx_i) = u(y,x_i)/u(x_i)$	Uncertainty evaluation
c_z (ng/g)	4.6921	0.008306	0.0018	1.19	4.0066E-04	0.0482	B
c_z (nmol/g)	0.0417	-	-	-	-	-	-
m_x (g)	20.016	0.0005	0.0000	0.00	-5.6429E-06	-0.0113	B
m_y (g)	1.0014	0.0005	0.0005	0.09	1.1301E-04	0.2260	B
m'_y (g)	1.0062	0.0005	0.0005	0.09	-1.1242E-04	-0.2248	B
m_z (g)	1.0004	0.0005	0.0005	0.09	1.1312E-04	0.2262	B
K_y	1	0	-	0.00	0.0000E+00	0.0000	Constant
R_y	0.0109	0.000044	0.0040	0.00	-1.7729E-07	-0.0040	B
K_x	0.9115	0.0039	0.0043	22.27	1.7362E-03	0.4432	A
R_x	1.0709	0.0054	0.0051	31.23	2.0558E-03	0.3775	A
K_a	1	0	-	0.00	0.0000E+00	0.0000	Constant
R_z	2.2473	0.0033	0.0015	2.59	-5.9247E-04	-0.1776	B
K_b	0.8955	0.0026	0.0029	10.16	-1.1724E-03	-0.4543	A
R'_b	1.1089	0.0051	0.0046	25.91	-1.8726E-03	-0.3663	A
K_z	1	0	-	0.00	0.0000E+00	0.0000	Constant
R_z	2.2473	0.0033	0.0015	2.68	6.0201E-04	0.1805	B
$\Sigma(K_{xi}.R_{xi})$	7.8156	0	-	0.00	0.0000E+00	0.0000	Constant
$\Sigma(K_{zi}.R_{zi})$	7.8156	0	-	0.00	0.0000E+00	0.0000	Constant
B (mmol)	0.00007744	0.0000143	0.1849	0.05	-8.0406E-05	-5.6162	A
D	1	0.0031	0.0031	3.65	7.0271E-04	0.2259	A
$c_{x,i}$ (nmol/g)	0.0020		$\Sigma A_{contrib}$ =	93.3			
$c_{x,i}$ (ng/g)	0.2259		$\Sigma B_{contrib}$ =	6.7			
			Total	100.0			
$\bar{c}_{x,i}$	0.2259 ng/g						
$u_c(c_{x,i})$	0.003679 ng/g						
U (k = 2)	0.007358 ng/g						
Relative standard uncertainty	1.63 %						
Relative expanded uncertainty (k = 2)	3.26 %						
Range	0.2185 ng/g		0.2333 ng/g				

Table 3. An example of uncertainty budget showing all uncertainty sources and their typical values in one of the replicate measurements of the mass fraction of Cu in CCQM-K155/P196.

Uncertainty budget								
Measured isotope ratio of	$^{63}Cu/^{65}Cu$							
Sample	CCQM-K155-38							
Sample-spike blend code	205							
Standard-spike blend code	220							
Symbol	**Value x**	**Standard uncertainty $u(x_i)$**	**Relative standard uncertainty $u(x_i)/x_i$**	**Contribution to total u_c (%)**	**$u(y,x_i) = (dy/dx_i)^* u(x_i)$**	**Sensitivity coefficient $(dy/dx_i) = u(y,x_i)/u(x_i)$**	**Uncertainty evaluation**
c_z (ng/g)	59.1459	0.089836	0.0015	1.44	4.6606E-03	0.0519	B
c_z (nmol/g)	0.9308	-	-	-	-	-	-
m_x (g)	20.0354	0.0005	0.0000	0.00	-7.6255E-05	-0.1525	B
m_y (g)	1.0043	0.0005	0.0005	0.15	1.5276E-03	3.0552	B
m'_y (g)	1.0032	0.0005	0.0005	0.15	-1.5285E-03	-3.0571	B
m_z (g)	1.0017	0.0005	0.0005	0.16	1.5316E-03	3.0632	B
K_y	1	0	-	0.00	0.0000E+00	0.0000	Constant
R_y	0.0029	0.000005	0.0016	0.00	2.7278E-07	0.0593	B
K_b	1.1217	0.0020	0.0018	6.59	9.9782E-03	5.0650	A
R_b	0.9158	0.0035	0.0038	30.44	2.1444E-02	6.2144	A
K_x	1	0	-	0.00	0.0000E+00	0.0000	Constant
R_x	2.2415	0.0060	0.0027	14.91	-1.5006E-02	-2.5147	B
K'_b	1.1271	0.0021	0.0018	6.87	-1.0187E-02	-4.9433	A
R'_b	0.8938	0.0029	0.0032	20.95	-1.7790E-02	-6.2254	A
K_z	1	0	-	0.00	0.0000E+00	0.0000	Constant
R_z	2.2415	0.0060	0.0027	14.57	1.4836E-02	2.4864	B
$\Sigma(K_{sz}, R_{sz})$	3.2415	0	-	0.00	0.0000E+00	0.0000	Constant
$\Sigma(K_{sz}, R_{sz})$	3.2415	0	-	0.00	0.0000E+00	0.0000	Constant
B (nmol)	0.00400465	0.0000023	0.0006	0.00	-7.2043E-06	-3.1717	A
D	1	0.0025	0.0025	3.77	7.5446E-03	3.0557	A
$c_{x,i}$ (nmol/g)	0.0481		$\Sigma A_{contrib}$ =	68.6			
$c_{x,i}$ (ng/g)	3.0557		$\Sigma B_{contrib}$ =	31.4			
			Total	100.0			
$c_{x,i}$	3.0557 ng/g						
$u_c(c_{x,i})$	0.038867 ng/g						
U (k = 2)	0.077733 ng/g						
Relative standard uncertainty	1.27 %						
Relative expanded uncertainty (k = 2)	2.54 %						
Range	2.9779 ng/g		3.1334 ng/g				

Table 4. An example of uncertainty budget showing all uncertainty sources and their typical values in one of the replicate measurements of the mass fraction of Pb in CCQM-K155

Concentration of sample	CCQM-K155-d1						
Unspiked sample solution	1000A						
Spiked sample solution	1000B						
Symbol							
Symbol	Type	Value x	Standard uncertainty $u(x_i)$	Relative standard uncertainty $u(x_i)/x_i$	Contribution to total u_c (%)	$u(y,x_i) = (dy/dx_i)*u(x_i)$	Sensitivity coefficient $(dy/dx_i) = u(y,x_i)/u(x_i)$
c_z (ng/g)	B	1.2427	0.0023	0.0019	0.35	2.0855E-03	0.8879
m_x (g)	B	10.2232	0.0005	0.0000	0.00	-5.3965E-05	-0.1079
m_d (g)	B	19.9978	0.0005	0.0000	0.00	2.7589E-05	0.0552
m_a (g)	B	5.1231	0.0005	0.0001	0.00	-1.0768E-04	-0.2154
m_z (g)	B	1.0035	0.0005	0.0005	0.02	5.4980E-04	1.0996
R_{us}	A	0.3194	0.0021	0.0065	47.17	2.4135E-02	11.6371
R_s	A	0.4572	0.0033	0.0071	52.44	-2.5446E-02	-7.8222
D	A	1	0.0003	0.0003	0.01	3.5427E-04	1.1034
				$\Sigma A_{contrib}$	99.62		combined u
$c_{x,i}$ (ng/g)		1.1034		$\Sigma B_{contrib}$	0.38		
				Total	100.00		
$c_{x,i}$		1.1034	ng/g				
$u_c(c_{x,i})$		0.0351	ng/g				
U (k=2)		0.0703	ng/g				
RSU		6.4	%				
Range		1.0332	ng/g	1.1737	ng/g		

Uncertainty Information from GUM (K155)

Uncertainty sources and their typical values

The combined standard uncertainty for measurement of each element, $u_c(\overline{w_x})$, was estimated using the following formula:

$$u_c(\overline{w_x}) = \sqrt{c_1^2 \cdot u^2\left(\frac{S_x}{S_{IS}}\right) + c_2^2 \cdot u^2(b) + c_3^2 \cdot u^2(a) + c_4^2 \cdot u^2(w_{IS}) + c_5^2 \cdot u^2(D) + c_6^2 \cdot u_c^2(cal) + c_7^2 \cdot u^2(blk) + c_8^2 \cdot u_c^2(recov) + c_9^2 \cdot u^2(drift) + s^2(\overline{w_x})}$$

where:

$u\left(\frac{S_x}{S_{IS}}\right)$ - standard uncertainty of the ratio of signal intensity of the analyte (x) to signal intensity of the internal standard (IS),

$u(b)$ - standard uncertainty of the intercept of the calibration curve,

$u(a)$ - standard uncertainty of the slope of the calibration curve,

$u(w_{IS})$ - standard uncertainty of the mass fraction of the internal standard (to simplify calculations, the concentration of IS solution was assumed as 10 μg kg^{-1}, instead of 10 μg L^{-1} given by producer. This assumption has no effect of reported mass fraction values of quantified elements as IS concentration was only used as reference for quantified elements concentration and the same working

IS solution was used for calibration and samples.),
$u(D)$ - standard uncertainty of the sample dilution factor,
$u_c(cal)$ - combined standard uncertainty of the calibration standards (standard uncertainty of the stock solution and its dilution to measured calibration standard and combined standard uncertainty of weighing),
$u(blk)$ - standard uncertainty of the blank sample,
$u_c(recov)$ - combined standard uncertainty of the recovery (standard uncertainty of spike and standard uncertainty of NMIA MX014); in case of Zn standard uncertainty of the recovery of spike only as there was no certified value for Zn in NMIA MX014,
$u(drift)$ - standard uncertainty of the instrument drift,
$s(\overline{w_x})$ - standard deviation of the mean,
$c_1 \div c_9$ - sensitivity coefficients.

Uncertainty budgets for the analytes

Table 3. Uncertainty budget for Arsenic

Uncertainty source	Estimate	Uncertainty distribution	Standard uncertainty	Sensitivity coefficient	Contribution to standard uncertainty
X_i	x_i		u_i	c_i	$u_i \cdot c_i$
Ratio of signals intensities, S_{As}/S_{Ge}	$9{,}614 \cdot 10^{-2}$ CPS(As) / CPS(Ge)	Normal	$1{,}741 \cdot 10^{-3}$ CPS(As) / CPS(Ge)	40,7 $\mu g_{As} \cdot kg^{-1} \cdot$CPS(Ge)/ CPS(As)	0,071 $\mu g_{As} \cdot kg^{-1}$
Intercept of the calibration curve, b	$-8{,}2 \cdot 10^{-5}$ CPS(As) / CPS(Ge)	Normal	$6{,}73 \cdot 10^{-4}$ CPS(As) / CPS(Ge)	-40,7 $\mu g_{As} \cdot kg^{-1} \cdot$CPS(Ge)/ CPS(As)	-0,027 $\mu g_{As} \cdot kg^{-1}$
Slope of the calibration curve, a	0,98313 CPS(As) / CPS(Ge) / $\mu g_{As} \cdot kg^{-1} / \mu g_{Ge} \cdot kg^{-1}$	Normal	$4{,}282 \cdot 10^{-3}$ CPS(As) / CPS(Ge) / $\mu g_{As} \cdot kg^{-1} / \mu g_{Ge} \cdot kg^{-1}$	-3,98 $(\mu g_{As} \cdot kg^{-1})^2 \cdot$CPS(Ge)/ $\mu g_{Ge} \cdot kg^{-1} \cdot$CPS(As)	-0,017 $\mu g_{As} \cdot kg^{-1}$
Mass fraction of the internal standard, w_{Ge}	10 $\mu g_{Ge} \cdot kg^{-1}$	Normal	$2 \cdot 10^{-5}$ $\mu g_{Ge} \cdot kg^{-1}$	$9{,}7868 \cdot 10^{-1}$ $\mu g_{As} \cdot kg^{-1} / \mu g_{Ge} \cdot kg^{-1}$	$6 \cdot 10^{-6}$ $\mu g_{As} \cdot kg^{-1}$
Sample dilution factor, D	4	Normal	$6 \cdot 10^{-5}$	$3{,}915 \cdot 10^{-1}$ $\mu g_{As} \cdot kg^{-1}$	$6 \cdot 10^{-5}$ $\mu g_{As} \cdot kg^{-1}$
Calibration standards, cal	983376 $\mu g_{As} \cdot kg^{-1}$	Rectangular	$1{,}613 \cdot 10^{-2}$ $\mu g_{As} \cdot kg^{-1}$	1	0,016 $\mu g_{As} \cdot kg^{-1}$
Blank, $blank$	$7{,}68 \cdot 10^{-3}$ $\mu g_{As} \cdot kg^{-1}$	Rectangular	$9{,}37 \cdot 10^{-3}$ $\mu g_{As} \cdot kg^{-1}$	1	0,009 $\mu g_{As} \cdot kg^{-1}$
Recovery, $recov$	99 %	Rectangular	$9{,}074 \cdot 10^{-2}$ $\mu g_{As} \cdot kg^{-1}$	1	0,091 $\mu g_{As} \cdot kg^{-1}$
Instrument drift, $drift$	6 %	Rectangular	$1{,}3994 \cdot 10^{-1}$ $\mu g_{As} \cdot kg^{-1}$	1	0,140 $\mu g_{As} \cdot kg^{-1}$
Repeatability, $s(\overline{w_{As}})$	3,881 $\mu g_{As} \cdot kg^{-1}$	Normal	$4{,}814 \cdot 10^{-2}$ $\mu g_{As} \cdot kg^{-1}$	1	0,048 $\mu g_{As} \cdot kg^{-1}$
$\overline{w_{As}}$	3,881 $\mu g_{As} \cdot kg^{-1}$				0,191 $\mu g_{As} \cdot kg^{-1}$

Standard uncertainty: 0,191 $\mu g_{As} \cdot kg^{-1}$
Expanded uncertainty (k=2): 0,382 $\mu g_{As} \cdot kg^{-1}$
Measurements result: $\overline{w_{As}} = (3{,}88 \pm 0{,}38)\ \mu g_{As} \cdot kg^{-1}$

Table 4. Uncertainty budget for Cadmium

Uncertainty source	Estimate	Uncertainty distribution	Standard uncertainty	Sensitivity coefficient	Contribution to standard uncertainty
X_i	x_i		u_i	c_i	$u_i \cdot c_i$
Ratio of signals intensities, S_{Cd}/S_{Bi}	$4{,}3 \cdot 10^{-4}$ CPS(Cd) / CPS(Bi)	Normal	$2 \cdot 10^{-5}$ CPS(Cd) / CPS(Bi)	$5{,}2 \cdot 10^{2}$ $\mu g_{Cd} \cdot kg^{-1} \cdot$ CPS(Bi)/ CPS(Cd)	0,0080 $\mu g_{Cd} \cdot kg^{-1}$
Intercept of the calibration curve, b	$-3 \cdot 10^{-6}$ CPS(Cd) / CPS(Bi)	Normal	$9 \cdot 10^{-6}$ CPS(Cd) / CPS(Bi)	$-5{,}19 \cdot 10^{2}$ $\mu g_{Cd} \cdot kg^{-1} \cdot$ CPS(Bi)/ CPS(Cd)	-0,0049 $\mu g_{Cd} \cdot kg^{-1}$
Slope of the calibration curve, a	$7{,}701 \cdot 10^{-2}$ CPS(Cd) / CPS(Bi) / $\mu g_{Cd} \cdot kg^{-1}$ / $\mu g_{Bi} \cdot kg^{-1}$	Normal	$4{,}3 \cdot 10^{-4}$ CPS(Cd) / CPS(Bi) / $\mu g_{Cd} \cdot kg^{-1}$ / $\mu g_{Bi} \cdot kg^{-1}$	$-2{,}9518$ $(\mu g_{As} \cdot kg^{-1})^2 \cdot$ CPS(Ge)/ $\mu g_{Ge} \cdot kg^{-1} \cdot$ CPS(As)	-0,0013 $\mu g_{Cd} \cdot kg^{-1}$
Mass fraction of the internal standard, w_{Bi}	10 $\mu g_{Bi} \cdot kg^{-1}$	Normal	$2 \cdot 10^{-5}$ $\mu g_{Bi} \cdot kg^{-1}$	$2{,}273 \cdot 10^{-2}$ $\mu g_{Cd} \cdot kg^{-1}$ / $\mu g_{Bi} \cdot kg^{-1}$	$4 \cdot 10^{-7}$ $\mu g_{Cd} \cdot kg^{-1}$
Sample dilution factor, D	4	Normal	$6 \cdot 10^{-5}$	$5{,}683 \cdot 10^{-2}$ $\mu g_{Cd} \cdot kg^{-1}$	$4 \cdot 10^{-6}$ $\mu g_{Cd} \cdot kg^{-1}$
Calibration standards, cal	987244 $\mu g_{Cd} \cdot kg^{-1}$	Rectangular	$2{,}92 \cdot 10^{-3}$ $\mu g_{Cd} \cdot kg^{-1}$	1	0,0029 $\mu g_{Cd} \cdot kg^{-1}$
Blank, $blank$	$1{,}35 \cdot 10^{-3}$ $\mu g_{Cd} \cdot kg^{-1}$	Rectangular	$2{,}54 \cdot 10^{-3}$ $\mu g_{Cd} \cdot kg^{-1}$	1	0,0025 $\mu g_{Cd} \cdot kg^{-1}$
Recovery, $recov$	98 %	Rectangular	$3{,}60 \cdot 10^{-3}$ $\mu g_{Cd} \cdot kg^{-1}$	1	0,0036 $\mu g_{Cd} \cdot kg^{-1}$
Instrument drift, $drift$	6 %	Rectangular	$7{,}53 \cdot 10^{-3}$ $\mu g_{Cd} \cdot kg^{-1}$	1	0,0075 $\mu g_{Cd} \cdot kg^{-1}$
Repeatability, $s(\overline{w_{Cd}})$	0,2321 $\mu g_{Cd} \cdot kg^{-1}$	Normal	$5{,}49 \cdot 10^{-3}$ $\mu g_{Cd} \cdot kg^{-1}$	1	0,0055 $\mu g_{Cd} \cdot kg^{-1}$
$\overline{w_{Cd}}$	0,2321 $\mu g_{Cd} \cdot kg^{-1}$				0,0143 $\mu g_{Cd} \cdot kg^{-1}$

Standard uncertainty: 0,0143 $\mu g_{Cd} \cdot kg^{-1}$
Expanded uncertainty (k=2): 0,0285 $\mu g_{Cd} \cdot kg^{-1}$
Measurements result: $\overline{w_{Cd}} = (0{,}232 \pm 0{,}029)\ \mu g_{Cd} \cdot kg^{-1}$

Table 5. Uncertainty budget for Copper

Uncertainty source	Estimate	Uncertainty distribution	Standard uncertainty	Sensitivity coefficient	Contribution to standard uncertainty
X_i	x_i		u_i	c_i	$u_i \cdot c_i$
Ratio of signals intensities, S_{Cu}/S_{Ge}	1,0963 CPS(Cu) / CPS(Ge)	Normal	$2{,}088 \cdot 10^{-2}$ CPS(Cu) / CPS(Ge)	3,375 $\mu g_{Cu} \cdot kg^{-1} \cdot$ CPS(Ge)/ CPS(Cu)	0,070 $\mu g_{Cu} \cdot kg^{-1}$
Intercept of the calibration curve, b	$3{,}190 \cdot 10^{-2}$ CPS(Cu) / CPS(Ge)	Normal	$1{,}172 \cdot 10^{-2}$ CPS(Cu) / CPS(Ge)	-3,375 $\mu g_{Cu} \cdot kg^{-1} \cdot$ CPS(Ge)/ CPS(Cu)	-0,040 $\mu g_{Cu} \cdot kg^{-1}$
Slope of the calibration curve, a	11,8503 CPS(Cu) / CPS(Ge) / $\mu g_{Cu} \cdot kg^{-1}$ / $\mu g_{Ge} \cdot kg^{-1}$	Normal	$7{,}497 \cdot 10^{-2}$ CPS(Cu) / CPS(Ge) / $\mu g_{Cu} \cdot kg^{-1}$ / $\mu g_{Ge} \cdot kg^{-1}$	$-3{,}0321 \cdot 10^{-1}$ $(\mu g_{Cu} \cdot kg^{-1})^2 \cdot$ CPS(Ge)/ $\mu g_{Ge} \cdot kg^{-1} \cdot$ CPS(Cu)	-0,023 $\mu g_{Cu} \cdot kg^{-1}$
Mass fraction of the internal standard, w_{Ge}	10 $\mu g_{Ge} \cdot kg^{-1}$	Normal	$2 \cdot 10^{-5}$ $\mu g_{Ge} \cdot kg^{-1}$	$3{,}5931 \cdot 10^{-1}$ $\mu g_{Cu} \cdot kg^{-1}$ / $\mu g_{Ge} \cdot kg^{-1}$	$6 \cdot 10^{-6}$ $\mu g_{Cu} \cdot kg^{-1}$
Sample dilution factor, D	4	Normal	$6 \cdot 10^{-5}$	$0{,}8927 \cdot 10^{-1}$ $\mu g_{Cu} \cdot kg^{-1}$	$6 \cdot 10^{-5}$ $\mu g_{Cu} \cdot kg^{-1}$
Calibration standards, cal	987258 $\mu g_{Cu} \cdot kg^{-1}$	Rectangular	$1{,}620 \cdot 10^{-2}$ $\mu g_{Cu} \cdot kg^{-1}$	1	0,016 $\mu g_{Cu} \cdot kg^{-1}$
Blank, $blank$	$8{,}52 \cdot 10^{-3}$ $\mu g_{Cu} \cdot kg^{-1}$	Rectangular	$2{,}196 \cdot 10^{-2}$ $\mu g_{Cu} \cdot kg^{-1}$	1	0,022 $\mu g_{Cu} \cdot kg^{-1}$
Recovery, $recov$	99 %	Rectangular	$7{,}636 \cdot 10^{-2}$ $\mu g_{Cu} \cdot kg^{-1}$	1	0,076 $\mu g_{Cu} \cdot kg^{-1}$
Instrument drift, $drift$	6 %	Rectangular	$1{,}0403 \cdot 10^{-1}$ $\mu g_{Cu} \cdot kg^{-1}$	1	0,104 $\mu g_{Cu} \cdot kg^{-1}$
Repeatability, $s(\overline{w_{Cu}})$	3,003 $\mu g_{Cu} \cdot kg^{-1}$	Normal	$3{,}158 \cdot 10^{-2}$ $\mu g_{Cu} \cdot kg^{-1}$	1	0,032 $\mu g_{Cu} \cdot kg^{-1}$
$\overline{w_{Cu}}$	3,003 $\mu g_{Cu} \cdot kg^{-1}$				0,160 $\mu g_{Cu} \cdot kg^{-1}$

Standard uncertainty: 0,160 $\mu g_{Cu} \cdot kg^{-1}$
Expanded uncertainty (k=2): 0,319 $\mu g_{Cu} \cdot kg^{-1}$
Measurements result: $\overline{w_{Cu}} = (3{,}00 \pm 0{,}32)\ \mu g_{Cu} \cdot kg^{-1}$

Table 9. Contribution of uncertainty sources to the total relative standard uncertainty for element

Source of uncertainty	Uncertainties contribution, %					
	As	Cd	Cu	Ni	Pb	Zn
$(\frac{s_x}{s_{IS}})$	14	31	20	4	1	5
b	2	12	6	3	3	4
a	1	1	2	2	0	3
w_{IS}	0	0	0	0	0	0
D	1	4	1	1	5	0
cal	0	0	0	0	0	0
blk	0	3	2	1	1	51
recov	23	6	23	18	5	4
drift	54	28	43	66	67	29
repeat	6	15	4	5	19	4

Uncertainty Information from HSA

2. Uncertainty evaluation

To calculate the uncertainty budgets for the mass fractions of **arsenic**, the standard addition measurement equation was expanded to include an appropriate additional factor as shown below:

$$C_X = MP.C_Z.\frac{M_D \times M_Z}{M_X \times M_S}.\frac{R'_U}{R'_S - R'_U}$$

Table 1: Uncertainty budget for result value of arsenic based on $^{75}As/^{69}Ga$ ion pair

Parameter	Source of uncertainty	Value (x_i)	Unit	Standard uncertainty $u(x_i)$
MP	Method precision	1	n/a	0.02653
C_Z	Concentration of calibration standard	0.06000	mg/kg	0.00005
M_X	Mass of sample used for digestion	9.99978	g	0.00008
M_D	Total mass of digest after dilution	49.99920	g	0.00008
M_S	Mass of diluted digest used to prepare spiked solution	4.99970	g	0.00008
M_Z	Mass of calibration standard	0.31349	g	0.00008
R'_U	Observed intensity ratio in unspiked solution	0.48560	Uncertainty included in method precision	
R'_S	Observed intensity ratio in unspiked solution	2.97510	Uncertainty included in method precision	

To calculate the uncertainty budgets for the mass fraction of **cadmium**, the exact-matching IDMS measurement was expanded to include appropriate additional factors as shown below:

$$C_X = MP.F_{conf}.C_Z.\frac{M_Y \times M_{ZC}}{M_{X1} \times M_{YC}}.\frac{R_Y - R_{SB}}{R_{SB} - R_X}.\frac{R_{CB} - R_Z}{R_Y - R_{CB}}$$

Table 2: Uncertainty budget for result value of cadmium based on $^{111}Cd/^{114}Cd$ ion pair

Parameter	Source of uncertainty	Value (x_i)	Unit	Standard uncertainty $u(x_i)$
MP	Method precision	1	n/a	0.01218
F(conf)	Comparison of results obtained using different ion pairs ($^{111}Cd/^{114}Cd$ and $^{111}Cd/^{112}Cd$)	1	n/a	0.01350
C_Z	Concentration of analyte in calibration standard	0.0002301	mg/kg	0.0000004
M_{X1}	Mass of sample	9.99769	g	0.00008
M_Y	Mass of spike added to sample	0.12517	g	0.00008
M_{ZC}	Mass of calibration standard	10.00686	g	0.00008
M_{YC}	Mass of spike added to calibration standard	0.12603	g	0.00008
$R_{X,Z}$	Isotope ratio in sample and standard	0.44553	n/a	0.00447
R_Y	Isotope ratio in spike	163.45763	n/a	2.77093
R_{SB}	Observed isotope ratio in sample blend	4.00915	Uncertainty included in method precision	
R_{CB}	Observed isotope ratio in calibration blend	4.09047	Uncertainty included in method precision	

To calculate the uncertainty budgets for the mass fractions of **copper**, the exact-matching IDMS measurement was expanded to include an appropriate additional factor as shown below:

$$C_X = MP.C_Z.\frac{A_X}{A_Z}.\frac{M_Y \times M_{ZC}}{M_{X1} \times M_{YC}}.\frac{R_Y - R_{SB}}{R_{SB} - R_X}.\frac{R_{CB} - R_Z}{R_Y - R_{CB}}.\frac{\sum R_{iX}}{\sum R_{iZ}}$$

Table 3: Uncertainty budget for result value of copper based on $^{65}Cu/^{63}Cu$ ion pair

Parameter	Source of uncertainty	Value (x_i)	Unit	Standard uncertainty $u(x_i)$
MP	Method precision	1	n/a	0.01935
C_z	Concentration of analyte in calibration standard	0.003037	mg/kg	0.000005
M_{x1} (SB)	Mass of sample	9.99798	g	0.00008
M_y (SB)	Mass of spike added to sample	1.17034	g	0.00008
M_{zc} (CB)	Mass of calibration standard	9.98612	g	0.00008
M_y (CB)	Mass of spike added to calibration standard	1.16842	g	0.00008
R_y	Isotope ratio in spike	332.33333	n/a	22.15566
A_x	Relative atomic mass of analyte in sample	63.55006	n/a	0.00613
A_z	Relative atomic mass of analyte in standard	63.54371	n/a	0.00581
R_x	Isotope ratio in sample	0.45037	n/a	0.00645
R_z	Isotope ratio in standard	0.44371	n/a	0.00609
$\sum R_{ix}$	Sum of ratios in sample	1.45037	n/a	0.00645
$\sum R_{iz}$	Sum of ratios in standard	1.44371	n/a	0.00609
R_{SB}	Observed isotope ratio in sample blend	0.97427	Uncertainty included in method precision	
R_{CB}	Observed isotope ratio in calibration blend	0.96517	Uncertainty included in method precision	

To calculate the uncertainty budgets for the mass fractions of **lead**, the exact-matching IDMS measurement was expanded to include appropriate additional factors as shown below:

$$C_X = MP.F_{conf}.C_Z.\frac{A_X}{A_Z}.\frac{M_Y \times M_{ZC}}{M_{X1} \times M_{YC}}.\frac{R_Y - R_{SB}}{R_{SB} - R_X}.\frac{R_{CB} - R_Z}{R_Y - R_{CB}}.\frac{\sum R_{iX}}{\sum R_{iZ}}$$

Table 4: Uncertainty budget for result value of lead based on $^{208}Pb/^{206}Pb$ ion pair

Parameter	Source of uncertainty	Value (x_i)	Unit	Standard uncertainty $u(x_i)$
MP	Method precision	1	n/a	0.01294
F(conf)	Factor representing any bias in the result value due to choice of ion pair ($^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$)	1	n/a	0.00267
C_z	Concentration of analyte in calibration standard	0.001067	mg/kg	0.000001
M_{x1} (SB)	Mass of sample	5.01066	g	0.00010
M_y (SB)	Mass of spike added to sample	0.15180	g	0.00010
M_{zc} (CB)	Mass of calibration standard	5.13511	g	0.00010
M_y (CB)	Mass of spike added to calibration standard	0.15596	g	0.00010
R_y	Isotope ratio in spike	0.00030	n/a	0.00030
A_x	Relative atomic mass of analyte in sample	207.20823	n/a	0.00313
A_z	Relative atomic mass of analyte in standard	207.20835	n/a	0.00055
R_x	Isotope ratio in sample	2.09253	n/a	0.01658
R_z	Isotope ratio in standard	2.09648	n/a	0.00360
$\sum R_{ix}$	Sum of ratios in sample	4.00200	n/a	0.02371
$\sum R_{iz}$	Sum of ratios in standard	4.00807	n/a	0.00572
R_{SB}	Observed isotope ratio in sample blend	0.99445	Uncertainty included in method precision	
R_{CB}	Observed isotope ratio in calibration blend	0.98520	Uncertainty included in method precision	

Uncertainty Information from INMETRO

6. Detail of the uncertainty estimation
   - Complete specification of the measurement equations

   $w = w_0 \times f_{rep} \times f_{bias} \times f_{repro}$, where w_0 is the mass fraction of Pb in the diluted solution, f_{rep} is the factor of the instrumental repeatability and f_{bias} is the uncertainty from the recovery testing and f_{repro} is the uncertainty from measurements performed in two days. The main sources of uncertainties are calibration curve, dilution factor, repeatability, and bias. A typical contribution from these sources of uncertainty is calibration curve (1.3 %), repeatability (1,5 %), bias (2.5 %), reproducibility (3.0 %). Combined standard uncertainty is the square-root of the linear sum of squared relative uncertainty components. The combined standard uncertainty ranged from 3.5 to 4.2 relative to the mass fraction of Pb in the sample.

   - Description of all uncertainty sources and their typical values

Uncertainty Information from ISP

6. Detail of the uncertainty estimation

   - Complete specification of the measurement equations

$$u_{comb} = \sqrt{c^2 \times u\,(\omega zB)^2 + c^2 \times u(mx)^2 + c^2 \times u(md1)^2 + c^2 \times u(mzB)^2 + c^2 \times u(mx1)^2 + c^2 \times u\,method^2}$$

   - Description of all uncertainty sources and their typical values

     Fraction mass (ω)
     Mass sample (mx)
     Mass dilution (md1)
     Mass portion SI (mzB)
     Method (Precision & Bias)
     Mass portion in dilution (mx1)

Uncertainty Information from KRISS

6. Detail of the uncertainty estimation
   a. Complete specification of the measurement equations

$$w_x = f_{dil} \cdot w_y \cdot \frac{m_y}{f_{dm} \cdot m_x} \cdot \frac{MM_x}{MM_y} \cdot \frac{R_y - R_b}{R_a - R_x} \cdot \frac{\sum R_{xi}}{\sum R_{yi}} - w_{blank} = f_{dil} \cdot w_z \cdot \frac{m_y m_z}{f_{dm} \cdot m_x m'_y} \cdot \frac{MM_x}{MM_y} \cdot \frac{R_y - R_b}{R_b - R_a} \cdot \frac{R_a - R_z}{R_y - R_b} \cdot \frac{\sum R_{xi}}{\sum R_{yi}} - w_{blank}$$

   b. Description of all uncertainty sources and their typical values

parameter	description	Cd		Cu		Ni		Pb		Zn	
		value	u	value	u	value	u	value	u	value	u
f_{dil}	dilution factor	1.5E-5	9.1E-9	2.0E-4	8.9E-8	1.5E-4	9.0E-8	5.1E-5	3.9E-8	5.1E-4	2.9E-7
w_Z	mass fraction of standard solution (µg /kg)	1000000	580	10000000	415	10000000	1582	10000000	623	10000000	787
f_{dm}	drymass correction factor	1.0	0	1.0	0	1.0	0	1.0	0	1.0	0
m_X	amount of subsample taken (g)	10.0	0.0005	10.0	0.0005	20.0	0.0005	20.0	0.0005	20.0	0.0005
m_Y	amount of spike solution taken for sample blend (g)	1.0	0.0005	1.0	0.0005	2.0	0.0005	2.0	0.0005	2.0	0.0005
m_Y'	amount of spike solution taken for calibration blend (g)	5.0	0.0005	5.0	0.0005	5.0	0.0005	5.0	0.0005	5.0	0.0005
m_Z	amount of standard solution taken for sample blend (g)	1.0	0.0005	1.0	0.0005	2.0	0.0005	2.0	0.0005	2.0	0.0005
MM_X	atomic weight of analyte element in standard solution (g/mol)	112.41	0.002	63.55	0.0015	58.69	0.0002	207.21	0.14	65.38	0.01
MM_Z	atomic weight of analyte element in sample (g/mol)	112.41	0.002	63.55	0.0015	58.69	0.0002	207.21	0.14	65.38	0.01
R_X	isotope ratio of sample	0.9746	0.0024	2.2415	0.0060	7.2151	0.0045	2.0958	0.0017	1.503	0.037
R_Y	isotope ratio of spike solution	0.0032	0.0032	0.00311	0.00030	0.00010	0.00010	2.0013	0.00001	0.0011	0.0001
R_Z	isotope ratio of standard solution	0.9746	0.0024	2.2415	0.0060	7.2151	0.0045	2.0724	0.0012	1.503	0.037
R_b	isotope ratio of sample blend	0.260	0	0.2645	0	1.4877	0	1.0348	0	0.29075	0
R_b'	isotope ratio of calibration blend	0.280	0	0.3322	0	1.0409	0	0.9793	0	0.31140	0
ΣR_X	sum of all isotope ratios of sample	7.8155	0.0037	3.2415	0.0060	27.514	0.012	4.0104	0.0019	5.420	0.062
ΣR_Z	sum of all isotope ratios of standard solution	7.8155	0.0037	3.2415	0.0060	27.514	0.012	3.9697	0.0019	5.420	0.062
w_{blank}	procedure blank (µg/kg)	0.00300	0.00076	0.0258	0.0022	0.0075	0.0009	0.0185	0.0052	0.688	0.008
SD_{mean} (subsample)	Standard deviation of the mean of subsamples (µg/kg)	0.280	0.007	3.093	0.003	4.534	0.009	1.113	0.026	8.297	0.023
SD (calib. blends)	Standard deviation of the mean of subsamples (µg/kg)	0.280	0.0006	3.093	0.0035	4.534	0.0046	1.113	0.001	8.297	0.135

Uncertainty Information from LNE

Combined uncertainties have been calculated by propagating the relative standard uncertainties from the standard solutions added, the intercept of the regression curve and the precision of the standard addition method:

$$u_{mass\_fract} = \sqrt{(u^2_{st\_sol} + u^2_{intercept} + u^2_{precision})}$$

Parameter	Source of uncertainty	Typical value	Standard uncertainty	Unit	Type
u_{stdsol}	Uncertainty on the standard solutions added for the regression curve	0.5, 1 and 2 fold the assessed concentration in the sample	0.2	Relative %	A
$u_{intercept}$	Uncertainty on of the intercepts of the regression curve (n=4)		5.36	Relative %	A
$u_{precision}$	Uncertainty on the standard addition method		3.14	Relative %	A

Uncertainty Information from NIM

Uncertainty budget:

As

Parameter	Description	Type A/B	Value	Unit	Standard Uncertainty
$_{Lc}$	uncertainty from calibration curve	B	3.798	μg/kg	0.039
c_z	amount content of the primary assay standard	B	4.290	μg/kg	0.031
m_x	mass fraction of sample	B	0.50679	g	0.00004
m_z	mass fraction of primary assay standard	B	0.32819	g	0.00004
c_x	measured result	A	3.798	μg/kg	0.053
u_c	combined uncertainty		0.071	μg/kg	
U_c	expanded uncertainty（k=2）		0.142	μg/kg	

Cd

Parameter	Description	Type A/B	Value	Unit	Standard uncertainty
c_y	concentration of ^{111}Cd spike	A	3.321	μg/kg	0.018
B	procedure blank control and subtraction	A	0.002	μg/kg	0.002
R_b	measured isotope amount ratio of blend b $R_{111/110}$	A	42.119		0.449
$R_{b'}$	measured isotope amount ratio of blend b' $R_{111/110}$	A	24.066		0.160
R_z	measured isotope amount ratio in the primary assay standard $R_{111/110}$	A	1.025		0.002
R_y	measured isotope amount ratio in the spike $R_{111/110}$	A	160.077		0.181
c_z	amount content of the primary assay standard	B	2.235	μg/kg	0.013
m_x	mass fraction of sample in blend b	B	1.22402	g	0.00008
m_y	mass fraction of spike in blend b	B	0.49922	g	0.00008
$m_{y'}$	mass fraction of spike in blend b'	B	2.02211	g	0.00008
m_z	mass fraction of primary assay standard in blend b'	B	0.99382	g	0.00008
c_x	measured result of Cd	A	0.225	μg/kg	0.004
u_c	combined uncertainty		0.006	μg/kg	
U_c	expanded uncertainty（k=2）		0.011	μg/kg	

Cu

Parameter	Description	Type A/B	Value	Unit	Standard uncertainty
c_y	concentration of ^{65}Cu spike	A	10.111	µg/kg	0.049
B	procedure blank control and subtraction	A	0.032	µg/kg	0.007
R_b	measured isotope amount ratio of blend b $R_{63/65}$	A	0.5231		0.004
$R_{b'}$	measured isotope amount ratio of blend b' $R_{63/65}$	A	0.6169		0.0021
R_z	measured isotope amount ratio in the primary assay standard $R_{63/65}$	A	2.2436		0.0062
R_y	measured isotope amount ratio in the spike $R_{63/65}$	A	0.1158		0.0003
c_z	amount content of the primary assay standard	B	22.123	µg/kg	0.120
m_x	mass fraction of sample in blend b	B	1.22137	g	0.00008
m_y	mass fraction of spike in blend b	B	0.49751	g	0.00008
$m_{y'}$	mass fraction of spike in blend b'	B	0.99399	g	0.00008
m_z	mass fraction of primary assay standard in blend b'	B	0.49582	g	0.00008
c_x	measured result of Cu	A	3.269	µg/kg	0.047
u_c	combined uncertainty		0.061	µg/kg	
U_c	expanded uncertainty（k=2）		0.122	µg/kg	

Pb

Parameter	Description	Type A/B	Value	Unit	Standard uncertainty
c_y	concentration of ^{207}Pb spike	A	2.222	µg/kg	0.006
B	procedure blank control and subtraction	A	0.019	µg/kg	0.007
R_b	measured isotope amount ratio of blend b $R_{20511/207}$	A	0.74491		0.0042
$R_{b'}$	measured isotope amount ratio of blend b' $R_{208/207}$	A	0.68521		0.0022
R_z	measured isotope amount ratio in the primary assay standard $R_{208/207}$	A	2.4514		0.0041
R_y	measured isotope amount ratio in the spike $R_{208/207}$	A	0.1819		0.0003
c_z	amount content of the primary assay standard	B	9.531	µg/kg	0.051
m_x	mass fraction of sample in blend b	B	1.22137	g	0.00008
m_y	mass fraction of spike in blend b	B	0.49749	g	0.00008
$m_{y'}$	mass fraction of spike in blend b'	B	1.00621	g	0.00008
m_z	mass fraction of primary assay standard in blend b'	B	0.50223	g	0.00008
c_x	measured result of Pb	A	1.088	µg/kg	0.012
u_c	combined uncertainty		0.017	µg/kg	
U_c	expanded uncertainty（k=2）		0.034	µg/kg	

Ni

Parameter	Description	Type A/B	Value	Unit	Standard uncertainty
c_y	concentration of ^{61}Ni spike	A	6.322	µg/kg	0.038
B	procedure blank control and subtraction	A	0.023	µg/kg	0.012
R_b	measured isotope amount ratio of blend b $R_{60/61}$	A	0.5877		0.0081
$R_{b'}$	measured isotope amount ratio of blend b' $R_{60/61}$	A	0.5962		0.0028
R_z	measured isotope amount ratio in the primary assay standard $R_{60/61}$	A	23.097		0.062
R_y	measured isotope amount ratio in the spike $R_{60/61}$	A	0.05610		0.00027

c_z	amount content of the primary assay standard	B	49.18	µg/kg	0.12
m_x	mass fraction of sample in blend *b*	B	1.20387	g	0.00008
m_y	mass fraction of spike in blend *b*	B	0.50221	g	0.00008
$m_{y'}$	mass fraction of spike in blend *b'*	B	0.50240	g	0.00008
m_z	mass fraction of primary assay standard in blend *b'*	B	1.20105	g	0.00008
c_x	measured result of Ni	A	4.744	µg/kg	0.040
u_c	combined uncertainty		0.090	µg/kg	
U_c	expanded uncertainty（k=2）		0.181	µg/kg	

Zn

Parameter	Description	Type A/B	Value	Unit	Standard uncertainty
c_y	concentration of ^{67}Zn spike	A	10.232	µg/kg	0.075
B	procedure blank control and subtraction	A	0.070	µg/kg	0.024
R_b	measured isotope amount ratio of blend *b* $R_{66/67}$	A	0.6840		0.0072
$R_{b'}$	measured isotope amount ratio of blend *b'* $R_{66/67}$	A	0.6547		0.0026
R_z	measured isotope amount ratio in the primary assay standard $R_{66/67}$	A	6.9027		0.0181
R_y	measured isotope amount ratio in the spike $R_{66/67}$	A	0.06362		0.00024
c_z	amount content of the primary assay standard	B	80.546	µg/kg	0.427
m_x	mass fraction of sample in blend *b*	B	1.20552	g	0.00008
m_y	mass fraction of spike in blend *b*	B	0.50046	g	0.00008
$m_{y'}$	mass fraction of spike in blend *b'*	B	0.49844	g	0.00008
m_z	mass fraction of primary assay standard in blend *b'*	B	1.20552	g	0.00008
c_x	measured result of Zn	A	8.764	µg/kg	0.089
u_c	combined uncertainty		0.162	µg/kg	
U_c	expanded uncertainty（k=2）		0.324	µg/kg	

Uncertainty Information from NIMT

6. Detail of the uncertainty estimation
   - Complete specification of the measurement equations

Quantification of trace elements in sea water by IDMS method.

$$C_x = f_{H_2O} \cdot f_P \cdot f_B \cdot f_D \cdot C_z \cdot \frac{M_y \cdot M_{zc}}{M_x \cdot M_{yc}} \cdot \frac{R_y - R_b}{R_b - R_x} \cdot \frac{R_{bc} - R_z}{R_y - R_{bc}}$$

Quantification of trace elements in sea water by GSA method.

$$C_x = C_0 * DF$$

   - Description of all uncertainty sources and their typical values

Uncertainty budget of **Pb** measurement by IDMS method

Parameter	Typical value (x)	Standard uncertainty u(x)	Type
Rb	0.5480	0.0051	A
Rbc	0.5281	0.0035	A
Rx	2.1681	0.0057	B
Rz	2.1681	0.0057	B
Digestion	1.00000	0.000	B
Blank correction	1.00000	0.004455	B
Method Precision	1.00000	0.012926	A
Cz	0.00306	0.000005	B
Ry	0.0030	0.000000	B
Mx	2.02518	0.000449	B
My	0.43186	0.000449	B
Myc	0.42850	0.000449	B
Mz	0.66820	0.000449	B
Moisture content	1.00000	0.00102	A

Uncertainty budget of **Ni** measurement by IDMS method

Parameter	Typical value (x)	Standard uncertainty u(x)	Type
Rb	0.6808	0.0036	A
Rbc	0.6899	0.0071	A
Rx	23.0047	0.0169	B
Rz	23.0047	0.0169	B
Digestion	1.00000	0.000	B
Blank correction	1.00000	0.010165	B
Method Precision	1.00000	0.005232	A
Cz	0.00310	0.000006	B
Ry	0.0019	0.000058	B
Mx	1.02784	0.000449	B
My	0.83839	0.000449	B
Myc	0.81499	0.000449	B
Mz	1.39496	0.000449	B
Moisture content	1.00000	0.00102	A

Uncertainty budget of **Cd** measurement by IDMS method

Parameter	Typical value (x)	Standard uncertainty u(x)	Type
Rb	0.0568	0.0000	A
Rbc	0.0569	0.0001	A
Rx	22.9928	0.0538	B
Rz	22.9928	0.0538	B
Digestion	1.00000	0.000	B
Blank correction	1.00000	0.002584	B
Method Precision	1.00000	0.010972	A
Cz	0.00151	0.000011	B
Ry	0.0527	0.000290	B
Mx	1.02119	0.000449	B
My	0.13556	0.000449	B
Myc	0.13168	0.000449	B
Mz	0.17307	0.000449	B
Moisture content	1.00000	0.00000	A

Uncertainty budget of As, Cd, Ni and Pb measurement by GSA-ICPMS method

Parameter	As	Cd	Ni	Pb
RSU_c (element in seawater)*	0.02633	0.04303	0.05180	0.02856
RSU Precision	0.01456	0.01176	0.04915	0.01274
RSU Calibration curve	0.02032	0.03924	0.01585	0.02450
RSU Calibration Standard	0.00129	0.00265	0.00139	0.00728
RSU Dilution factor (sample dilution)	0.00031	0.00031	0.00031	0.00031
RSU Dilution factor (measured sample)	0.00021	0.00021	0.00021	0.00021
RSU Blank factor	0.00814	0.01287	0.00380	0.00015

* RSU is relative standard uncertainty.

Uncertainty Information from NMIA

6. Detail of the uncertainty estimation
   - Complete specification of the measurement equations

$$W_X = F(MP)\cdot F(MT)\cdot W_Z \cdot \frac{MM_X}{MM_Z}\cdot\frac{M_{Y(SB)}}{M_X}\cdot\frac{M_Z}{M_{Y(CB)}}\cdot\frac{R_{SB}-R_Y}{R_X-R_{SB}}\cdot\frac{R_Z-R_{CB}}{R_{CB}-R_Y}\cdot\frac{a(RI)_Z}{a(RI)_X}$$

   - Description of all uncertainty sources and their typical values

Uncertainty Budget for Ni:

Name of Component	*Symbol*	*Units*	*Value*	*Standard Uncertainty*	*Relative Standard Uncertainty*	*Degrees of Freedom*
Xi			xi	u(xi)	u(xi)/xi (%)	vi
Method Precision	F(MP)	dimensionless	1.0000	0.0052	0.52%	8
Method Trueness	F(MT)	dimensionless	1.000	0.013	1.3%	30
Calibration Standard	Wz	ug/kg	74.48	0.10	0.14%	232
Sample Mass in Calibration Blend (Gravimetry)	Mx	g	4.01933	0.00020	0.0050%	100
Isotopic Internal Standard Mass in Sample Blend (Gravimetry)	My(SB)	g	0.25244	0.00020	0.079%	100
Standard Mass in Calibration Blend (Gravimetry)	Mz	g	1.21907	0.00020	0.016%	100
Isotopic Internal Standard Mass in Calibration Blend (Gravimetry)	My(CB)	g	1.23935	0.00020	0.016%	100
Sample Isotope Amount Ratio	Rx	mol/mol	23.005	0.015	0.064%	100
Standard Isotope Amount Ratio	Rz	mol/mol	23.005	0.015	0.064%	100

Isotopic Standard Isotope Amount Ratio	Ry	mol/mol	0.00191	0.00191	100 %	10
Isotopic Composition	a(RI)z/a(RI)x	dimensionless	1.00000	0.00081	0.081%	100
Molar Mass Ratio	MMx/ MMz	dimensionless	1.000000	0.000010	0.0010%	100
Sample Blend Isotope Amount Ratio	R(SB)	mol/mol	0.191	Included in F(MP)		8
Calibration Blend Isotope Amount Ratio	R(CB)	mol/mol	0.193	Included in F(MP)		8

Uncertainty Budget for Cu:

Name of Component	*Symbol*	*Units*	*Value*	*Standard Uncertainty*	*Relative Standard Uncertainty*	*Degrees of Freedom*
Xi			xi	u(xi)	u(xi)/xi (%)	vi
Method Precision	F(MP)	dimensionless	1.0000	0.0050	0.50%	8
Method Trueness	F(MT)	dimensionless	1.000	0.041	4.1%	30
Calibration Standard	Wz	ug/kg	73.302	0.096	0.13%	1063
Sample Mass in Calibration Blend (Gravimetry)	Mx	g	4.01693	0.00020	0.0050%	100
Isotopic Internal Standard Mass in Sample Blend (Gravimetry)	My(SB)	g	0.19218	0.00020	0.10%	100
Standard Mass in Calibration Blend (Gravimetry)	Mz	g	0.90043	0.00020	0.022%	100
Isotopic Internal Standard Mass in Calibration Blend (Gravimetry)	My(CB)	g	0.93303	0.00020	0.021%	100
Sample Isotope Amount Ratio	Rx	mol/mol	2.2415	0.0060	0.27%	100
Standard Isotope Amount Ratio	Rz	mol/mol	2.2415	0.0060	0.27%	100
Isotopic Standard Isotope Amount Ratio	Ry	mol/mol	0.0030	0.0030	100%	10
Isotopic Composition	a(RI)z/a(RI)x	dimensionless	1.0000	0.0034	0.34%	100
Molar Mass Ratio	MMx/ MMz	dimensionless	1.00000	0.000067	0.0067%	100
Sample Blend Isotope Amount Ratio	R(SB)	mol/mol	0.0824	Included in F(MP)		8
Calibration Blend Isotope Amount Ratio	R(CB)	mol/mol	0.0863	Included in F(MP)		8

Uncertainty Information from NMIJ

6. Detail of the uncertainty estimation

(1) For standard addition ICP-MS/MS.

Calibration and uncertainty estimation in standard addition ICP-MS/MS was carried out based on Eq (1).

$$c_{x1} = \frac{m_{tot}}{m_{tak}} \cdot r \cdot d \cdot \frac{c_{x2} \cdot m_2}{\left(\frac{b}{a} - 1\right) \cdot m_1} \qquad (1)$$

m_{tak}: mass of the sample solution taken for dilution [g]
m_{tot}: mass of the sample solution after dilution [g]
c_{x1}: the concentration of the element in the sample [mg kg^{-1}]
c_{x2}: the concentration of the element in the calibration standard solution [mg kg^{-1}]
m_1: mass of sample solution taken for standard addition (g)
m_2: mass of calibration standard solution for making the spiked sample (g)
a: the signal intensity ratio of analyte/(internal standard) in non-spiked sample
b: the signal intensity ratio of analyte/(internal standard) in spiked sample
B: observed blank [mg kg^{-1}]
r: the reproducibility factor of measurement
d: the signal drift of ICP-MS/MS

Uncertainty sources and their typical values for standard addition ICP-MS/MS

Symbol	As		Zn		Unit
	Typical value	Standard uncertainty	Typical value	Standard uncertainty	
m_{tak}	0.5057	0.0002	5.1302	0.0002	g
m_{tot}	25.1079	0.0002	51.2755	0.0002	g
r	1.0000	0.0117	1.0000	0.0086	-
d	1.0000	0.0066	1.0000	0.0065	-
c_{x2}	93.98	0.19	114.5	0.2	µg/kg
m_1	10.1074	0.0002	24.7137	0.0002	g
m_2	0.4972	0.0002	0.4905	0.0002	g
a	0.3869	0.0056	5.5E-04	4.7E-06	-
b	21.75	0.15	2.1E-03	9.1E-06	-
B	0.0000	0.0980	0.0000	0.0069	µg/kg

(2) For ID-MS.

Calibration and uncertainty estimation in ID-MS was carried out based on Eq (2), with Cu as the example.

$$c_x = c_z \cdot r \cdot \frac{m_y \cdot m_z}{m_x \cdot m'_y} \cdot \frac{K_y \cdot R_y - K_b \cdot R_b}{K_b \cdot R_b - K_x \cdot R_x} \cdot \frac{K_{b'} \cdot R_{b'} - K_z \cdot R_z}{K_y \cdot R_y - K_{b'} \cdot R_{b'}} \cdot \frac{\sum_i (K_{xi} \cdot R_{xi})}{\sum_i (K_{zi} \cdot R_{zi})} - B \qquad (2)$$

In Eq. (2), the subscripts of x, y, z, b, and b' represent the sample, the isotope enriched spike, the standard, the blend solution of x and y for ID, and the blend solution of y and z for reverse ID, respectively. The meanings of other factors were as follows: m_x and m_y, masses of x and y in blend b (g); m'_y and m_z, masses of y and z in blend b' (g); c_x, c_y, and c_z, concentrations of the Cu [µg kg^{-1}] in x, y, and z, respectively; B, observed blank [mol g^{-1}]; R_x, R_y, R_z, R_b, and $R_{b'}$, measured ratios of $^{63}Cu/^{65}Cu$ in x, y, z, b and b', respectively; K_x, K_y, K_z, K_b, and $K_{b'}$, mass bias correction factors of R_x, R_y, R_z, R_b, and $R_{b'}$, respectively; R_{xi} and R_{zi}, all ratios in the sample and in the standard, respectively; K_{xi} and K_{zi}, mass bias correction factors of R_{xi} and R_{zi}, respectively. The r is the reproducibility factor. For the purpose of calculating the measurement uncertainty of r, the relative standard deviation (RSD) of 5-sample analysis was taken into consideration.

Uncertainty sources and their typical values for ID-MS

	Cd		Cu		Pb		Ni		
Factor	Typical Value	Standard Uncertainty	Typical Value	Standard Uncertainty	Typical Value	Standard Uncertainty	Typical Value	Standard Uncertainty	Unit
R_b	0.0118	0.0001	0.3942	0.0011	0.3139	0.0011	0.2320	0.0012	-
K_b	1.0313	0.0023	1.0782	0.0027	0.8924	0.0013	1.0225	0.0025	-
R_b'	0.2043	0.0005	0.8813	0.0027	1.3597	0.0022	0.5051	0.0013	-
K_b'	1.0364	0.0021	1.0680	0.0046	0.8850	0.0013	1.0136	0.0063	-
R_x	0.9758	0.0084	2.2436	0.0015	2.1057	0.0101	23.0046	0.0169	-
K_x	1.0000	0.0000	1.0000	0.0000	1.0000	0.0027	1.0000	0.0000	-
R_z	0.9758	0.0084	2.2436	0.0015	2.1340	0.0154	23.0046	0.0169	-
K_z	1.0000	0.0000	1.0000	0.0000	1.0000	0.0027	1.0000	0.0000	-
B	0.0010	0.0003	0.1178	0.0175	0.0685	0.0154	0.1174	0.0088	µ g kg^{-1}
C_z	965.6	3.4	964.0	3.4	979.1	3.4	984.7	3.4	µ g kg^{-1}
R_y	0.0065	0.0000	0.0030	0.0000	0.0136	0.0000	0.0019	0.0001	-
K_y	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000	-
m_x	5.1644	0.0002	5.1644	0.0002	5.0771	0.0002	5.0771	0.0002	g
m_y	5.0258	0.0002	5.0258	0.0002	5.0382	0.0002	5.0382	0.0002	g
m'_y	10.0824	0.0002	10.0824	0.0002	10.0824	0.0002	10.0824	0.0002	g
m_z	0.1073	0.0002	0.1073	0.0002	0.1073	0.0002	0.1073	0.0002	g
$\Sigma(K_{xi}R_{xi})$	8.0096	0.0132	3.2415	0.0043	4.0049	0.0187	3.8134	0.0009	-
$\Sigma(K_{zi}R_{zi})$	8.0096	0.0132	3.2415	0.0043	4.0534	0.0257	3.8134	0.0009	-
r	1.0000	0.0058	1.0000	0.0047	1.0000	0.0048	1.0000	0.0086	-
c_x	0.217		3.099		1.098		4.623		µ g kg^{-1}
u_c	0.005		0.043		0.030		0.063		µ g kg^{-1}
u%	2.3%		1.4%		2.7%		1.4%		-

Uncertainty Information from NRC

6. Detail of the uncertainty estimation

For double IDMS, the following equation was used for the calculation of measurand mass fraction in the sample:

$$w_x = w_z \cdot \frac{m_y}{m_x} \cdot \frac{m_z}{m'_y} \cdot \frac{A_y - B_y \cdot K \cdot r}{B_{xz} \cdot K \cdot r - A_{xz}} \cdot \frac{B_{xz} \cdot K \cdot r' - A_{xz}}{A_y - B_y \cdot K \cdot r'_b} - w_b \qquad (1)$$

where:

w_x is the mass fraction of the measurand in the sample (µg/kg);
w_z is the mass fraction of the measurand in primary standard solution (µg/kg);
m_y is the mass of spike solution used to prepare the mixture of sample and spike (g);
m_x is the mass of sample used (g);
m_z is the mass of primary assay standard used (g);
m'_y is the mass of spike used to prepare the mixture of spike and primary assay standard (g);
A_y is the abundance of the reference isotope in the spike;
B_y is the abundance of the spike isotope in the spike;
A_{xz} is the abundance of the reference isotope in the sample or primary standard;
B_{xz} is the abundance of the spike isotope in the sample or primary standard;
K is the mass bias correction factor;

r is the measured reference/spike isotope ratio in the mixture solution of sample and spike;
r' is the measured reference/spike isotope ratio in the mixture solution of spike and primary assay standard;
w_b is the mass fraction of the measurand in the sample blank (µg/kg).

Equation 2 is used for the calculation of the mass fraction of As using two additions of standard addition calibration:

$$\frac{m_{\text{std-i}} \cdot w_{\text{std}}}{m_{\text{s-i}}} = b \cdot I_i \cdot \frac{m_{\text{sf-i}}}{m_{\text{s-i}}} \cdot \frac{m_{\text{df-i}}}{m_{\text{d0-i}}} + a \text{ and } w_x = -a \qquad (2)$$

where:

w_x is the mass fraction of the measurand in the sample (µg/kg);
w_{std} is the mass fraction of the measurand in the primary standard solution (µg/kg);
I_i is the measured intensity in the prepared set of samples, i=0, 1, 2;
$m_{\text{std-i}}$ is the mass of natural abundance standard added to the spiked sample (g), i=1, 2;
$m_{\text{s-i}}$ is the mass of aliquot of sample used to prepared spiked sample (g), i=0, 1, 2;
$m_{\text{sf-i}}$ is the final mass of spiked sample (g), i=0, 1, 2;
$m_{\text{d0-i}}$ is the mass of aliquots of spiked samples for dilution (g), i=0, 1, 2;
$m_{\text{d0-f}}$ is the final mass of aliquots of spiked samples after dilution (g), i=0, 1, 2.

According to JCGM 100:28 Evaluation of Measurement Data-Guide to the Expression of Uncertainty in Measurement, the combined standard uncertainty of a measurement result y, designated by u_{ci} (y) can be obtained from the following equation (3):

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) + 2 \cdot \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left(\frac{\partial f}{\partial x_i} \right) \cdot \left(\frac{\partial f}{\partial x_j} \right) \cdot u(x_i, x_j) \qquad (3)$$

where $y = f(x_1, x_2, \ldots, x_N)$. Equation 3 is conveniently referred to as *the law of propagation of uncertainty*. The partial derivatives $\partial f/\partial x_i$ are often referred to as *sensitivity coefficients*, $u(x_i)$ is the standard uncertainty associated with the input x_i, and $u(x_i, x_j)$ is the estimated covariance associated with x_i and x_j.

Individual combined standard uncertainty was estimated based on equations 1-3 for individual data. Given that the majority of the uncertainty originates from the isotope ratio measurements, random effects model was used to combine all measurement results from 3 different days and 3 to 6 sample aliquots. For this Bayesian random effects model was used and we assigned 5 degrees of freedom to each result as implemented in the NIST consensus builder.

Table 1. Uncertainty budget for Ni in CCQM-K155 seawater

Parameter	Typical value	Standard uncertainty	Unit
w_z	166.72	0.21	µg/kg
m_y	0.2963	0.0003	g
m_x	10.0933	0.0003	g
m_z	1.0137	0.0003	g
m'_y	1.0046	0.0003	g
A_y	0.0612	0.0003	mol/mol
B_y	0.8884	0.0003	mol/mol
A_{xz}	0.26223	0.000075	mol/mol
B_{xz}	0.011399	0.0000065	mol/mol
K	1.0323	0.0061	
r	0.9440	0.0050	
r'	1.0131	0.0022	
w_b	0.0018	0.0002	µg/kg
w_x, µg/kg	4.522		
u_c, µg/kg	0.022		
k	2		
U, µg/kg	0.044		

Table 2. Uncertainty budget for Zn in CCQM-K155 seawater

Parameter	Typical value	Standard uncertainty	Unit
w_z	325.35	0.36	µg/kg
m_y	0.2963	0.0003	g
m_x	10.0933	0.0003	g
m_z	1.0137	0.0003	g
m'_y	1.0046	0.0003	g
A_y	0.0258	0.0003	mol/mol
B_y	0.9311	0.0003	mol/mol
A_{xz}	0.2773	0.0049	mol/mol
B_{xz}	0.0404	0.0008	mol/mol
K	0.9936	0.02265	
r	0.9066	0.0018	
r'	0.9850	0.0013	
w_b	0.064	0.008	µg/kg
w_x, µg/kg	8.572		
u_c, µg/kg	0.034		
k	2		
U, µg/kg	0.068		

Table 3. Uncertainty budget for As in CCQM-K155 seawater

Parameter	Typical value	Standard uncertainty	Unit
w_z	68.15	0.075	µg/kg
a	3.82	0.08	µg/kg
w_x, µg/kg	3.82		
u_c, µg/kg	0.08		
k	2		
U, µg/kg	0.16		

7. Authors for NRC CCQM-K155 project
Kenny Nadeau, Juris Meija, Lu Yang and Zoltan Mester

Uncertainty Information from RISE

	Ni determination CCQM K155	

Ni determination CCQM K155

Ni is determined using ICP-MS after concentration (with a concentration factor of 2) and removal of salt using two identical Chelex columns. Co is used as internal standard and is added prior to the Chelex concentration step. Ni is measured using 60Ni, with 59Co as internal standard. Measurements are performed at 3 different occasions on totally 16 replicates. Calibration is performed using a Ni standard solution at the same concentration as the sample concentration prepared from NIST SRM 3136.

Calculation of measurement uncertainty for Ni is performed based on the precision of mean values obtained at 3 different occasions. Uncertainty contributions that are not included in this precision are added. Hence, the calculated measurement uncertainty is for the mean value.

Model Equation:

$$C_{Ni}=C_{Ni.mean}/C_{Chelex.concentration}*f_{C.CRM}*f_{dil}*f_{sample.mass}*f_{recovery}*f_{Co.blank}*f_{ICPMS}*f_{IS}+f_{blank};$$

$$f_{dil}=f_{dil1}*f_{dil2}*f_{dil3}*f_{dil4};$$

List of Quantities:

Quantity	Unit	Definition
C_{Ni}	µg/kg	Ni content in the sample
$C_{Ni.mean}$	µg/kg	Mean Ni content of measurements performed at 3 different occasions (totally 16 replicates have been measured)
$C_{Chelex.concentration}$	1	Increase in concentration in the Chelex purification step
$f_{recovery}$	1	Factor taking into account uncertainty of recovery correction
$f_{sample.mass}$	1	Factor taking into account uncertainty of sample mass (10 g)
$f_{Co.blank}$	1	Factor taking into account uncertainty of Co blank correction
f_{ICPMS}	1	Factor taking into account uncertainty for systematic effects in ICP-MS measurement (not included in the precision of the Ni measurement)
$f_{C.CRM}$	1	Factor taking into account uncertainty of Ni concentration in Ni standard stock solution (10000 mg/kg) from NIST (SRM 3136)
f_{dil}	1	Factor taking into account uncertainty of dilution of Ni standard stock solution (10000 mg/kg)
f_{dil1}	1	Factor taking into account uncertainty of mass of Ni standard stock solution (10 g) first dilution step
f_{dil2}	1	Factor taking into account uncertainty of mass of diluted Ni standard solution (1000 g) first dilution step
f_{dil3}	1	Factor taking into account uncertainty of mass of Ni standard solution (10 g) second dilution step
f_{dil4}	1	Factor taking into account uncertainty of mass of diluted Ni standard solution (1000 g) second dilution step
f_{blank}	1	Factor taking into account blank correction
f_{IS}	1	Factor taking into account uncertainty of internal standard correction

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	Ni determination CCQM K155	

$C_{Ni.mean}$: Type A
Method of observation: Direct
Number of observations: 3

No.	Observation
1	8.704 µg/kg
2	9.325 µg/kg
3	8.872 µg/kg

Arithmetic Mean: 8.967 µg/kg
Standard Deviation: 0.32 µg/kg
Standard Uncertainty: 0.185 µg/kg

Mean Ni content of measurements performed at 3 different occasions (totally 16 replicates have been measured)

$C_{Chelex.concentration}$: Type B rectangular distribution
Value: 2 1
Halfwidth of Limits: 0.01 %

Increase in concentration in Chelex purification step.

$f_{recovery}$: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.04 1

Values are corrected for recovery and this is an estimated uncertainty of the recovery correction. It is based on the variation in recoveries at the different occasions.

$f_{sample.mass}$: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.003 %

Uncertainty of sample mass used on Chelex column.

$f_{Co.blank}$: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 1 %

Sample contains Co corresponding to approx. 2 % of Co added as internal standard and the result has been corrected for this. The uncertainty of the Co content in the sample is estimated to +/- 50 % (rel.)

f_{ICPMS}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.01 %

$f_{C.CRM}$: Type B normal distribution
Value: 1 1
Expanded Uncertainty: 0.26 %
Coverage Factor: 1.970

Ni standard solution SRM 3136 from NIST containing 10003 +/- 26 mg/kg (95 %)

f_{dil1}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.05 %

f_{dil2}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.01 %

f_{dil3}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.05 %

f_{dil4}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.01 %

f_{blank}: Type B t-distribution
Value: 0 1
Standard Uncertainty: 0.06 1
Degrees of Freedom: 2

Uncertainty for blank correction

f_{IS}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.5 %

Uncertainty for internal standard correction.

Uncertainty Budgets:

C_{Ni}: Ni content in the sample

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$C_{Ni.mean}$	8.967 µg/kg	0.185 µg/kg	normal	0.50	0.093 µg/kg	36.1 %
$C_{Chelex.concentration}$	2.000000 1	$115 \cdot 10^{-6}$ 1	rectangular	-2.2	$-260 \cdot 10^{-6}$ µg/kg	0.0 %
$f_{recovery}$	1.0000 1	0.0231 1	rectangular	4.5	0.10 µg/kg	45.1 %
$f_{sample.mass}$	1.0000000 1	$17.3 \cdot 10^{-6}$ 1	rectangular	4.5	$78 \cdot 10^{-6}$ µg/kg	0.0 %
$f_{Co.blank}$	1.00000 1	$5.77 \cdot 10^{-3}$ 1	rectangular	4.5	0.026 µg/kg	2.8 %
f_{ICPMS}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	4.5	$260 \cdot 10^{-6}$ µg/kg	0.0 %
$f_{C.CRM}$	1.00000 1	$1.32 \cdot 10^{-3}$ 1	normal	4.5	$5.9 \cdot 10^{-3}$ µg/kg	0.1 %
f_{dil1}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	4.5	$1.3 \cdot 10^{-3}$ µg/kg	0.0 %
f_{dil2}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	4.5	$260 \cdot 10^{-6}$ µg/kg	0.0 %
f_{dil3}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	4.5	$1.3 \cdot 10^{-3}$ µg/kg	0.0 %
f_{dil4}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	4.5	$260 \cdot 10^{-6}$ µg/kg	0.0 %
f_{blank}	0.0 1	0.0600 1	t-distr.	1.0	0.060 µg/kg	15.1 %
f_{IS}	1.00000 1	$2.89 \cdot 10^{-3}$ 1	rectangular	4.5	0.013 µg/kg	0.7 %
C_{Ni}	4.484 µg/kg	0.154 µg/kg				

Ni content in the sample

f_{dil}: Factor taking into account uncertainty of dilution of Ni standard stock solution (10000 mg/kg)

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
f_{dil1}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	1.0	$290 \cdot 10^{-6}$ 1	48.1 %
f_{dil2}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	1.0	$58 \cdot 10^{-6}$ 1	1.9 %
f_{dil3}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	1.0	$290 \cdot 10^{-6}$ 1	48.1 %
f_{dil4}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	1.0	$58 \cdot 10^{-6}$ 1	1.9 %
f_{dil}	1.000000 1	$416 \cdot 10^{-6}$ 1				

Uncertainty for dilution of Ni standard stock solution. 10 g och stock solution is diluted to 1000 g, and then 40 g is diluted to 1000 g. standard solution for calibration.

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
C_{Ni}	4.48 µg/kg	0.31 µg/kg	2.00	95% (normal)
f_{dil}	1.00000 1	$830 \cdot 10^{-6}$ 1	2.00	95% (normal)

Pb determination CCQM K155

Pb is determined using ICP-MS after concentration (with a concentration factor of 2) and removal of salt using two identical Chelex columns. Co is used as internal standard and is added prior to the Chelex concentration step. Pb is measured using 208Pb, with 59Co as internal standard. Measurements are performed at 4 different occasions on totally 20 replicates. Calibration is performed using a Pb standard solution at the same concentration as the sample concentration prepared from NIST SRM 3128 .

Calculation of measurement uncertainty for Pb is performed based on the precision of mean values obtained at 4 different occasions. Uncertainty contributions that are not included in this precision are added. Hence, the calculated measurement uncertainty is for the mean value.

Model Equation:

$$C_{Pb}=C_{Pb.mean}/C_{Chelex.concentration}*f_{C.CRM}*f_{dil}*f_{sample.mass}*f_{recovery}*f_{Co.blank}*f_{ICPMS}*f_{IS}+f_{blank};$$

$$f_{dil}=f_{dil1}*f_{dil2}*f_{dil3}*f_{dil4};$$

List of Quantities:

Quantity	Unit	Definition
C_{Pb}	µg/kg	Pb content in the sample
$C_{Pb.mean}$	µg/kg	Mean Pb content of measurements performed at 4 different occasions (totally 20 replicates have been measured)
$C_{Chelex.concentration}$	1	Increase in concentration in the Chelex purification step
$f_{recovery}$	1	Factor taking into account uncertainty of recovery correction
$f_{sample.mass}$	1	Factor taking into account uncertainty of sample mass (10 g)
$f_{Co.blank}$	1	Factor taking into account uncertainty of Co blank correction
f_{ICPMS}	1	Factor taking into account uncertainty for systematic effects in ICP-MS measurement (not included in the precision of the Pb measurement)
$f_{C.CRM}$	1	Factor taking into account uncertainty of Pb concentration in Pb standard stock solution (10000 mg/kg) from NIST (SRM 3128)
f_{dil}	1	Factor taking into account uncertainty of dilution of Pb standard stock solution (10000 mg/kg)
f_{dil1}	1	Factor taking into account uncertainty of mass of Pb standard stock solution (10 g) first dilution step
f_{dil2}	1	Factor taking into account uncertainty of mass of diluted Pb standard solution (1000 g) first dilution step
f_{dil3}	1	Factor taking into account uncertainty of mass of Pb standard solution (10 g) second dilution step
f_{dil4}	1	Factor taking into account uncertainty of mass of diluted Pb standard solution (1000 g) second dilution step
f_{blank}	1	Factor taking into account blank correction
f_{IS}	1	Factor taking account internal standard correction

	Pb determination CCQM K155	

$c_{Pb.mean}$: Type A
Method of observation: Direct
Number of observations: 4

No.	Observation
1	1.98516 µg/kg
2	1.94428 µg/kg
3	2.04480 µg/kg
4	2.07447 µg/kg

Arithmetic Mean: 2.0122 µg/kg
Standard Deviation: 0.059 µg/kg
Standard Uncertainty: 0.0293 µg/kg

Mean Pb content of measurements performed at 4 different occasions (totally 20 replicates have been measured)

$c_{Chelex.concentration}$: Type B rectangular distribution
Value: 2 1
Halfwidth of Limits: 0.01 %

Increase in concentration in Chelex purification step.

$f_{recovery}$: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.05 1

Values are corrected for recovery and this is an estimated uncertainty of the recovery correction. It is based on the variation in recoveries at the different occasions.

$f_{sample.mass}$: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.003 %

Uncertainty of sample mass used on Chelex column.

$f_{Co.blank}$: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 1 %

Sample contains Co corresponding to approx. 2 % of Co added as internal standard and the result has been corrected for this. The uncertainty of the Co content in the sample is estimated to +/- 50 % (rel.)

f_{ICPMS}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 1 %

$f_{C.CRM}$: Type B normal distribution
Value: 1 1
Expanded Uncertainty: 0.140 %
Coverage Factor: 2.007

Pb standard solution SRM 3128 from NIST containing 9995 +/- 14 mg/kg (95 %)

f_{dil1}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.05 %

f_{dil2}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.01 %

f_{dil3}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.05 %

f_{dil4}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.01 %

f_{blank}: Type B t-distribution
Value: 0 1
Standard Uncertainty: 0.02 1
Degrees of Freedom: 3

Uncertainty for blank correction

f_{IS}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.5 %

Uncertainty for internal standard correction.

Uncertainty Budgets:

C_{Pb}: **Pb content in the sample**

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$C_{Pb.mean}$	2.0122 µg/kg	0.0293 µg/kg	normal	0.50	0.015 µg/kg	14.0 %
$C_{Chelex.concentration}$	2.000000 1	$115 \cdot 10^{-6}$ 1	rectangular	-0.50	$-58 \cdot 10^{-6}$ µg/kg	0.0 %
$f_{recovery}$	1.0000 1	0.0289 1	rectangular	1.0	0.029 µg/kg	55.0 %
$f_{sample.mass}$	1.0000000 1	$17.3 \cdot 10^{-6}$ 1	rectangular	1.0	$17 \cdot 10^{-6}$ µg/kg	0.0 %
$f_{Co.blank}$	1.00000 1	$5.77 \cdot 10^{-3}$ 1	rectangular	1.0	$5.8 \cdot 10^{-3}$ µg/kg	2.2 %
f_{ICPMS}	1.00000 1	$5.77 \cdot 10^{-3}$ 1	rectangular	1.0	$5.8 \cdot 10^{-3}$ µg/kg	2.2 %
$f_{C.CRM}$	1.000000 1	$698 \cdot 10^{-6}$ 1	normal	1.0	$700 \cdot 10^{-6}$ µg/kg	0.0 %
f_{dil1}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	1.0	$290 \cdot 10^{-6}$ µg/kg	0.0 %
f_{dil2}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	1.0	$58 \cdot 10^{-6}$ µg/kg	0.0 %
f_{dil3}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	1.0	$290 \cdot 10^{-6}$ µg/kg	0.0 %
f_{dil4}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	1.0	$58 \cdot 10^{-6}$ µg/kg	0.0 %
f_{blank}	0.0 1	0.0200 1	t-distr.	1.0	0.020 µg/kg	26.1 %
f_{IS}	1.00000 1	$2.89 \cdot 10^{-3}$ 1	rectangular	1.0	$2.9 \cdot 10^{-3}$ µg/kg	0.6 %
C_{Pb}	1.0061 µg/kg	0.0392 µg/kg				

Pb content in the sample

	Pb determination CCQM K155	

f_{dil}: Factor taking into account uncertainty of dilution of Pb standard stock solution (10000 mg/kg)

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
f_{dil1}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	1.0	$290 \cdot 10^{-6}$ 1	48.1 %
f_{dil2}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	1.0	$58 \cdot 10^{-6}$ 1	1.9 %
f_{dil3}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	1.0	$290 \cdot 10^{-6}$ 1	48.1 %
f_{dil4}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	1.0	$58 \cdot 10^{-6}$ 1	1.9 %
f_{dil}	1.000000 1	$416 \cdot 10^{-6}$ 1				

Uncertainty for dilution of Pb standard stock solution. 10 g och stock solution is diluted to 1000 g, and then 10 g is diluted to 1000 g. standard solution for calibration.

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
C_{Pb}	1.006 µg/kg	0.078 µg/kg	2.00	95% (normal)
f_{dil}	1.00000 1	$830 \cdot 10^{-6}$ 1	2.00	95% (normal)

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	Zn determination CCQM K155	

Zn determination CCQM K155

Zn is determined using ICP-MS after concentration (with a concentration factor of 2) and removal of salt using two identical Chelex columns. Co is used as internal standard and is added prior to the Chelex concentration step. Zn is measured using 66Zn, with 59Co as internal standard. Measurements are performed at 3 different occasions on totally 16 replicates. Calibration is performed using a Zn standard solution at the same concentration as the sample concentration prepared from NIST SRM 3168a .

Calculation of measurement uncertainty for Zn is performed based on the precision of mean values obtained at 3 different occasions. Uncertainty contributions that are not included in this precision are added. Hence, the calculated measurement uncertainty is for the mean value.

Model Equation:

$$C_{Zn}=C_{Zn.mean}/C_{Chelex.concentration}*f_{C.CRM}*f_{dil}*f_{sample.mass}*f_{recovery}*f_{Co.blank}*f_{ICPMS}*f_{IS}+f_{blank};$$

$$f_{dil}=f_{dil1}*f_{dil2}*f_{dil3}*f_{dil4};$$

List of Quantities:

Quantity	Unit	Definition
C_{Zn}	µg/kg	Zn content in the sample
$C_{Zn.mean}$	µg/kg	Mean Zn content of measurements performed at 3 different occasions (totally 16 replicates have been measured)
$C_{Chelex.concentration}$	1	Increase in concentration in the Chelex purification step
$f_{recovery}$	1	Factor taking into account uncertainty of apparent recovery correction
$f_{sample.mass}$	1	Factor taking into account uncertainty of sample mass (10 g)
$f_{Co.blank}$	1	Factor taking into account uncertainty of Co blank correction
f_{ICPMS}	1	Factor taking into account uncertainty for systematic effects in ICP-MS measurement (not included in the precision of the Zn measurement)
$f_{C.CRM}$	1	Factor taking into account uncertainty of Zn concentration in Zn standard stock solution (10000 mg/kg) from NIST (SRM 3168a)
f_{dil}	1	Factor taking into account uncertainty of dilution of Zn standard stock solution (10000 mg/kg)
f_{dil1}	1	Factor taking into account uncertainty of mass of Zn standard stock solution (10 g) first dilution step
f_{dil2}	1	Factor taking into account uncertainty of mass of diluted Zn standard solution (1000 g) first dilution step
f_{dil3}	1	Factor taking into account uncertainty of mass of Zn standard solution (10 g) second dilution step
f_{dil4}	1	Factor taking into account uncertainty of mass of diluted Zn standard solution (1000 g) second dilution step
f_{blank}	1	Factor taking into account blank correction
f_{IS}	1	Factor taking into account uncertainty of internal standard correction

	Zn determination CCQM K155	

$C_{Zn.mean}$: Type A
Method of observation: Direct
Number of observations: 3

No.	Observation
1	16.102 µg/kg
2	16.550 µg/kg
3	15.970 µg/kg

Arithmetic Mean: 16.207 µg/kg
Standard Deviation: 0.30 µg/kg
Standard Uncertainty: 0.176 µg/kg

Mean Ni content of measurements performed at 3 different occasions (totally 16 replicates have been measured)

$C_{Chelex.concentration}$: Type B rectangular distribution
Value: 2 1
Halfwidth of Limits: 0.01 %

Increase in concentration in Chelex purification step.

$f_{recovery}$: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.07 1

Values are corrected for apparent recovery and this is an estimated uncertainty of the apparent recovery correction. It is based on the variation in apparent recoveries at the different occasions.

$f_{sample.mass}$: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.003 %

Uncertainty of sample mass used on Chelex column.

$f_{Co.blank}$: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 1 %

Sample contains Co corresponding to approx. 2 % of Co added as internal standard and the result has been corrected for this. The uncertainty of the Co content in the sample is estimated to +/- 50 % (rel.)

f_{ICPMS}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.01 %

$f_{C.CRM}$: Type B normal distribution
Value: 1 1
Expanded Uncertainty: 0.20 %
Coverage Factor: 1.963

Zn standard solution SRM 3168a from NIST containing 10007 +/- 20 mg/kg (95 %)

f_{dil1}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.05 %

f_{dil2}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.01 %

f_{dil3}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.05 %

f_{dil4}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.01 %

f_{blank}: Type B t-distribution
Value: 0 1
Standard Uncertainty: 0.05 1
Degrees of Freedom: 2

Uncertainty for blank correction

f_{IS}: Type B rectangular distribution
Value: 1 1
Halfwidth of Limits: 0.5 %

Uncertainty for internal standard correction.

Uncertainty Budgets:

C_{Zn}: Zn content in the sample

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$C_{Zn.mean}$	16.207 µg/kg	0.176 µg/kg	normal	0.50	0.088 µg/kg	6.4 %
$C_{Chelex.concentration}$	2.000000 1	$115 \cdot 10^{-6}$ 1	rectangular	-4.1	$-470 \cdot 10^{-6}$ µg/kg	0.0 %
$f_{recovery}$	1.0000 1	0.0404 1	rectangular	8.1	0.33 µg/kg	89.2 %
$f_{sample.mass}$	1.0000000 1	$17.3 \cdot 10^{-6}$ 1	rectangular	8.1	$140 \cdot 10^{-6}$ µg/kg	0.0 %
$f_{Co.blank}$	1.00000 1	$5.77 \cdot 10^{-3}$ 1	rectangular	8.1	0.047 µg/kg	1.8 %
f_{ICPMS}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	8.1	$470 \cdot 10^{-6}$ µg/kg	0.0 %
$f_{C.CRM}$	1.00000 1	$1.02 \cdot 10^{-3}$ 1	normal	8.1	$8.3 \cdot 10^{-3}$ µg/kg	0.0 %
f_{dil1}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	8.1	$2.3 \cdot 10^{-3}$ µg/kg	0.0 %
f_{dil2}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	8.1	$470 \cdot 10^{-6}$ µg/kg	0.0 %
f_{dil3}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	8.1	$2.3 \cdot 10^{-3}$ µg/kg	0.0 %
f_{dil4}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	8.1	$470 \cdot 10^{-6}$ µg/kg	0.0 %
f_{blank}	0.0 1	0.0500 1	t-distr.	1.0	0.050 µg/kg	2.1 %
f_{IS}	1.00000 1	$2.89 \cdot 10^{-3}$ 1	rectangular	8.1	0.023 µg/kg	0.5 %
C_{Zn}	8.104 µg/kg	0.347 µg/kg				

Ni content in the sample

	Zn determination CCQM K155	

f_{dil}: Factor taking into account uncertainty of dilution of Zn standard stock solution (10000 mg/kg)

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
f_{dil1}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	1.0	$290 \cdot 10^{-6}$ 1	48.1 %
f_{dil2}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	1.0	$58 \cdot 10^{-6}$ 1	1.9 %
f_{dil3}	1.000000 1	$289 \cdot 10^{-6}$ 1	rectangular	1.0	$290 \cdot 10^{-6}$ 1	48.1 %
f_{dil4}	1.0000000 1	$57.7 \cdot 10^{-6}$ 1	rectangular	1.0	$58 \cdot 10^{-6}$ 1	1.9 %
f_{dil}	1.000000 1	$416 \cdot 10^{-6}$ 1				

Uncertainty for dilution of Zn standard stock solution. 10 g och stock solution is diluted to 1000 g, and then 80 g is diluted to 1000 g. standard solution for calibration.

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
C_{Zn}	8.10 µg/kg	0.69 µg/kg	2.00	95% (normal)
f_{dil}	1.00000 1	$830 \cdot 10^{-6}$ 1	2.00	95% (normal)

Uncertainty Information from UME

The model equation of IDMS measurements;

$$C_x = \frac{m_{y_1}}{m_{x_1}} \cdot \left(C_{z_2} \cdot \frac{m_{z_2}}{m_{y_2}} \cdot \frac{(r_{zy_2} - R_z) \cdot (r_{zy_3} - r_{xy_1})}{(r_{xy_1} - R_x) \cdot (r_{zy_3} - r_{zy_2})} + C_{z_3} \cdot \frac{m_{z_3}}{m_{y_3}} \cdot \frac{(r_{zy_3} - R_z) \cdot (r_{xy_1} - r_{zy_2})}{(r_{xy_1} - R_x) \cdot (r_{zy_3} - r_{zy_2})} \right)$$

Parameter	Unit	Definition
X	-	Sample
Y	-	Isotopically enriched standard, iCRM
Z	-	Primary standard reference material with natural isotopic composition, PSRM
xy	-	Blend of X and Y
yz	-	Blend of Y and Z
C_X, C_Y, C_Z	mol/kg	Mass fraction of sample, iCRM and PSRM
m_x	kg	Mass of sample
m_y, m_{y2}, m_{y3},	kg	Mass of isotopically enriched standard
m_y, m_{y2}, m_{y3},	kg	Mass of isotopically enriched standard
m_{z2}, m_{z3}	kg	Mass of PSRM
R_X, R_y, R_Z	-	Isotope ratio in sample, iCRM and PSRM
r_{xy}, r_{zy2}, R_{zy3}	-	Measured isotope ratio in sample-iCRM (sample blend) , iCRM-PSRM (calibration blend)
K_{xy},K_{zy}	-	Mass bias correction factor
ΣR_X, ΣR_Y	-	Sum of all isotope amount ratios of the same denominator

Uncertainty contributor -Cd	
Weighing	1.6%
Measurements of sample blends ratio	2.2%
Measurements of calibration blends ratio	1.4%
Intermediate precision	94.8%

Uncertainty contributor -Cu	
Weighing	4.1%
Measurements of sample blends ratio	0.9%
Measurements of calibration blends ratio	0.8%
Intermediate precision	93.8%
Other	0.45%

Uncertainty contributor -Ni	
Measurements of sample blends ratio	0.3%
Measurements of calibration blends ratio	2.6%
Intermediate precision	95.8%
Other	1.3%

Uncertainty contributor -Pb	
Primary Standard Reference Material	1.1%
Measurements of sample blends ratio	1.1%
Measurements of calibration blends ratio	0.9%
Intermediate precision	96.3%
Other	0.6%

Uncertainty contributor -Zn	
Primary Standard Reference Material	7.8%
Uncertainty on IUPAC (col 9) isotopic abundance of analyte	1.0%
Measurements of sample blends ratio	1.4%
Measurements of calibration blends ratio	2.1%
Intermediate precision	86.2%
Other	1.5%

The model equation of standard addition calibration;

$C_{1.1} = \frac{C_{1.1}}{m_1} * D_{f1.1}$,

$C_1 = \frac{C_{1.1}+C_{1.2}+C_{1.3}+C_{1.4}+C_{1.5}+C_{1.6}}{6} * \alpha_{Rep}$, *where IP: repeatability*

$C = (C_1 + C_2 + C_3) * \alpha_{IP}$, *where IP: intermediate precision*

Uncertainty contributor -As	
Weighing	0.8%
Intensity measurements of samples	1.6%
Intensity measurements of standards	9.5%
Repeatability	1.7%
Intermediate precision	85.4%
Other	1.0%

Uncertainty Information from UNIIM

6. Detail of the uncertainty estimation
   - Complete specification of the measurement equations
   - Description of all uncertainty sources and their typical values

$$W = \frac{{}^{b}M}{{}^{a}M} \cdot \frac{wm_{al}}{m_s} \cdot \left[\frac{A' - \frac{{}^{a}I}{{}^{b}I} B'}{\frac{{}^{a}I}{{}^{b}I} B - A} \right] \tag{1}$$

$$u_A = \sqrt{\frac{\sum_{k=1}^{M} \left(W_k - \overline{W} \right)^2}{M(M-1)}} \tag{2}$$

$$u_B = \sqrt{\sum_{i=1}^{N} \left(\frac{\partial W}{\partial X_i} \right)^2 \left(u_B(X_i) \right)^2} \tag{3}$$

$$u_c = \sqrt{u_A^2 + u_B^2} \tag{4}$$

$$U = k \cdot u_c \tag{5}$$

$$W = \frac{xm_r}{m_n} = x \frac{m_r}{m_n} \cdot M \cdot R \tag{6}$$

$$u(x) = \frac{1}{b} \sqrt{\left(\frac{1}{N} + \frac{(x - \overline{x})^2}{\sum_{j=1}^{N} (x_j - \overline{x})^2} \right) u^2(\overline{y}) + b^2 u_B^2(x)} \tag{7}$$

$$u_B = W \sqrt{\left(\frac{u_B(x_j)}{x_j} \right)^2 + \left(\frac{u(m_r)}{m_r} \right)^2 + \left(\frac{u(m_n)}{m_n} \right)^2 + \left(\frac{u(M)}{M} \right)^2} \tag{8}$$

Note: Please complete this form and return it to TÜBITAK UME (E-mail: betul.ari@tubitak.gov.tr) and GLHK (E-mail: yttsoi@govtlab.gov.hk) on or before the deadline (29 February 2020) for submission of results.

Uncertainty Information from VNIIFTRI

5. Detail of the uncertainty estimation
   - Complete specification of the measurement equations

$$C = (b/a - C_{Blank}) \cdot k_{Dilution}$$

Description of all uncertainty sources and their typical values for Cd

Parameter	Source of unceratinty	Typical value	Unit	Uncertainty contribution, %	Type
C	Replicate of element concentration in sample	0.535	µg/kg	35.1	A
b/a regression intercept and slope	concentration of additions; IS, sample, additions signals	0.0188	µg/kg	59.9	B
C_{Blank}	concentration of additions; blank, blank+add1, blank+add2, blank+add3 signals	0.001	µg/kg	5.0	B
$k_{Dilution}$	mass of the aliquot and solution	30.003	-	insignificant	B

Description of all uncertainty sources and their typical values for Cu

Parameter	Source of unceratinty	Typical value	Unit	Uncertainty contribution, %	Type
C	Replicate of element concentration in sample	7.93	µg/kg	25.3	A
b/a regression intercept and slope	concentration of additions; IS, sample, additions signals	0.504	µg/kg	62.4	B
C_{Blank}	concentration of additions; blank, blank+add1, blank+add2, blank+add3 signals	0.24	µg/kg	12.3	B
$k_{Dilution}$	mass of the aliquot and solution	29.998	-	insignificant	B

Description of all uncertainty sources and their typical values for Pb

Parameter	Source of unceratinty	Typical value	Unit	Uncertainty contribution, %	Type
C	Replicate of element concentration in sample	1.68	µg/kg	33.1	A
b/a regression intercept and slope	concentration of additions; IS, sample, additions signals	0.085	µg/kg	58.3	B
C_{Blank}	concentration of additions; blank, blank+add1, blank+add2, blank+add3 signals	0.028	µg/kg	8.6	B
$k_{Dilution}$	mass of the aliquot and solution	29.773	-	insignificant	B

Description of all uncertainty sources and their typical values for Ni

Parameter	Source of unceratinty	Typical value	Unit	Uncertainty contribution, %	Type
C	Replicate of element concentration in sample	6.67	µg/kg	35.8	A
b/a regression intercept and slope	concentration of additions; IS, sample, additions signals	0.268	µg/kg	62.3	B
C_{Blank}	concentration of additions; blank, blank+add1, blank+add2, blank+add3 signals	0.045	µg/kg	1.9	B
$k_{Dilution}$	mass of the aliquot and solution	30.010	-	insignificant	B

Description of all uncertainty sources and their typical values for Zn

Parameter	Source of unceratinty	Typical value	Unit	Uncertainty contribution, %	Type
C	Replicate of element concentration in sample	13.54	µg/kg	45.5	A
b/a regression intercept and slope	concentration of additions; IS, sample, additions signals	0.631	µg/kg	51.3	B
C_{Blank}	concentration of additions; blank, blank+add1, blank+add2, blank+add3 signals	0.18	µg/kg	3.2	B
$k_{Dilution}$	mass of the aliquot and solution	30.016	-	insignificant	B

Uncertainty Information from GUM (P196)

Uncertainty sources and their typical values

The combined standard uncertainty for measurement of each element, $u_c(\overline{w_x})$, was estimated using the following formula:

$$u_c(\overline{w_x}) = \sqrt{c_1^2 \cdot u^2\left(\frac{S_x}{S_{IS}}\right) + c_2^2 \cdot u^2(b) + c_3^2 \cdot u^2(a) + c_4^2 \cdot u^2(w_{IS}) + c_5^2 \cdot u^2(D) + c_6^2 \cdot u_c^2(cal) + c_7^2 \cdot u^2(blk) + c_8^2 \cdot u_c^2(recov) + c_9^2 \cdot u^2(drift) + s^2(\overline{w_x})}$$

where:

$u\left(\frac{S_x}{S_{IS}}\right)$ - standard uncertainty of the ratio of signal intensity of the analyte (x) to signal intensity of the internal standard (IS),

$u(b)$ - standard uncertainty of the intercept of the calibration curve,

$u(a)$ - standard uncertainty of the slope of the calibration curve,

$u(w_{IS})$ - standard uncertainty of the mass fraction of the internal standard (to simplify calculations, the concentration of IS solution was assumed as 10 µg kg^{-1}, instead of 10 µg L^{-1} given by producer. This assumption has no effect of reported mass fraction values of quantified elements as IS concentration was only used as reference for quantified elements concentration and the same working IS solution was used for calibration and samples.),

$u(D)$ - standard uncertainty of the sample dilution factor,

$u_c(cal)$ - combined standard uncertainty of the calibration standards (standard uncertainty of the stock solution and its dilution to measured calibration standard and combined standard uncertainty of weighing),

$u(blk)$ - standard uncertainty of the blank sample,

$u_c(recov)$ - combined standard uncertainty of the recovery (standard uncertainty of spike and standard uncertainty of NMIA MX014); in case of Zn standard uncertainty of the recovery of spike only as there was no certified value for Zn in NMIA MX014,

$u(drift)$ - standard uncertainty of the instrument drift,

$s(\overline{w_x})$ - standard deviation of the mean,

$c_1 \div c_9$ - sensitivity coefficients.

Uncertainty budgets for the analytes

Table 6. Uncertainty budget for Nickel

Uncertainty source	Estimate	Uncertainty distribution	Standard uncertainty	Sensitivity coefficient	Contribution to standard uncertainty
X_i	x_i		u_i	c_i	$u_i \cdot c_i$
Ratio of signals intensities, S_{Ni}/S_{Bi}	$2{,}162 \cdot 10^{-2}$ CPS(Ni) / CPS(Bi)	Normal	$1{,}7 \cdot 10^{-4}$ CPS(Ni) / CPS(Bi)	$2{,}54 \cdot 10^{2}$ $\mu g_{Ni} \cdot kg^{-1} \cdot$ CPS(Bi)/ CPS(Ni)	0,043 $\mu g_{Ni} \cdot kg^{-1}$
Intercept of the calibration Curve, b	$2{,}1 \cdot 10^{-4}$ CPS(Ni) / CPS(Bi)	Normal	$1{,}5 \cdot 10^{-4}$ CPS(Ni) / CPS(Bi)	$-2{,}54 \cdot 10^{2}$ $\mu g_{Ni} \cdot kg^{-1} \cdot$ CPS(Bi)/ CPS(Ni)	-0,039 $\mu g_{Ni} \cdot kg^{-1}$
Slope of the calibration Curve, a	$1{,}5769 \cdot 10^{-1}$ CPS(Ni) / CPS(Bi) / $\mu g_{Ni} \cdot kg^{-1}$ / $\mu g_{Bi} \cdot kg^{-1}$	Normal	$1{,}00 \cdot 10^{-3}$ CPS(Ni) / CPS(Bi) / $\mu g_{Ni} \cdot kg^{-1}$ / $\mu g_{Bi} \cdot kg^{-1}$	$-3{,}45 \cdot 10^{1}$ $(\mu g_{Ni} \cdot kg^{-1})^2 \cdot$ CPS(Bi)/ $\mu g_{Bi} \cdot kg^{-1} \cdot$ CPS(Ni)	-0,035 $\mu g_{Ni} \cdot kg^{-1}$
Mass fraction of the internal standard, w_{Bi}	10 $\mu g_{Bi} \cdot kg^{-1}$	Normal	$2 \cdot 10^{-5}$ $\mu g_{Bi} \cdot kg^{-1}$	$5{,}4332 \cdot 10^{-1}$ $\mu g_{Ni} \cdot kg^{-1}$ / $\mu g_{Bi} \cdot kg^{-1}$	$9 \cdot 10^{-6}$ $\mu g_{Ni} \cdot kg^{-1}$
Sample dilution factor, D	4	Normal	$6 \cdot 10^{-5}$	1,358 $\mu g_{Ni} \cdot kg^{-1}$	$9 \cdot 10^{-5}$ $\mu g_{Ni} \cdot kg^{-1}$
Calibration standards, *cal*	990909 $\mu g_{Ni} \cdot kg^{-1}$	Rectangular	$1{,}626 \cdot 10^{-2}$ $\mu g_{Ni} \cdot kg^{-1}$	1	0,016 $\mu g_{Ni} \cdot kg^{-1}$
Blank, *blank*	$1{,}28 \cdot 10^{-2}$ $\mu g_{Ni} \cdot kg^{-1}$	Rectangular	$2{,}111 \cdot 10^{-2}$ $\mu g_{Ni} \cdot kg^{-1}$	1	0,021 $\mu g_{Ni} \cdot kg^{-1}$
Recovery, *recov*	103 %	Rectangular	$9{,}469 \cdot 10^{-2}$ $\mu g_{Ni} \cdot kg^{-1}$	1	0,095 $\mu g_{Ni} \cdot kg^{-1}$
Instrument drift, *drift*	7 %	Rectangular	$1{,}8097 \cdot 10^{-1}$ $\mu g_{Ni} \cdot kg^{-1}$	1	0,181 $\mu g_{Ni} \cdot kg^{-1}$
Repeatability, $s(\overline{w_{Ni}})$	4,478 $\mu g_{Ni} \cdot kg^{-1}$	Normal	$4{,}768 \cdot 10^{-2}$ $\mu g_{Ni} \cdot kg^{-1}$	1	0,048 $\mu g_{Ni} \cdot kg^{-1}$
$\overline{w_{Ni}}$	4,478 $\mu g_{Ni} \cdot kg^{-1}$				0,222 $\mu g_{Ni} \cdot kg^{-1}$

Standard uncertainty: 0,222 $\mu g_{Ni} \cdot kg^{-1}$
Expanded uncertainty (k=2): 0,444 $\mu g_{Ni} \cdot kg^{-1}$
Measurements result: $\overline{w_{Ni}} = (4{,}48 \pm 0{,}44)\ \mu g_{Ni} \cdot kg^{-1}$

Table 7. Uncertainty budget for Lead

Uncertainty source	Estimate	Uncertainty distribution	Standard uncertainty	Sensitivity coefficient	Contribution to standard uncertainty
X_i	x_i		u_i	c_i	$u_i \cdot c_i$
Ratio of signals intensities, S_{Pb}/S_{Bi}	$3{,}958 \cdot 10^{-2}$ CPS(Pb) / CPS(Bi)	Normal	$9{,}8 \cdot 10^{-5}$ CPS(Pb) / CPS(Bi)	28 $\mu g_{Pb} \cdot kg^{-1} \cdot$ CPS(Bi)/ CPS(Pb)	0,0027 $\mu g_{Pb} \cdot kg^{-1}$
Intercept of the calibration Curve, b	$1{,}50 \cdot 10^{-3}$ CPS(Pb) / CPS(Bi)	Normal	$2{,}2 \cdot 10^{-4}$ CPS(Pb) / CPS(Bi)	-28 $\mu g_{Pb} \cdot kg^{-1} \cdot$ CPS(Bi)/ CPS(Pb)	-0,0061 $\mu g_{Pb} \cdot kg^{-1}$
Slope of the calibration Curve, a	1,4287 CPS(Pb) / CPS(Bi) / $\mu g_{Pb} \cdot kg^{-1}$ / $\mu g_{Bi} \cdot kg^{-1}$	Normal	$2{,}90 \cdot 10^{-3}$ CPS(Pb) / CPS(Bi) / $\mu g_{Pb} \cdot kg^{-1}$ / $\mu g_{Bi} \cdot kg^{-1}$	$-7{,}4619 \cdot 10^{-1}$ $(\mu g_{Pb} \cdot kg^{-1})^2 \cdot$ CPS(Bi)/ $\mu g_{Bi} \cdot kg^{-1} \cdot$ CPS(Pb)	-0,0022 $\mu g_{Pb} \cdot kg^{-1}$
Mass fraction of the internal standard, w_{Bi}	10 $\mu g_{Bi} \cdot kg^{-1}$	Normal	$2 \cdot 10^{-5}$ $\mu g_{Bi} \cdot kg^{-1}$	$1{,}0661 \cdot 10^{-1}$ $\mu g_{Pb} \cdot kg^{-1}$ / $\mu g_{Bi} \cdot kg^{-1}$	$2 \cdot 10^{-6}$ $\mu g_{Pb} \cdot kg^{-1}$
Sample dilution factor, D	4	Normal	$6 \cdot 10^{-5}$	$2{,}6652 \cdot 10^{-1}$ $\mu g_{Pb} \cdot kg^{-1}$	$2 \cdot 10^{-5}$ $\mu g_{Pb} \cdot kg^{-1}$
Calibration standards, *cal*	988917 $\mu g_{Pb} \cdot kg^{-1}$	Rectangular	$8{,}26 \cdot 10^{-3}$ $\mu g_{Pb} \cdot kg^{-1}$	1	0,0083 $\mu g_{Pb} \cdot kg^{-1}$
Blank, *blank*	$1{,}42 \cdot 10^{-3}$ $\mu g_{Pb} \cdot kg^{-1}$	Rectangular	$3{,}92 \cdot 10^{-3}$ $\mu g_{Pb} \cdot kg^{-1}$	1	0,0039 $\mu g_{Pb} \cdot kg^{-1}$
Recovery, *recov*	100 %	Rectangular	$8{,}29 \cdot 10^{-3}$ $\mu g_{Pb} \cdot kg^{-1}$	1	0,0083 $\mu g_{Pb} \cdot kg^{-1}$
Instrument drift, *drift*	5 %	Rectangular	$3{,}106 \cdot 10^{-2}$ $\mu g_{Pb} \cdot kg^{-1}$	1	0,0311 $\mu g_{Pb} \cdot kg^{-1}$
Repeatability, $s(\overline{w_{Pb}})$	1,0758 $\mu g_{Pb} \cdot kg^{-1}$	Normal	$1{,}665 \cdot 10^{-2}$ $\mu g_{Pb} \cdot kg^{-1}$	1	0,0166 $\mu g_{Pb} \cdot kg^{-1}$
$\overline{w_{Pb}}$	1,0758 $\mu g_{Pb} \cdot kg^{-1}$				0,0380 $\mu g_{Pb} \cdot kg^{-1}$

Standard uncertainty: 0,0380 $\mu g_{Pb} \cdot kg^{-1}$
Expanded uncertainty (k=2): 0,0760 $\mu g_{Pb} \cdot kg^{-1}$
Measurements result: $\overline{w_{Pb}} = (1{,}076 \pm 0{,}076)\ \mu g_{Pb} \cdot kg^{-1}$

Table 8. Uncertainty budget for Zinc

Uncertainty source	Estimate	Uncertainty distribution	Standard uncertainty	Sensitivity coefficient	Contribution to standard uncertainty
X_i	x_i		u_i	c_i	$u_i c_i$
Ratio of signals intensities, S_{Zn}/S_{Ge}	$3{,}7061 \cdot 10^{-1}$ CPS(Zn) / CPS(Ge)	Normal	$6{,}30 \cdot 10^{-3}$ CPS(Zn) / CPS(Ge)	33,3 $\mu g_{Zn} \cdot kg^{-1} \cdot$ CPS(Ge)/ CPS(Zn)	0,210 $\mu g_{Zn} \cdot kg^{-1}$
Intercept of the calibration Curve, b	$8{,}334 \cdot 10^{-2}$ CPS(Zn) / CPS(Ge)	Normal	$6{,}04 \cdot 10^{-3}$ CPS(Zn) / CPS(Ge)	-33,3 $\mu g_{Zn} \cdot kg^{-1} \cdot$ CPS(Ge)/ CPS(Zn)	-0,201 $\mu g_{Zn} \cdot kg^{-1}$
Slope of the calibration Curve, a	1,2009 CPS(Zn) / CPS(Ge) / $\mu g_{Zn} \cdot kg^{-1}$ / $\mu g_{Ge} \cdot kg^{-1}$	Normal	$2{,}00 \cdot 10^{-2}$ CPS(Zn) / CPS(Ge) / $\mu g_{Zn} \cdot kg^{-1}$ / $\mu g_{Ge} \cdot kg^{-1}$	-7,97 $(\mu g_{Zn} \cdot kg^{-1})^2 \cdot$ CPS(Ge)/ $\mu g_{Ge} \cdot kg^{-1} \cdot$ CPS(Zn)	-0,159 $\mu g_{Zn} \cdot kg^{-1}$
Mass fraction of the internal standard, w_{Ge}	10 $\mu g_{Ge} \cdot kg^{-1}$	Normal	$2 \cdot 10^{-5}$ $\mu g_{Ge} \cdot kg^{-1}$	$9{,}5687 \cdot 10^{-1}$ $\mu g_{Zn} \cdot kg^{-1}$ / $\mu g_{Ge} \cdot kg^{-1}$	$2 \cdot 10^{-5}$ $\mu g_{Zn} \cdot kg^{-1}$
Sample dilution factor, D	4	Normal	$6 \cdot 10^{-5}$	2,392 $\mu g_{Zn} \cdot kg^{-1}$	$2 \cdot 10^{-4}$ $\mu g_{Zn} \cdot kg^{-1}$
Calibration standards, *cal*	987547 $\mu g_{Zn} \cdot kg^{-1}$	Rectangular	$3{,}225 \cdot 10^{-2}$ $\mu g_{Zn} \cdot kg^{-1}$	1	0,032 $\mu g_{Zn} \cdot kg^{-1}$
Blank, *blank*	$2{,}74 \cdot 10^{-1}$ $\mu g_{Zn} \cdot kg^{-1}$	Rectangular	$7{,}0774 \cdot 10^{-1}$ $\mu g_{Zn} \cdot kg^{-1}$	1	0,708 $\mu g_{Zn} \cdot kg^{-1}$
Recovery, *recov*	99 %	Rectangular	$2{,}0890 \cdot 10^{-1}$ $\mu g_{Zn} \cdot kg^{-1}$	1	0,209 $\mu g_{Zn} \cdot kg^{-1}$
Instrument drift, *drift*	10 %	Rectangular	$5{,}3146 \cdot 10^{-1}$ $\mu g_{Zn} \cdot kg^{-1}$	1	0,531 $\mu g_{Zn} \cdot kg^{-1}$
Repeatability, $s(\overline{w_{Zn}})$	9,205 $\mu g_{Zn} \cdot kg^{-1}$	Normal	$1{,}9399 \cdot 10^{-1}$ $\mu g_{Zn} \cdot kg^{-1}$	1	0,194 $\mu g_{Zn} \cdot kg^{-1}$
$\overline{w_{Zn}}$	9,205 $\mu g_{Zn} \cdot kg^{-1}$				0,988 $\mu g_{Zn} \cdot kg^{-1}$

Standard uncertainty: 0,988 $\mu g_{Zn} \cdot kg^{-1}$
Expanded uncertainty (k=2): 1,975 $\mu g_{Zn} \cdot kg^{-1}$
Measurements result: $\overline{w_{Zn}}$ = (9,21± 1,98) $\mu g_{Zn} \cdot kg^{-1}$

Table 9. Contribution of uncertainty sources to the total relative standard uncertainty for element

Source of uncertainty	Uncertainties contribution, %					
	As	Cd	Cu	Ni	Pb	Zn
$(\frac{S_x}{S_{IS}})$	14	31	20	4	1	5
b	2	12	6	3	3	4
a	1	1	2	2	0	3
w_{IS}	0	0	0	0	0	0
D	1	4	1	1	5	0
cal	0	0	0	0	0	0
blk	0	3	2	1	1	51
recov	23	6	23	18	5	4
drift	54	28	43	66	67	29
repeat	6	15	4	5	19	4

Uncertainty Information from NML

6. Detail of the uncertainty estimation
   - Complete specification of the measurement equations:

$$Conc\left(\frac{ug}{kg}\right) = \text{conc from linear regression} * \text{df}$$

$$\boldsymbol{u_{Conc}} = Conc * \sqrt{\left(\frac{u_{Creg}}{Creg}\right)^2 + \left(\frac{u_{mass\ sample}}{mass\ sample}\right)^2 + \left(\frac{u_{mass\ soln}}{mass\ soln}\right)^2 + (Precision\ RSD)^2 + \left(\frac{u_{recovery}}{recovery}\right)^2}$$

   - Description of all uncertainty sources and their typical values:

Uncertainty sources	u/x
Concentration of analyte in solution	0.0878561
Sample Preparation (mass sample)	0.0008696
Sample Preparation (mass solution)	0.0000122
Method Precision	0.0229789
Method recovery	0.0079051

APPENDIX E: NDT Reports of Arsenic, Cadmium, Copper, Lead, Nickel, Zinc and Tributyltin in CCQM-K155

Arsenic

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	FTMC*	2.650	0.490	9
TRUE	UME	3.590	0.090	60
TRUE	HSA	3.770	0.100	5
TRUE	NIMT	3.790	0.100	60
TRUE	NIM	3.798	0.071	60
TRUE	NRC	3.820	0.080	60
TRUE	LNE	3.820	0.240	60
TRUE	ISP	3.880	0.247	4
TRUE	GUM	3.880	0.190	60
TRUE	GLHK	3.900	0.140	60
TRUE	UNIIM	4.100	0.250	60
TRUE	NMIJ	4.210	0.130	60
FALSE	NML*	3.760	0.340	60

Date: 2023-11-08
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 1000
Selected Procedure: Adaptive Weighted Average
Consensus estimate: 3.832
Standard uncertainty: 0.04927
Standard uncertainty (using parametric bootstrap): 0.05
95% coverage interval: (3.736, 3.929)
95% coverage interval (using parametric bootstrap): (3.733, 3.932)
Dark uncertainty (tau): 0.1016

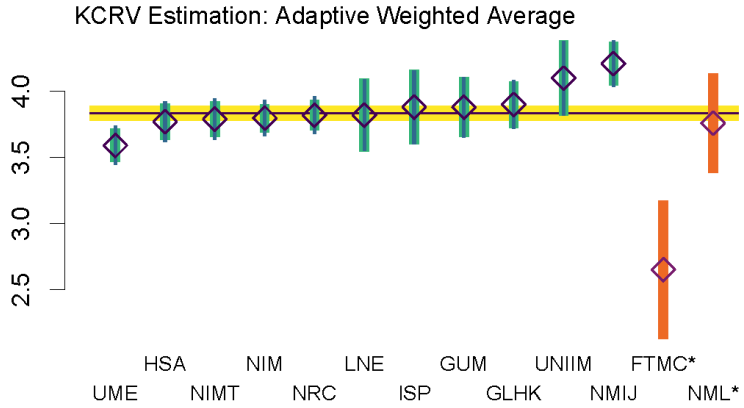
Decision Tree Hypothesis test results

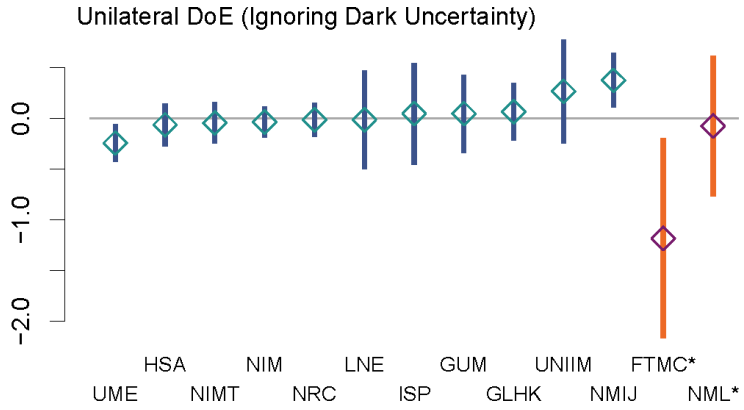
Cochran's test for Homogeneity:
p-value: 0.061
Q = 17.66 (Reference Distribution: Chi-Square with 10 Degrees of Freedom)
tau est. = 0.1016
tau/median(x) = 0.02659
tau/median(u) = 0.7812

Shapiro-Wilk test for Normality: p = 0.1554

Miao-Gel-Gastwirth test of Symmetry: p = 0.1096

Plots


KCRV Estimation: Adaptive Weighted Average
4.0
3.5
3.0
2.5
HSA
NIM
LNE
GUM
UNIIM
FTMC*
UME
NIMT
NRC
ISP
GLHK
NMIJ
NML*


Unilateral DoE (Ignoring Dark Uncertainty)
0.0
−1.0
−2.0
HSA
NIM
LNE
GUM
UNIIM
FTMC*
UME
NIMT
NRC
ISP
GLHK
NMIJ
NML*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
UME	UME	-0.24240	0.1635	-0.4060	-0.07891
HSA	HSA	-0.06244	0.1854	-0.2478	0.12290
NIMT	NIMT	-0.04244	0.1827	-0.2251	0.14020
NIM	NIM	-0.03444	0.1320	-0.1664	0.09754
NRC	NRC	-0.01244	0.1417	-0.1541	0.12930
LNE	LNE	-0.01244	0.4606	-0.4730	0.44810
ISP	ISP	0.04756	0.4781	-0.4305	0.52570
GUM	GUM	0.04756	0.3630	-0.3154	0.41060
GLHK	GLHK	0.06756	0.2620	-0.1944	0.32960
UNIIM	UNIIM	0.26760	0.4868	-0.2192	0.75440
NMIJ	NMIJ	0.37760	0.2457	0.1319	0.62320
FTMC*	FTMC*	-1.18200	0.9629	-2.1450	-0.21960
NML*	NML*	-0.07244	0.6700	-0.7424	0.59750

Lab Uncertainties Table

lab	x	u	nu	ut
FTMC*	2.650	0.490	9	0.5004
UME	3.590	0.090	60	0.1357
HSA	3.770	0.100	5	0.1425
NIMT	3.790	0.100	60	0.1425
NIM	3.798	0.071	60	0.1239
NRC	3.820	0.080	60	0.1293
LNE	3.820	0.240	60	0.2606
ISP	3.880	0.247	4	0.2671
GUM	3.880	0.190	60	0.2154
GLHK	3.900	0.140	60	0.1730
UNIIM	4.100	0.250	60	0.2698
NMIJ	4.210	0.130	60	0.1650
NML*	3.760	0.340	60	0.3548

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
FTMC*	-1.18200	0.5029	0.9857	-2.16800	-0.196700	0.49130	0.9629	-2.1450	-0.21960
UME	-0.24240	0.1252	0.2481	-0.49050	0.005633	0.08322	0.1635	-0.4060	-0.07891
HSA	-0.06244	0.1396	0.2790	-0.34150	0.216600	0.09462	0.1854	-0.2478	0.12290
NIMT	-0.04244	0.1353	0.2666	-0.30900	0.224100	0.09346	0.1827	-0.2251	0.14020
NIM	-0.03444	0.1176	0.2433	-0.27770	0.208800	0.06618	0.1320	-0.1664	0.09754
NRC	-0.01244	0.1205	0.2475	-0.26000	0.235100	0.07274	0.1417	-0.1541	0.12930
LNE	-0.01244	0.2584	0.5005	-0.51290	0.488100	0.23720	0.4606	-0.4730	0.44810
ISP	0.04756	0.2678	0.5237	-0.47610	0.571200	0.24460	0.4781	-0.4305	0.52570
GUM	0.04756	0.2119	0.4165	-0.36900	0.464100	0.18600	0.3630	-0.3154	0.41060
GLHK	0.06756	0.1649	0.3171	-0.24950	0.384600	0.13430	0.2620	-0.1944	0.32960
UNIIM	0.26760	0.2704	0.5268	-0.25920	0.794300	0.25070	0.4868	-0.2192	0.75440
NMIJ	0.37760	0.1599	0.3120	0.06554	0.689600	0.12650	0.2457	0.1319	0.62320
NML*	-0.07244	0.3584	0.7024	-0.77490	0.630000	0.34180	0.6700	-0.7424	0.59750

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

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	FTMC*	2.650	0.490	9
TRUE	UME	3.590	0.090	60
TRUE	HSA	3.770	0.100	5
TRUE	NIMT	3.790	0.100	60
TRUE	NIM	3.798	0.071	60
TRUE	NRC	3.820	0.080	60
TRUE	LNE	3.820	0.240	60
TRUE	ISP	3.880	0.247	4
TRUE	GUM	3.880	0.190	60
TRUE	GLHK	3.900	0.140	60
TRUE	UNIIM	4.100	0.250	60
TRUE	NMIJ	4.210	0.130	60
FALSE	NML*	3.760	0.340	60

Date: 2023-11-08
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 1000
Selected Procedure: Adaptive Weighted Average
Consensus estimate: 3.832
Standard uncertainty: 0.04927
Standard uncertainty (using parametric bootstrap): 0.05
95% coverage interval: (3.736, 3.929)
95% coverage interval (using parametric bootstrap): (3.733, 3.932)
Dark uncertainty (tau): 0.1016

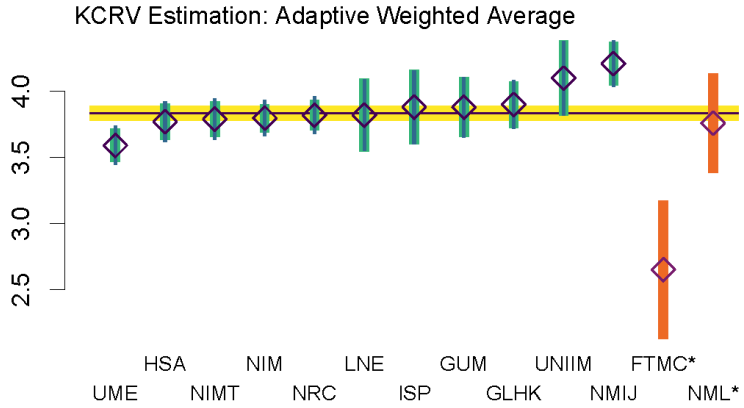
Decision Tree Hypothesis test results

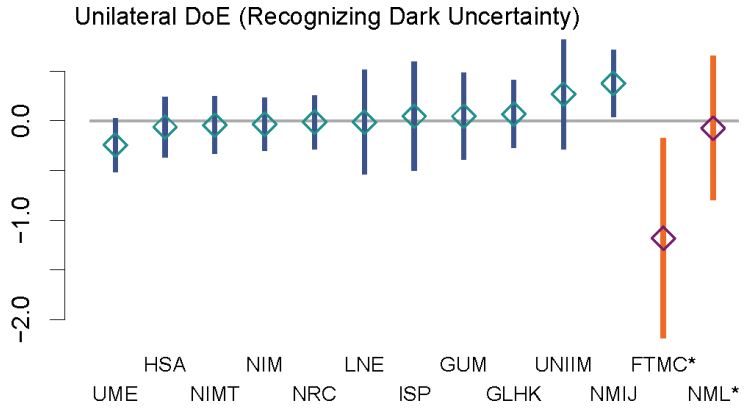
Cochran's test for Homogeneity:
p-value: 0.061
Q = 17.66 (Reference Distribution: Chi-Square with 10 Degrees of Freedom)
tau est. = 0.1016
tau/median(x) = 0.02659
tau/median(u) = 0.7812

Shapiro-Wilk test for Normality: p = 0.1554

Miao-Gel-Gastwirth test of Symmetry: p = 0.1162

Plots


KCRV Estimation: Adaptive Weighted Average
4.0
3.5
3.0
2.5
HSA
NIM
LNE
GUM
UNIIM
FTMC*
UME
NIMT
NRC
ISP
GLHK
NMIJ
NML*


Unilateral DoE (Recognizing Dark Uncertainty)
0.0
−1.0
−2.0
HSA
NIM
LNE
GUM
UNIIM
FTMC*
UME
NIMT
NRC
ISP
GLHK
NMIJ
NML*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
UME	UME	-0.24240	0.2481	-0.49050	0.005633
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NIM	NIM	-0.03444	0.2433	-0.27770	0.208800
NRC	NRC	-0.01244	0.2475	-0.26000	0.235100
LNE	LNE	-0.01244	0.5005	-0.51290	0.488100
ISP	ISP	0.04756	0.5237	-0.47610	0.571200
GUM	GUM	0.04756	0.4165	-0.36900	0.464100
GLHK	GLHK	0.06756	0.3171	-0.24950	0.384600
UNIIM	UNIIM	0.26760	0.5268	-0.25920	0.794300
NMIJ	NMIJ	0.37760	0.3120	0.06554	0.689600
FTMC*	FTMC*	-1.18200	0.9857	-2.16800	-0.196700
NML*	NML*	-0.07244	0.7024	-0.77490	0.630000

Lab Uncertainties Table

lab	x	u	nu	ut
FTMC*	2.650	0.490	9	0.5004
UME	3.590	0.090	60	0.1357
HSA	3.770	0.100	5	0.1425
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NIM	3.798	0.071	60	0.1239
NRC	3.820	0.080	60	0.1293
LNE	3.820	0.240	60	0.2606
ISP	3.880	0.247	4	0.2671
GUM	3.880	0.190	60	0.2154
GLHK	3.900	0.140	60	0.1730
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NMIJ	4.210	0.130	60	0.1650
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lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
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HSA	-0.06244	0.1396	0.2790	-0.34150	0.216600	0.09462	0.1854	-0.2478	0.12290
NIMT	-0.04244	0.1353	0.2666	-0.30900	0.224100	0.09346	0.1827	-0.2251	0.14020
NIM	-0.03444	0.1176	0.2433	-0.27770	0.208800	0.06618	0.1320	-0.1664	0.09754
NRC	-0.01244	0.1205	0.2475	-0.26000	0.235100	0.07274	0.1417	-0.1541	0.12930
LNE	-0.01244	0.2584	0.5005	-0.51290	0.488100	0.23720	0.4606	-0.4730	0.44810
ISP	0.04756	0.2678	0.5237	-0.47610	0.571200	0.24460	0.4781	-0.4305	0.52570
GUM	0.04756	0.2119	0.4165	-0.36900	0.464100	0.18600	0.3630	-0.3154	0.41060
GLHK	0.06756	0.1649	0.3171	-0.24950	0.384600	0.13430	0.2620	-0.1944	0.32960
UNIIM	0.26760	0.2704	0.5268	-0.25920	0.794300	0.25070	0.4868	-0.2192	0.75440
NMIJ	0.37760	0.1599	0.3120	0.06554	0.689600	0.12650	0.2457	0.1319	0.62320
NML*	-0.07244	0.3584	0.7024	-0.77490	0.630000	0.34180	0.6700	-0.7424	0.59750

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.

Cadmium

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	ISP*	0.1940	0.0069	2
TRUE	NMIJ	0.2190	0.0050	60
TRUE	UME	0.2232	0.0028	60
TRUE	NIM	0.2250	0.0060	60
TRUE	GLHK	0.2254	0.0042	60
TRUE	HSA	0.2301	0.0042	60
TRUE	GUM	0.2320	0.0140	60
FALSE	NIMT*	0.2580	0.0060	60
TRUE	UNIIM	0.2600	0.0150	60
TRUE	KRISS	0.2800	0.0070	4
FALSE	FTMC*	0.3290	0.0370	9
FALSE	VNIIFTRI*	0.5350	0.0380	60

Date: 2024-04-22
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 1000
Selected Procedure: Hierarchical Laplace-Gauss
Consensus estimate: 0.2283
Standard uncertainty: 0.004409
95% coverage interval: (0.2196, 0.2371)
Dark uncertainty (tau): 0.01008
Tau posterior 0.025 and 0.975 quantiles: (0.0003426,0.03277)

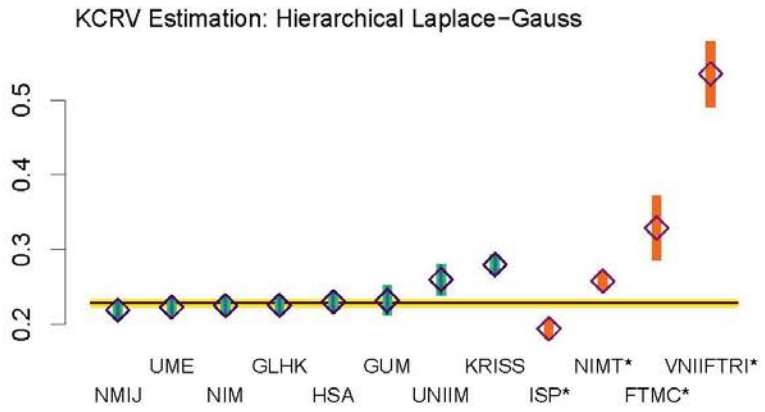
Decision Tree Hypothesis test results

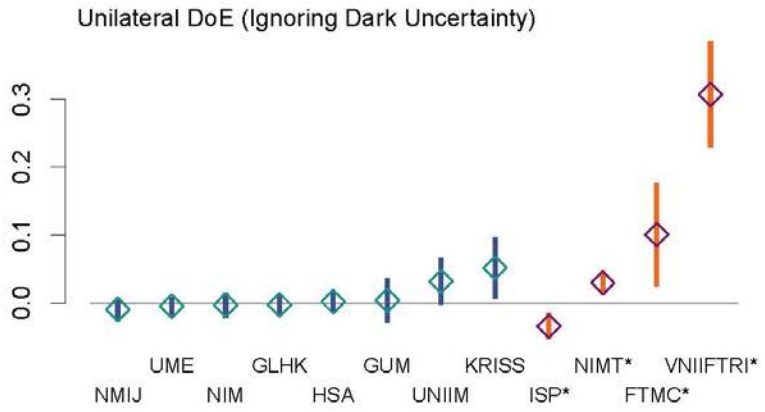
Cochran's test for Homogeneity:
p-value: $p < 0.001$
$Q = 66.82$ (Reference Distribution: Chi-Square with 7 Degrees of Freedom)
tau est. = 0.01507
tau/median(x) = 0.06619
tau/median(u) = 2.741

Shapiro-Wilk test for Normality: $p = 0.02118$

Miao-Gel-Gastwirth test of Symmetry: $p = 0.0268$

Plots


KCRV Estimation: Hierarchical Laplace−Gauss
0.2
0.3
0.4
0.5
NMIJ
UME
NIM
GLHK
HSA
GUM
UNIIM
KRISS
ISP*
NIMT*
FTMC*
VNIIFTRI*


Unilateral DoE (Ignoring Dark Uncertainty)
0.0
0.1
0.2
0.3
NMIJ
UME
NIM
GLHK
HSA
GUM
UNIIM
KRISS
ISP*
NIMT*
FTMC*
VNIIFTRI*

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
UNIIM	0.031650	0.02163	0.04312	-0.011460	0.0747700	0.015930	0.03142	0.0002333	0.063080
KRISS	0.051650	0.02509	0.05045	0.001200	0.1021000	0.020400	0.04220	0.0094510	0.093860
FTMC*	0.100700	0.04004	0.07871	0.021940	0.1794000	0.037320	0.07298	0.0276700	0.173600
VNIIFTRI*	0.306700	0.04086	0.08051	0.226100	0.3872000	0.038310	0.07511	0.2315000	0.381800

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	9500
lambda[1]	1.001	15000
lambda[2]	1.001	27000
lambda[3]	1.001	50000
lambda[4]	1.001	22000
lambda[5]	1.001	16000
lambda[6]	1.001	25000
lambda[7]	1.001	6400
lambda[8]	1.001	8100
mu	1.001	29000
sigma[1]	1.001	33000
sigma[2]	1.001	50000
sigma[3]	1.001	50000
sigma[4]	1.001	24000
sigma[5]	1.001	50000
sigma[6]	1.001	22000
sigma[7]	1.001	27000
sigma[8]	1.001	13000
tau	1.001	7000

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
ISP*	ISP*	-0.034350	0.01609	-0.0504400	-0.018260
NMIJ	NMIJ	-0.009346	0.01333	-0.0226800	0.003987
UME	UME	-0.005146	0.01036	-0.0155100	0.005215
NIM	NIM	-0.003346	0.01481	-0.0181600	0.011470
GLHK	GLHK	-0.002946	0.01216	-0.0151100	0.009214
HSA	HSA	0.001754	0.01214	-0.0103900	0.013900
GUM	GUM	0.003654	0.02888	-0.0252300	0.032530
NIMT*	NIMT*	0.029650	0.01458	0.0150800	0.044230
UNIIM	UNIIM	0.031650	0.03142	0.0002333	0.063080
KRISS	KRISS	0.051650	0.04220	0.0094510	0.093860
FTMC*	FTMC*	0.100700	0.07298	0.0276700	0.173600
VNIIFTRI*	VNIIFTRI*	0.306700	0.07511	0.2315000	0.381800

Lab Uncertainties Table

lab	x	u	nu	ut
ISP*	0.1940	0.0069	2	0.01222
NMIJ	0.2190	0.0050	60	0.01125
UME	0.2232	0.0028	60	0.01046
NIM	0.2250	0.0060	60	0.01173
GLHK	0.2254	0.0042	60	0.01092
HSA	0.2301	0.0042	60	0.01092
GUM	0.2320	0.0140	60	0.01725
NIMT*	0.2580	0.0060	60	0.01173
UNIIM	0.2600	0.0150	60	0.01807
KRISS	0.2800	0.0070	4	0.01227
FTMC*	0.3290	0.0370	9	0.03835
VNIIFTRI*	0.5350	0.0380	60	0.03931

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
ISP*	-0.034350	0.01662	0.03450	-0.068840	0.0001518	0.008210	0.01609	-0.0504400	-0.018260
NMIJ	-0.009346	0.01590	0.03329	-0.042640	0.0239400	0.006739	0.01333	-0.0226800	0.003987
UME	-0.005146	0.01548	0.03309	-0.038230	0.0279400	0.005232	0.01036	-0.0155100	0.005215
NIM	-0.003346	0.01648	0.03418	-0.037520	0.0308300	0.007533	0.01481	-0.0181600	0.011470
GLHK	-0.002946	0.01568	0.03318	-0.036130	0.0302300	0.006137	0.01216	-0.0151100	0.009214
HSA	0.001754	0.01578	0.03331	-0.031560	0.0350600	0.006136	0.01214	-0.0103900	0.013900
GUM	0.003654	0.02077	0.04126	-0.037610	0.0449200	0.014780	0.02888	-0.0252300	0.032530
NIMT*	0.029650	0.01645	0.03435	-0.004695	0.0640000	0.007427	0.01458	0.0150800	0.044230

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	ISP*	0.1940	0.0069	2
TRUE	NMIJ	0.2190	0.0050	60
TRUE	UME	0.2232	0.0028	60
TRUE	NIM	0.2250	0.0060	60
TRUE	GLHK	0.2254	0.0042	60
TRUE	HSA	0.2301	0.0042	60
TRUE	GUM	0.2320	0.0140	60
FALSE	NIMT*	0.2580	0.0060	60
TRUE	UNIIM	0.2600	0.0150	60
TRUE	KRISS	0.2800	0.0070	4
FALSE	FTMC*	0.3290	0.0370	9
FALSE	VNIIFTRI*	0.5350	0.0380	60

Date: 2024-04-22
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 1000
Selected Procedure: Hierarchical Laplace-Gauss
Consensus estimate: 0.2283
Standard uncertainty: 0.004409
95% coverage interval: (0.2196, 0.2371)
Dark uncertainty (tau): 0.01008
Tau posterior 0.025 and 0.975 quantiles: (0.0003426,0.03277)

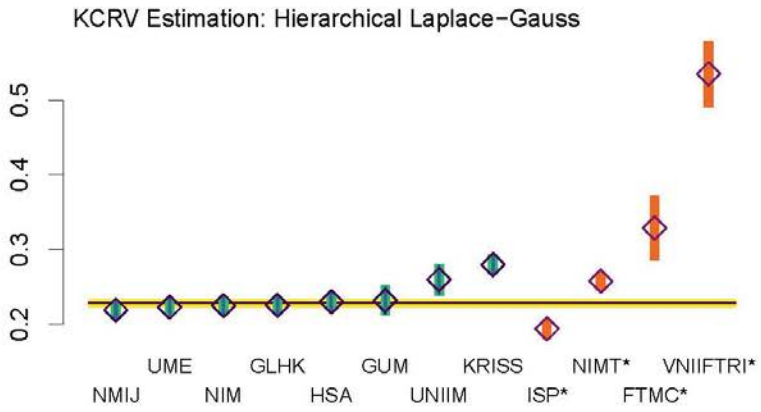
Decision Tree Hypothesis test results

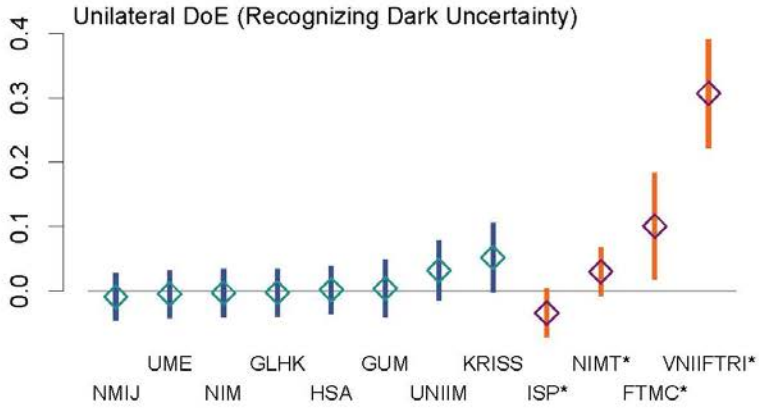
Cochran's test for Homogeneity:
p-value: $p < 0.001$
$Q = 66.82$ (Reference Distribution: Chi-Square with 7 Degrees of Freedom)
tau est. $= 0.01507$
tau/median(x) $= 0.06619$
tau/median(u) $= 2.741$

Shapiro-Wilk test for Normality: $p = 0.02118$

Miao-Gel-Gastwirth test of Symmetry: $p = 0.023$

Plots


KCRV Estimation: Hierarchical Laplace−Gauss
0.2
0.3
0.4
0.5
NMIJ
UME
NIM
GLHK
HSA
GUM
UNIIM
KRISS
ISP*
NIMT*
FTMC*
VNIIFTRI*


Unilateral DoE (Recognizing Dark Uncertainty)
0.0
0.1
0.2
0.3
0.4
NMIJ
UME
NIM
GLHK
HSA
GUM
UNIIM
KRISS
ISP*
NIMT*
FTMC*
VNIIFTRI*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
ISP*	ISP*	-0.034350	0.03450	-0.068840	0.0001518
NMIJ	NMIJ	-0.009346	0.03329	-0.042640	0.0239400
UME	UME	-0.005146	0.03309	-0.038230	0.0279400
NIM	NIM	-0.003346	0.03418	-0.037520	0.0308300
GLHK	GLHK	-0.002946	0.03318	-0.036130	0.0302300
HSA	HSA	0.001754	0.03331	-0.031560	0.0350600
GUM	GUM	0.003654	0.04126	-0.037610	0.0449200
NIMT*	NIMT*	0.029650	0.03435	-0.004695	0.0640000
UNIIM	UNIIM	0.031650	0.04312	-0.011460	0.0747700
KRISS	KRISS	0.051650	0.05045	0.001200	0.1021000
FTMC*	FTMC*	0.100700	0.07871	0.021940	0.1794000
VNIIFTRI*	VNIIFTRI*	0.306700	0.08051	0.226100	0.3872000

Lab Uncertainties Table

lab	x	u	nu	ut
ISP*	0.1940	0.0069	2	0.01222
NMIJ	0.2190	0.0050	60	0.01125
UME	0.2232	0.0028	60	0.01046
NIM	0.2250	0.0060	60	0.01173
GLHK	0.2254	0.0042	60	0.01092
HSA	0.2301	0.0042	60	0.01092
GUM	0.2320	0.0140	60	0.01725
NIMT*	0.2580	0.0060	60	0.01173
UNIIM	0.2600	0.0150	60	0.01807
KRISS	0.2800	0.0070	4	0.01227
FTMC*	0.3290	0.0370	9	0.03835
VNIIFTRI*	0.5350	0.0380	60	0.03931

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
ISP*	-0.034350	0.01662	0.03450	-0.068840	0.0001518	0.008210	0.01609	-0.0504400	-0.018260
NMIJ	-0.009346	0.01590	0.03329	-0.042640	0.0239400	0.006739	0.01333	-0.0226800	0.003987
UME	-0.005146	0.01548	0.03309	-0.038230	0.0279400	0.005232	0.01036	-0.0155100	0.005215
NIM	-0.003346	0.01648	0.03418	-0.037520	0.0308300	0.007533	0.01481	-0.0181600	0.011470
GLHK	-0.002946	0.01568	0.03318	-0.036130	0.0302300	0.006137	0.01216	-0.0151100	0.009214
HSA	0.001754	0.01578	0.03331	-0.031560	0.0350600	0.006136	0.01214	-0.0103900	0.013900
GUM	0.003654	0.02077	0.04126	-0.037610	0.0449200	0.014780	0.02888	-0.0252300	0.032530
NIMT*	0.029650	0.01645	0.03435	-0.004695	0.0640000	0.007427	0.01458	0.0150800	0.044230

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
UNIIM	0.031650	0.02163	0.04312	-0.011460	0.0747700	0.015930	0.03142	0.0002333	0.063080
KRISS	0.051650	0.02509	0.05045	0.001200	0.1021000	0.020400	0.04220	0.0094510	0.093860
FTMC*	0.100700	0.04004	0.07871	0.021940	0.1794000	0.037320	0.07298	0.0276700	0.173600
VNIIFTRI*	0.306700	0.04086	0.08051	0.226100	0.3872000	0.038310	0.07511	0.2315000	0.381800

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	9500
lambda[1]	1.001	15000
lambda[2]	1.001	27000
lambda[3]	1.001	50000
lambda[4]	1.001	22000
lambda[5]	1.001	16000
lambda[6]	1.001	25000
lambda[7]	1.001	6400
lambda[8]	1.001	8100
mu	1.001	29000
sigma[1]	1.001	33000
sigma[2]	1.001	50000
sigma[3]	1.001	50000
sigma[4]	1.001	24000
sigma[5]	1.001	50000
sigma[6]	1.001	22000
sigma[7]	1.001	27000
sigma[8]	1.001	13000
tau	1.001	7000

Copper

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	ISP	2.950	0.110	7
TRUE	GUM	3.000	0.160	60
TRUE	UME	3.022	0.022	60
TRUE	NMIJ	3.050	0.040	60
TRUE	GLHK	3.090	0.050	60
TRUE	KRISS	3.093	0.008	50
TRUE	HSA	3.107	0.082	60
TRUE	NIM	3.269	0.061	60
TRUE	NMIA	3.280	0.140	30
FALSE	FTMC*	3.310	0.310	9
TRUE	UNIIM	4.000	0.400	60
FALSE	VNIIFTRI*	7.930	0.490	60

Date: 2023-11-04
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 1000
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 3.099
Standard uncertainty: 0.03544
95% coverage interval: (3.028, 3.17)
Dark uncertainty (tau): 0.06788
Tau posterior 0.025 and 0.975 quantiles: (0.01648,0.1693)

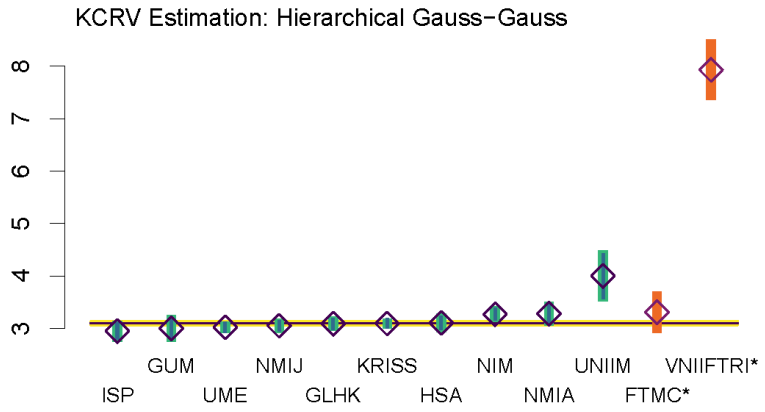
Decision Tree Hypothesis test results

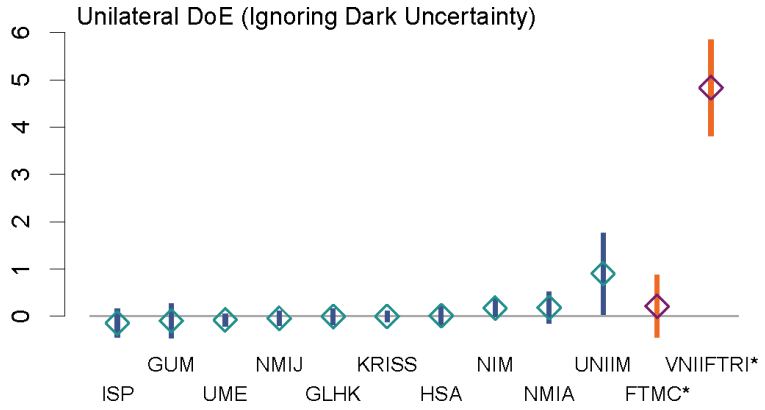
Cochran's test for Homogeneity:
p-value: $p < 0.001$
$Q = 28.06$ (Reference Distribution: Chi-Square with 9 Degrees of Freedom)
tau est. = 0.05451
tau/median(x) = 0.01763
tau/median(u) = 0.7624

Shapiro-Wilk test for Normality: $p = 0.9204$

Miao-Gel-Gastwirth test of Symmetry: $p = 0.2356$

Plots


KCRV Estimation: Hierarchical Gauss−Gauss
3
4
5
6
7
8
ISP
GUM
UME
NMIJ
GLHK
KRISS
HSA
NIM
NMIA
UNIIM
FTMC*
VNIIFTRI*


Unilateral DoE (Ignoring Dark Uncertainty)
0
1
2
3
4
5
6
ISP
GUM
UME
NMIJ
GLHK
KRISS
HSA
NIM
NMIA
UNIIM
FTMC*
VNIIFTRI*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
ISP	ISP	-0.148900	0.25550	-0.40440	0.106600
GUM	GUM	-0.098870	0.32250	-0.42130	0.223600
UME	UME	-0.076870	0.08266	-0.15950	0.005792
NMIJ	NMIJ	-0.048870	0.10660	-0.15540	0.057710
GLHK	GLHK	-0.008867	0.12230	-0.13120	0.113400
KRISS	KRISS	-0.005867	0.07215	-0.07801	0.066280
HSA	HSA	0.008133	0.17790	-0.16980	0.186100
NIM	NIM	0.170100	0.14220	0.02794	0.312300
NMIA	NMIA	0.181100	0.29030	-0.10920	0.471400
FTMC*	FTMC*	0.211100	0.60870	-0.39750	0.819800
UNIIM	UNIIM	0.901100	0.81600	0.08516	1.717000
VNIIFTRI*	VNIIFTRI*	4.831000	0.96660	3.86500	5.798000

Lab Uncertainties Table

lab	x	u	nu	ut
ISP	2.950	0.110	7	0.12930
GUM	3.000	0.160	60	0.17380
UME	3.022	0.022	60	0.07136
NMIJ	3.050	0.040	60	0.07879
GLHK	3.090	0.050	60	0.08431
KRISS	3.093	0.008	50	0.06835
HSA	3.107	0.082	60	0.10650
NIM	3.269	0.061	60	0.09126
NMIA	3.280	0.140	30	0.15560
FTMC*	3.310	0.310	9	0.31730
UNIIM	4.000	0.400	60	0.40570
VNIIFTRI*	7.930	0.490	60	0.49470

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
ISP	-0.148900	0.15210	0.3044	-0.45330	0.1556	0.12860	0.25550	-0.40440	0.106600
GUM	-0.098870	0.18460	0.3619	-0.46070	0.2630	0.16520	0.32250	-0.42130	0.223600
UME	-0.076870	0.09393	0.1933	-0.27020	0.1164	0.04196	0.08266	-0.15950	0.005792
NMIJ	-0.048870	0.10050	0.2018	-0.25070	0.1529	0.05419	0.10660	-0.15540	0.057710
GLHK	-0.008867	0.10280	0.2067	-0.21560	0.1979	0.06219	0.12230	-0.13120	0.113400
KRISS	-0.005867	0.09153	0.1886	-0.19450	0.1828	0.03634	0.07215	-0.07801	0.066280
HSA	0.008133	0.12320	0.2447	-0.23660	0.2529	0.09054	0.17790	-0.16980	0.186100
NIM	0.170100	0.11090	0.2216	-0.05143	0.3917	0.07231	0.14220	0.02794	0.312300
NMIA	0.181100	0.17020	0.3356	-0.15450	0.5168	0.14710	0.29030	-0.10920	0.471400
FTMC*	0.211100	0.32390	0.6351	-0.42390	0.8462	0.31170	0.60870	-0.39750	0.819800
UNIIM	0.901100	0.42550	0.8406	0.06049	1.7420	0.41800	0.81600	0.08516	1.717000
VNIIFTRI*	4.831000	0.49770	0.9764	3.85500	5.8080	0.49200	0.96660	3.86500	5.798000

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	50000
lambda[2]	1.001	50000
lambda[3]	1.001	38000
lambda[4]	1.001	50000
lambda[5]	1.001	50000
lambda[6]	1.001	50000
lambda[7]	1.001	50000
lambda[8]	1.001	23000
lambda[9]	1.001	50000
lambda[10]	1.001	50000
mu	1.001	50000
sigma[1]	1.001	50000
sigma[2]	1.001	48000
sigma[3]	1.001	32000
sigma[4]	1.001	50000
sigma[5]	1.001	34000
sigma[6]	1.001	50000
sigma[7]	1.001	18000
sigma[8]	1.001	32000
sigma[9]	1.001	50000
sigma[10]	1.001	50000
tau	1.001	23000

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	ISP	2.950	0.110	7
TRUE	GUM	3.000	0.160	60
TRUE	UME	3.022	0.022	60
TRUE	NMIJ	3.050	0.040	60
TRUE	GLHK	3.090	0.050	60
TRUE	KRISS	3.093	0.008	50
TRUE	HSA	3.107	0.082	60
TRUE	NIM	3.269	0.061	60
TRUE	NMIA	3.280	0.140	30
FALSE	FTMC*	3.310	0.310	9
TRUE	UNIIM	4.000	0.400	60
FALSE	VNIIFTRI*	7.930	0.490	60

Date: 2023-11-04
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 1000
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 3.099
Standard uncertainty: 0.03544
95% coverage interval: (3.028, 3.17)
Dark uncertainty (tau): 0.06788
Tau posterior 0.025 and 0.975 quantiles: (0.01648,0.1693)

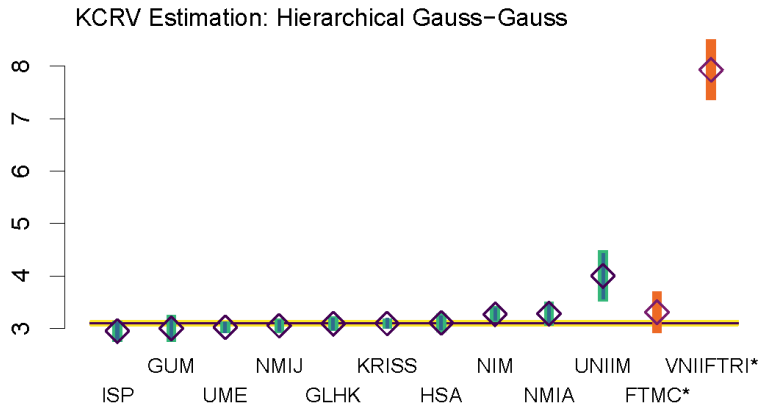
Decision Tree Hypothesis test results

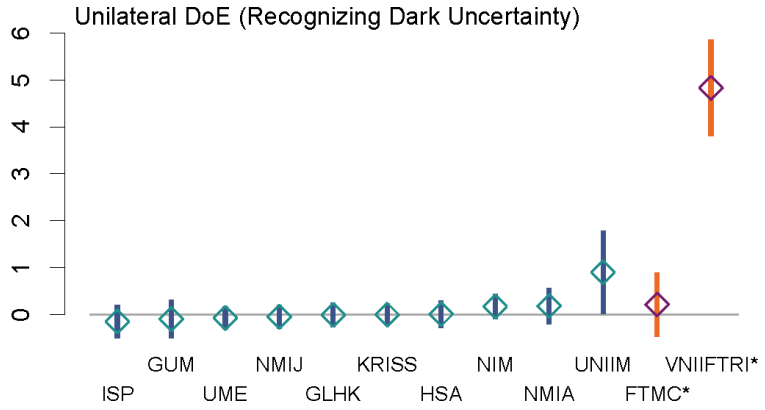
Cochran's test for Homogeneity:
p-value: $p < 0.001$
$Q = 28.06$ (Reference Distribution: Chi-Square with 9 Degrees of Freedom)
tau est. = 0.05451
tau/median(x) = 0.01763
tau/median(u) = 0.7624

Shapiro-Wilk test for Normality: $p = 0.9204$

Miao-Gel-Gastwirth test of Symmetry: $p = 0.2248$

Plots


KCRV Estimation: Hierarchical Gauss−Gauss
3
4
5
6
7
8
ISP
GUM
UME
NMIJ
GLHK
KRISS
HSA
NIM
NMIA
UNIIM
FTMC*
VNIIFTRI*


Unilateral DoE (Recognizing Dark Uncertainty)
0
1
2
3
4
5
6
ISP
GUM
UME
NMIJ
GLHK
KRISS
HSA
NIM
NMIA
UNIIM
FTMC*
VNIIFTRI*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
ISP	ISP	-0.148900	0.3044	-0.45330	0.1556
GUM	GUM	-0.098870	0.3619	-0.46070	0.2630
UME	UME	-0.076870	0.1933	-0.27020	0.1164
NMIJ	NMIJ	-0.048870	0.2018	-0.25070	0.1529
GLHK	GLHK	-0.008867	0.2067	-0.21560	0.1979
KRISS	KRISS	-0.005867	0.1886	-0.19450	0.1828
HSA	HSA	0.008133	0.2447	-0.23660	0.2529
NIM	NIM	0.170100	0.2216	-0.05143	0.3917
NMIA	NMIA	0.181100	0.3356	-0.15450	0.5168
FTMC*	FTMC*	0.211100	0.6351	-0.42390	0.8462
UNIIM	UNIIM	0.901100	0.8406	0.06049	1.7420
VNIIFTRI*	VNIIFTRI*	4.831000	0.9764	3.85500	5.8080

Lab Uncertainties Table

lab	x	u	nu	ut
ISP	2.950	0.110	7	0.12930
GUM	3.000	0.160	60	0.17380
UME	3.022	0.022	60	0.07136
NMIJ	3.050	0.040	60	0.07879
GLHK	3.090	0.050	60	0.08431
KRISS	3.093	0.008	50	0.06835
HSA	3.107	0.082	60	0.10650
NIM	3.269	0.061	60	0.09126
NMIA	3.280	0.140	30	0.15560
FTMC*	3.310	0.310	9	0.31730
UNIIM	4.000	0.400	60	0.40570
VNIIFTRI*	7.930	0.490	60	0.49470

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
ISP	-0.148900	0.15210	0.3044	-0.45330	0.1556	0.12860	0.25550	-0.40440	0.106600
GUM	-0.098870	0.18460	0.3619	-0.46070	0.2630	0.16520	0.32250	-0.42130	0.223600
UME	-0.076870	0.09393	0.1933	-0.27020	0.1164	0.04196	0.08266	-0.15950	0.005792
NMIJ	-0.048870	0.10050	0.2018	-0.25070	0.1529	0.05419	0.10660	-0.15540	0.057710
GLHK	-0.008867	0.10280	0.2067	-0.21560	0.1979	0.06219	0.12230	-0.13120	0.113400
KRISS	-0.005867	0.09153	0.1886	-0.19450	0.1828	0.03634	0.07215	-0.07801	0.066280
HSA	0.008133	0.12320	0.2447	-0.23660	0.2529	0.09054	0.17790	-0.16980	0.186100
NIM	0.170100	0.11090	0.2216	-0.05143	0.3917	0.07231	0.14220	0.02794	0.312300
NMIA	0.181100	0.17020	0.3356	-0.15450	0.5168	0.14710	0.29030	-0.10920	0.471400
FTMC*	0.211100	0.32390	0.6351	-0.42390	0.8462	0.31170	0.60870	-0.39750	0.819800
UNIIM	0.901100	0.42550	0.8406	0.06049	1.7420	0.41800	0.81600	0.08516	1.717000
VNIIFTRI*	4.831000	0.49770	0.9764	3.85500	5.8080	0.49200	0.96660	3.86500	5.798000

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	50000
lambda[2]	1.001	50000
lambda[3]	1.001	38000
lambda[4]	1.001	50000
lambda[5]	1.001	50000
lambda[6]	1.001	50000
lambda[7]	1.001	50000
lambda[8]	1.001	23000
lambda[9]	1.001	50000
lambda[10]	1.001	50000
mu	1.001	50000
sigma[1]	1.001	50000
sigma[2]	1.001	48000
sigma[3]	1.001	32000
sigma[4]	1.001	50000
sigma[5]	1.001	34000
sigma[6]	1.001	50000
sigma[7]	1.001	18000
sigma[8]	1.001	32000
sigma[9]	1.001	50000
sigma[10]	1.001	50000
tau	1.001	23000

Lead

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	ISP*	0.543	0.018	4
TRUE	INMETRO	0.982	0.041	60
TRUE	RISE	1.006	0.039	60
TRUE	NIMT	1.020	0.023	60
TRUE	UME	1.068	0.008	60
TRUE	NMIJ	1.070	0.030	60
TRUE	HSA	1.073	0.023	8
TRUE	GLHK	1.084	0.035	60
TRUE	NIM	1.088	0.017	60
TRUE	KRISS	1.113	0.026	4
TRUE	UNIIM	1.300	0.100	60
FALSE	FTMC*	1.360	0.130	9
FALSE	VNIIFTRI*	1.680	0.110	60
FALSE	GUM*	1.076	0.038	60

Date: 2023-11-04
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 1000
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 1.067
Standard uncertainty: 0.01212
95% coverage interval: (1.043, 1.092)
Dark uncertainty (tau): 0.02143
Tau posterior 0.025 and 0.975 quantiles: (0.001417,0.06419)

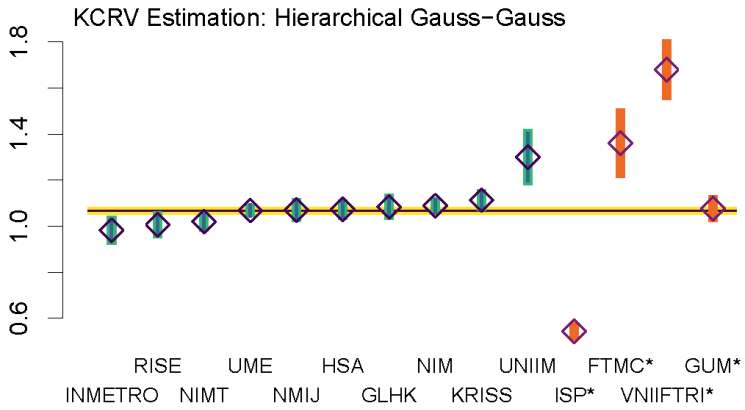
Decision Tree Hypothesis test results

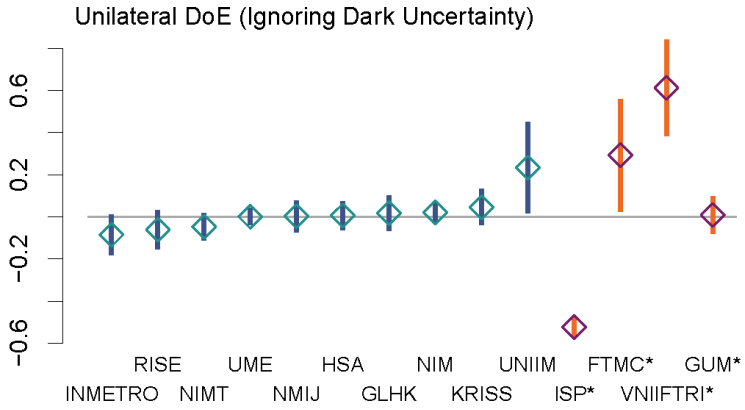
Cochran's test for Homogeneity:
p-value: 0.011
Q = 21.31 (Reference Distribution: Chi-Square with 9 Degrees of Freedom)
tau est. = 0.02621
tau/median(x) = 0.02446
tau/median(u) = 0.9359

Shapiro-Wilk test for Normality: p = 0.6361

Miao-Gel-Gastwirth test of Symmetry: p = 0.8262

Plots


KCRV Estimation: Hierarchical Gauss−Gauss
0.6
1.0
1.4
1.8
RISE
UME
HSA
NIM
UNIIM
FTMC*
GUM*
INMETRO
NIMT
NMIJ
GLHK
KRISS
ISP*
VNIIFTRI*


Unilateral DoE (Ignoring Dark Uncertainty)
−0.6
−0.2
0.2
0.6
RISE
UME
HSA
NIM
UNIIM
FTMC*
GUM*
INMETRO
NIMT
NMIJ
GLHK
KRISS
ISP*
VNIIFTRI*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
ISP*	ISP*	-0.5241000	0.04259	-0.56670	-0.481500
INMETRO	INMETRO	-0.0851200	0.08619	-0.17130	0.001069
RISE	RISE	-0.0611200	0.08125	-0.14240	0.020120
NIMT	NIMT	-0.0471200	0.05263	-0.09976	0.005511
UME	UME	0.0008763	0.02899	-0.02811	0.029860
NMIJ	NMIJ	0.0028760	0.06432	-0.06145	0.067200
HSA	HSA	0.0058760	0.05623	-0.05035	0.062110
GLHK	GLHK	0.0168800	0.07293	-0.05605	0.089810
NIM	NIM	0.0208800	0.04157	-0.02070	0.062450
KRISS	KRISS	0.0458800	0.07456	-0.02869	0.120400
UNIIM	UNIIM	0.2329000	0.20520	0.02769	0.438100
FTMC*	FTMC*	0.2929000	0.25590	0.03693	0.548800
VNIIFTRI*	VNIIFTRI*	0.6129000	0.21750	0.39540	0.830400
GUM*	GUM*	0.0088760	0.07843	-0.06955	0.087300

Lab Uncertainties Table

lab	x	u	nu	ut
ISP*	0.543	0.018	4	0.02799
INMETRO	0.982	0.041	60	0.04626
RISE	1.006	0.039	60	0.04450
NIMT	1.020	0.023	60	0.03144
UME	1.068	0.008	60	0.02288
NMIJ	1.070	0.030	60	0.03687
HSA	1.073	0.023	8	0.03144
GLHK	1.084	0.035	60	0.04104
NIM	1.088	0.017	60	0.02736
KRISS	1.113	0.026	4	0.03370
UNIIM	1.300	0.100	60	0.10230
FTMC*	1.360	0.130	9	0.13180
VNIIFTRI*	1.680	0.110	60	0.11210
GUM*	1.076	0.038	60	0.04363

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
ISP*	-0.5241000	0.03645	0.07368	-0.59780	-0.45040	0.02167	0.04259	-0.56670	-0.481500
INMETRO	-0.0851200	0.05256	0.10360	-0.18880	0.01851	0.04398	0.08619	-0.17130	0.001069
RISE	-0.0611200	0.05106	0.10070	-0.16180	0.03958	0.04137	0.08125	-0.14240	0.020120
NIMT	-0.0471200	0.03953	0.07933	-0.12650	0.03221	0.02673	0.05263	-0.09976	0.005511
UME	0.0008763	0.03261	0.06811	-0.06723	0.06899	0.01462	0.02899	-0.02811	0.029860
NMIJ	0.0028760	0.04388	0.08697	-0.08410	0.08985	0.03269	0.06432	-0.06145	0.067200
HSA	0.0058760	0.04061	0.08233	-0.07645	0.08821	0.02829	0.05623	-0.05035	0.062110
GLHK	0.0168800	0.04738	0.09447	-0.07760	0.11130	0.03714	0.07293	-0.05605	0.089810
NIM	0.0208800	0.03605	0.07297	-0.05209	0.09384	0.02110	0.04157	-0.02070	0.062450

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
KRISS	0.0458800	0.04735	0.09563	-0.04975	0.14150	0.03744	0.07456	-0.02869	0.120400
UNIIM	0.2329000	0.10890	0.21340	0.01943	0.44630	0.10500	0.20520	0.02769	0.438100
FTMC*	0.2929000	0.13370	0.26180	0.03103	0.55470	0.13080	0.25590	0.03693	0.548800
VNIIFTRI*	0.6129000	0.11470	0.22530	0.38750	0.83820	0.11080	0.21750	0.39540	0.830400
GUM*	0.0088760	0.04945	0.09773	-0.08885	0.10660	0.04003	0.07843	-0.06955	0.087300

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	50000
lambda[2]	1.001	50000
lambda[3]	1.001	36000
lambda[4]	1.001	50000
lambda[5]	1.001	50000
lambda[6]	1.001	47000
lambda[7]	1.001	50000
lambda[8]	1.001	37000
lambda[9]	1.001	50000
lambda[10]	1.001	50000
mu	1.001	50000
sigma[1]	1.001	50000
sigma[2]	1.001	36000
sigma[3]	1.001	50000
sigma[4]	1.001	50000
sigma[5]	1.001	50000
sigma[6]	1.001	36000
sigma[7]	1.001	47000
sigma[8]	1.001	50000
sigma[9]	1.001	38000
sigma[10]	1.001	32000
tau	1.003	3700

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	ISP*	0.543	0.018	4
TRUE	INMETRO	0.982	0.041	60
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TRUE	UME	1.068	0.008	60
TRUE	NMIJ	1.070	0.030	60
TRUE	HSA	1.073	0.023	8
TRUE	GLHK	1.084	0.035	60
TRUE	NIM	1.088	0.017	60
TRUE	KRISS	1.113	0.026	4
TRUE	UNIIM	1.300	0.100	60
FALSE	FTMC*	1.360	0.130	9
FALSE	VNIIFTRI*	1.680	0.110	60
FALSE	GUM*	1.076	0.038	60

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Standard uncertainty: 0.01212
95% coverage interval: (1.043, 1.092)
Dark uncertainty (tau): 0.02143
Tau posterior 0.025 and 0.975 quantiles: (0.001417,0.06419)

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p-value: 0.011
Q = 21.31 (Reference Distribution: Chi-Square with 9 Degrees of Freedom)
tau est. = 0.02621
tau/median(x) = 0.02446
tau/median(u) = 0.9359

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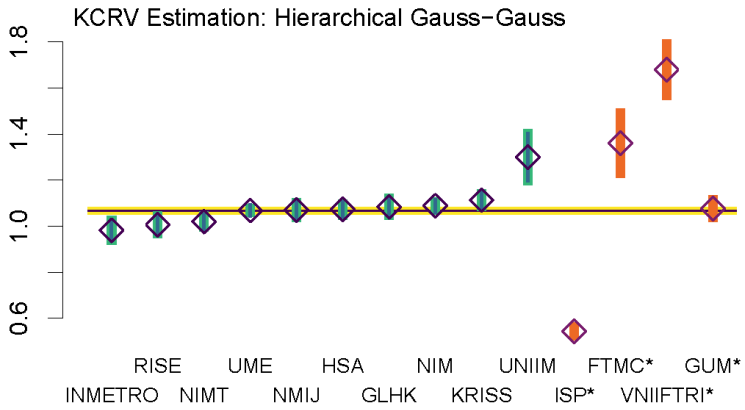
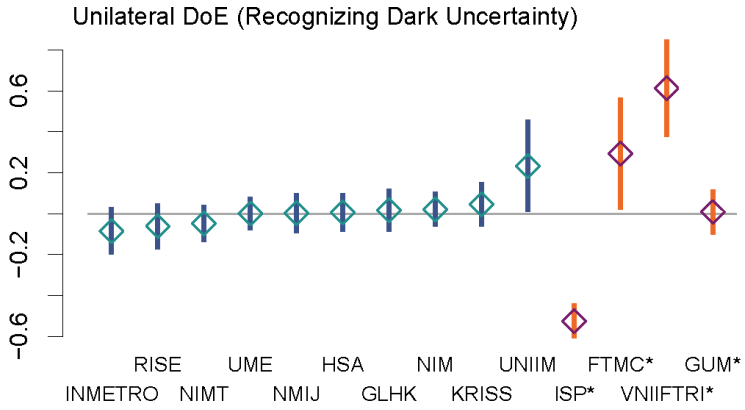
Miao-Gel-Gastwirth test of Symmetry: p = 0.8226

Plots


KCRV Estimation: Hierarchical Gauss−Gauss
0.6
1.0
1.4
1.8
RISE
UME
HSA
NIM
UNIIM
FTMC*
GUM*
INMETRO
NIMT
NMIJ
GLHK
KRISS
ISP*
VNIIFTRI*


Unilateral DoE (Recognizing Dark Uncertainty)
−0.6
−0.2
0.2
0.6
RISE
UME
HSA
NIM
UNIIM
FTMC*
GUM*
INMETRO
NIMT
NMIJ
GLHK
KRISS
ISP*
VNIIFTRI*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
ISP*	ISP*	-0.5241000	0.07368	-0.59780	-0.45040
INMETRO	INMETRO	-0.0851200	0.10360	-0.18880	0.01851
RISE	RISE	-0.0611200	0.10070	-0.16180	0.03958
NIMT	NIMT	-0.0471200	0.07933	-0.12650	0.03221
UME	UME	0.0008763	0.06811	-0.06723	0.06899
NMIJ	NMIJ	0.0028760	0.08697	-0.08410	0.08985
HSA	HSA	0.0058760	0.08233	-0.07645	0.08821
GLHK	GLHK	0.0168800	0.09447	-0.07760	0.11130
NIM	NIM	0.0208800	0.07297	-0.05209	0.09384
KRISS	KRISS	0.0458800	0.09563	-0.04975	0.14150
UNIIM	UNIIM	0.2329000	0.21340	0.01943	0.44630
FTMC*	FTMC*	0.2929000	0.26180	0.03103	0.55470
VNIIFTRI*	VNIIFTRI*	0.6129000	0.22530	0.38750	0.83820
GUM*	GUM*	0.0088760	0.09773	-0.08885	0.10660

Lab Uncertainties Table

lab	x	u	nu	ut
ISP*	0.543	0.018	4	0.02799
INMETRO	0.982	0.041	60	0.04626
RISE	1.006	0.039	60	0.04450
NIMT	1.020	0.023	60	0.03144
UME	1.068	0.008	60	0.02288
NMIJ	1.070	0.030	60	0.03687
HSA	1.073	0.023	8	0.03144
GLHK	1.084	0.035	60	0.04104
NIM	1.088	0.017	60	0.02736
KRISS	1.113	0.026	4	0.03370
UNIIM	1.300	0.100	60	0.10230
FTMC*	1.360	0.130	9	0.13180
VNIIFTRI*	1.680	0.110	60	0.11210
GUM*	1.076	0.038	60	0.04363

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
ISP*	-0.5241000	0.03645	0.07368	-0.59780	-0.45040	0.02167	0.04259	-0.56670	-0.481500
INMETRO	-0.0851200	0.05256	0.10360	-0.18880	0.01851	0.04398	0.08619	-0.17130	0.001069
RISE	-0.0611200	0.05106	0.10070	-0.16180	0.03958	0.04137	0.08125	-0.14240	0.020120
NIMT	-0.0471200	0.03953	0.07933	-0.12650	0.03221	0.02673	0.05263	-0.09976	0.005511
UME	0.0008763	0.03261	0.06811	-0.06723	0.06899	0.01462	0.02899	-0.02811	0.029860
NMIJ	0.0028760	0.04388	0.08697	-0.08410	0.08985	0.03269	0.06432	-0.06145	0.067200
HSA	0.0058760	0.04061	0.08233	-0.07645	0.08821	0.02829	0.05623	-0.05035	0.062110
GLHK	0.0168800	0.04738	0.09447	-0.07760	0.11130	0.03714	0.07293	-0.05605	0.089810
NIM	0.0208800	0.03605	0.07297	-0.05209	0.09384	0.02110	0.04157	-0.02070	0.062450

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
KRISS	0.0458800	0.04735	0.09563	-0.04975	0.14150	0.03744	0.07456	-0.02869	0.120400
UNIIM	0.2329000	0.10890	0.21340	0.01943	0.44630	0.10500	0.20520	0.02769	0.438100
FTMC*	0.2929000	0.13370	0.26180	0.03103	0.55470	0.13080	0.25590	0.03693	0.548800
VNIIFTRI*	0.6129000	0.11470	0.22530	0.38750	0.83820	0.11080	0.21750	0.39540	0.830400
GUM*	0.0088760	0.04945	0.09773	-0.08885	0.10660	0.04003	0.07843	-0.06955	0.087300

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	50000
lambda[2]	1.001	50000
lambda[3]	1.001	36000
lambda[4]	1.001	50000
lambda[5]	1.001	50000
lambda[6]	1.001	47000
lambda[7]	1.001	50000
lambda[8]	1.001	37000
lambda[9]	1.001	50000
lambda[10]	1.001	50000
mu	1.001	50000
sigma[1]	1.001	50000
sigma[2]	1.001	36000
sigma[3]	1.001	50000
sigma[4]	1.001	50000
sigma[5]	1.001	50000
sigma[6]	1.001	36000
sigma[7]	1.001	47000
sigma[8]	1.001	50000
sigma[9]	1.001	38000
sigma[10]	1.001	32000
tau	1.003	3700

Nickel

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	FTMC*	4.280	0.650	9
TRUE	NIMT	4.320	0.071	60
TRUE	RISE	4.480	0.150	60
TRUE	NRC	4.522	0.022	60
TRUE	KRISS	4.534	0.020	8
TRUE	UME	4.568	0.019	60
TRUE	NMIA	4.580	0.070	40
TRUE	NMIJ	4.620	0.060	60
TRUE	UNIIM	4.700	0.450	60
TRUE	NIM	4.744	0.090	60
FALSE	VNIIFTRI*	6.670	0.380	60
FALSE	GUM*	4.480	0.220	60

Date: 2023-11-04
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 1000
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 4.549
Standard uncertainty: 0.027
95% coverage interval: (4.493, 4.604)
Dark uncertainty (tau): 0.05233
Tau posterior 0.025 and 0.975 quantiles: (0.003282,0.154)

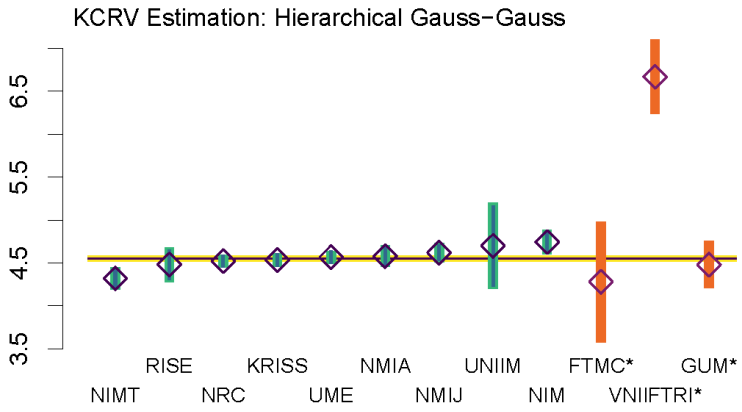
Decision Tree Hypothesis test results

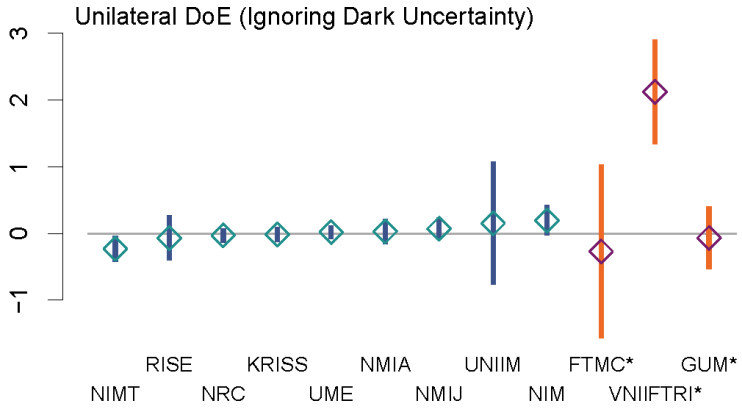
Cochran's test for Homogeneity:
p-value: 0.011
Q = 19.91 (Reference Distribution: Chi-Square with 8 Degrees of Freedom)
tau est. = 0.04475
tau/median(x) = 0.009796
tau/median(u) = 0.6393

Shapiro-Wilk test for Normality: p = 0.8835

Miao-Gel-Gastwirth test of Symmetry: p = 0.8878

Plots


KCRV Estimation: Hierarchical Gauss−Gauss
6.5
5.5
4.5
3.5
NIMT
RISE
NRC
KRISS
UME
NMIA
NMIJ
UNIIM
NIM
FTMC*
VNIIFTRI*
GUM*


Unilateral DoE (Ignoring Dark Uncertainty)
3
2
1
0
−1
NIMT
RISE
NRC
KRISS
UME
NMIA
NMIJ
UNIIM
NIM
FTMC*
VNIIFTRI*
GUM*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
FTMC*	FTMC*	-0.26890	1.26800	-1.537000	0.99920
NIMT	NIMT	-0.22890	0.15620	-0.385100	-0.07263
RISE	RISE	-0.06885	0.30050	-0.369400	0.23160
NRC	NRC	-0.02685	0.07003	-0.096890	0.04318
KRISS	KRISS	-0.01485	0.07247	-0.087330	0.05762
UME	UME	0.01915	0.06652	-0.047380	0.08567
NMIA	NMIA	0.03115	0.15040	-0.119300	0.18160
NMIJ	NMIJ	0.07115	0.13120	-0.060020	0.20230
UNIIM	UNIIM	0.15110	0.88350	-0.732400	1.03500
NIM	NIM	0.19510	0.19050	0.004627	0.38570
VNIIFTRI*	VNIIFTRI*	2.12100	0.74490	1.376000	2.86600
GUM*	GUM*	-0.06885	0.43470	-0.503500	0.36580

Lab Uncertainties Table

lab	x	u	nu	ut
FTMC*	4.280	0.650	9	0.65210
NIMT	4.320	0.071	60	0.08820
RISE	4.480	0.150	60	0.15890
NRC	4.522	0.022	60	0.05677
KRISS	4.534	0.020	8	0.05602
UME	4.568	0.019	60	0.05568
NMIA	4.580	0.070	40	0.08740
NMIJ	4.620	0.060	60	0.07962
UNIIM	4.700	0.450	60	0.45300
NIM	4.744	0.090	60	0.10410
VNIIFTRI*	6.670	0.380	60	0.38360
GUM*	4.480	0.220	60	0.22610

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
FTMC*	-0.26890	0.65050	1.2740	-1.5430	1.00500	0.65130	1.26800	-1.537000	0.99920
NIMT	-0.22890	0.10700	0.2118	-0.4407	-0.01701	0.07951	0.15620	-0.385100	-0.07263
RISE	-0.06885	0.16990	0.3350	-0.4038	0.26610	0.15280	0.30050	-0.369400	0.23160
NRC	-0.02685	0.07991	0.1687	-0.1956	0.14190	0.03520	0.07003	-0.096890	0.04318
KRISS	-0.01485	0.08004	0.1687	-0.1835	0.15380	0.03625	0.07247	-0.087330	0.05762
UME	0.01915	0.07842	0.1659	-0.1467	0.18500	0.03328	0.06652	-0.047380	0.08567
NMIA	0.03115	0.10460	0.2079	-0.1767	0.23900	0.07655	0.15040	-0.119300	0.18160
NMIJ	0.07115	0.09768	0.1967	-0.1255	0.26780	0.06644	0.13120	-0.060020	0.20230
UNIIM	0.15110	0.45660	0.8972	-0.7461	1.04800	0.44840	0.88350	-0.732400	1.03500
NIM	0.19510	0.12040	0.2380	-0.0429	0.43320	0.09649	0.19050	0.004627	0.38570
VNIIFTRI*	2.12100	0.38790	0.7636	1.3580	2.88500	0.38160	0.74490	1.376000	2.86600
GUM*	-0.06885	0.23290	0.4548	-0.5237	0.38590	0.22200	0.43470	-0.503500	0.36580

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	15000
lambda[1]	1.001	15000
lambda[2]	1.001	50000
lambda[3]	1.001	43000
lambda[4]	1.001	50000
lambda[5]	1.001	50000
lambda[6]	1.001	34000
lambda[7]	1.001	31000
lambda[8]	1.001	47000
lambda[9]	1.001	38000
mu	1.001	21000
sigma[1]	1.001	50000
sigma[2]	1.001	50000
sigma[3]	1.001	41000
sigma[4]	1.001	50000
sigma[5]	1.001	50000
sigma[6]	1.001	50000
sigma[7]	1.001	38000
sigma[8]	1.001	50000
sigma[9]	1.001	31000
tau	1.001	12000

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
FALSE	FTMC*	4.280	0.650	9
TRUE	NIMT	4.320	0.071	60
TRUE	RISE	4.480	0.150	60
TRUE	NRC	4.522	0.022	60
TRUE	KRISS	4.534	0.020	8
TRUE	UME	4.568	0.019	60
TRUE	NMIA	4.580	0.070	40
TRUE	NMIJ	4.620	0.060	60
TRUE	UNIIM	4.700	0.450	60
TRUE	NIM	4.744	0.090	60
FALSE	VNIIFTRI*	6.670	0.380	60
FALSE	GUM*	4.480	0.220	60

Date: 2023-11-04
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 1000
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 4.549
Standard uncertainty: 0.027
95% coverage interval: (4.493, 4.604)
Dark uncertainty (tau): 0.05233
Tau posterior 0.025 and 0.975 quantiles: (0.003282,0.154)

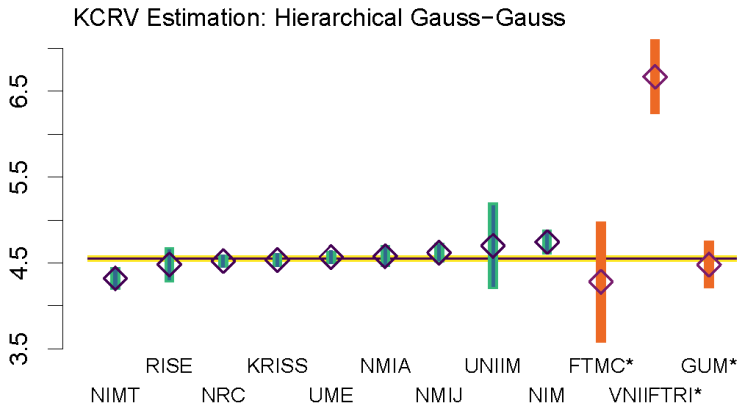
Decision Tree Hypothesis test results

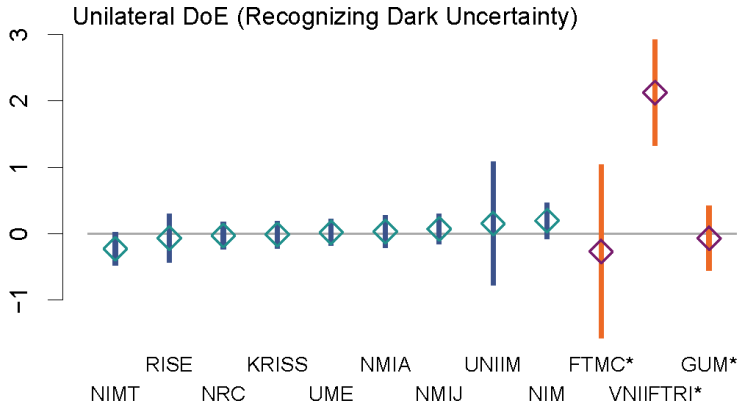
Cochran's test for Homogeneity:
p-value: 0.011
Q = 19.91 (Reference Distribution: Chi-Square with 8 Degrees of Freedom)
tau est. = 0.04475
tau/median(x) = 0.009796
tau/median(u) = 0.6393

Shapiro-Wilk test for Normality: p = 0.8835

Miao-Gel-Gastwirth test of Symmetry: p = 0.8786

Plots


KCRV Estimation: Hierarchical Gauss−Gauss
6.5
5.5
4.5
3.5
RISE
KRISS
NMIA
UNIIM
FTMC*
GUM*
NIMT
NRC
UME
NMIJ
NIM
VNIIFTRI*


Unilateral DoE (Recognizing Dark Uncertainty)
3
2
1
0
−1
RISE
KRISS
NMIA
UNIIM
FTMC*
GUM*
NIMT
NRC
UME
NMIJ
NIM
VNIIFTRI*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
FTMC*	FTMC*	-0.26890	1.2740	-1.5430	1.00500
NIMT	NIMT	-0.22890	0.2118	-0.4407	-0.01701
RISE	RISE	-0.06885	0.3350	-0.4038	0.26610
NRC	NRC	-0.02685	0.1687	-0.1956	0.14190
KRISS	KRISS	-0.01485	0.1687	-0.1835	0.15380
UME	UME	0.01915	0.1659	-0.1467	0.18500
NMIA	NMIA	0.03115	0.2079	-0.1767	0.23900
NMIJ	NMIJ	0.07115	0.1967	-0.1255	0.26780
UNIIM	UNIIM	0.15110	0.8972	-0.7461	1.04800
NIM	NIM	0.19510	0.2380	-0.0429	0.43320
VNIIFTRI*	VNIIFTRI*	2.12100	0.7636	1.3580	2.88500
GUM*	GUM*	-0.06885	0.4548	-0.5237	0.38590

Lab Uncertainties Table

lab	x	u	nu	ut
FTMC*	4.280	0.650	9	0.65210
NIMT	4.320	0.071	60	0.08820
RISE	4.480	0.150	60	0.15890
NRC	4.522	0.022	60	0.05677
KRISS	4.534	0.020	8	0.05602
UME	4.568	0.019	60	0.05568
NMIA	4.580	0.070	40	0.08740
NMIJ	4.620	0.060	60	0.07962
UNIIM	4.700	0.450	60	0.45300
NIM	4.744	0.090	60	0.10410
VNIIFTRI*	6.670	0.380	60	0.38360
GUM*	4.480	0.220	60	0.22610

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
FTMC*	-0.26890	0.65050	1.2740	-1.5430	1.00500	0.65130	1.26800	-1.537000	0.99920
NIMT	-0.22890	0.10700	0.2118	-0.4407	-0.01701	0.07951	0.15620	-0.385100	-0.07263
RISE	-0.06885	0.16990	0.3350	-0.4038	0.26610	0.15280	0.30050	-0.369400	0.23160
NRC	-0.02685	0.07991	0.1687	-0.1956	0.14190	0.03520	0.07003	-0.096890	0.04318
KRISS	-0.01485	0.08004	0.1687	-0.1835	0.15380	0.03625	0.07247	-0.087330	0.05762
UME	0.01915	0.07842	0.1659	-0.1467	0.18500	0.03328	0.06652	-0.047380	0.08567
NMIA	0.03115	0.10460	0.2079	-0.1767	0.23900	0.07655	0.15040	-0.119300	0.18160
NMIJ	0.07115	0.09768	0.1967	-0.1255	0.26780	0.06644	0.13120	-0.060020	0.20230
UNIIM	0.15110	0.45660	0.8972	-0.7461	1.04800	0.44840	0.88350	-0.732400	1.03500
NIM	0.19510	0.12040	0.2380	-0.0429	0.43320	0.09649	0.19050	0.004627	0.38570
VNIIFTRI*	2.12100	0.38790	0.7636	1.3580	2.88500	0.38160	0.74490	1.376000	2.86600
GUM*	-0.06885	0.23290	0.4548	-0.5237	0.38590	0.22200	0.43470	-0.503500	0.36580

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	15000
lambda[1]	1.001	15000
lambda[2]	1.001	50000
lambda[3]	1.001	43000
lambda[4]	1.001	50000
lambda[5]	1.001	50000
lambda[6]	1.001	34000
lambda[7]	1.001	31000
lambda[8]	1.001	47000
lambda[9]	1.001	38000
mu	1.001	21000
sigma[1]	1.001	50000
sigma[2]	1.001	50000
sigma[3]	1.001	41000
sigma[4]	1.001	50000
sigma[5]	1.001	50000
sigma[6]	1.001	50000
sigma[7]	1.001	38000
sigma[8]	1.001	50000
sigma[9]	1.001	31000
tau	1.001	12000

Zinc

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	RISE	8.100	0.350	60
TRUE	KRISS	8.300	0.450	200
TRUE	NMIJ	8.310	0.150	60
TRUE	UME	8.521	0.038	60
TRUE	NRC	8.572	0.034	60
TRUE	UNIIM	8.600	0.500	60
TRUE	NIM	8.764	0.162	60
FALSE	VNIIFTRI*	13.540	0.960	60
FALSE	GUM*	9.210	0.990	60

Date: 2023-11-04
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 1000
Selected Procedure: Adaptive Weighted Average
Consensus estimate: 8.54
Standard uncertainty: 0.03427
Standard uncertainty (using parametric bootstrap): 0.04163
95% coverage interval: (8.473, 8.607)
95% coverage interval (using parametric bootstrap): (8.454, 8.625)
Dark uncertainty (tau): 0.03678

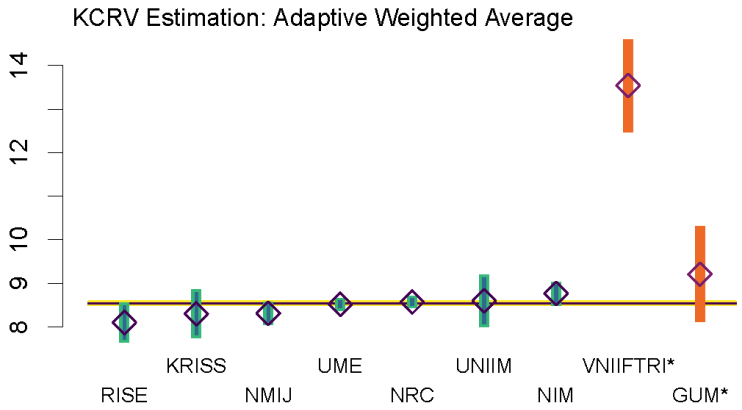
Decision Tree Hypothesis test results

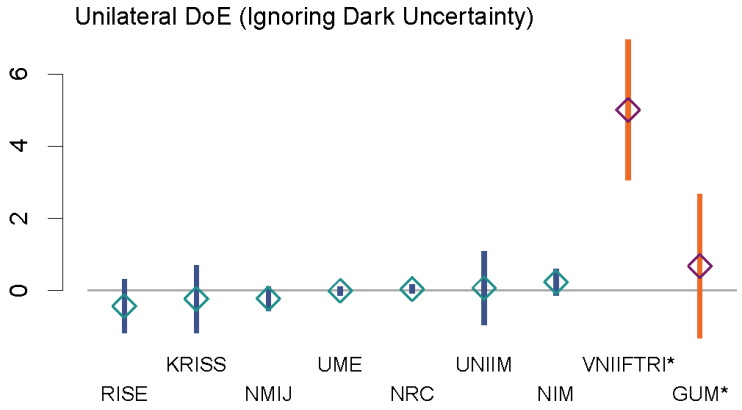
Cochran's test for Homogeneity:
p-value: 0.3
Q = 7.237 (Reference Distribution: Chi-Square with 6 Degrees of Freedom)
tau est. = 0.03678
tau/median(x) = 0.004316
tau/median(u) = 0.227

Shapiro-Wilk test for Normality: p = 0.3584

Miao-Gel-Gastwirth test of Symmetry: p = 0.465

Plots


KCRV Estimation: Adaptive Weighted Average
8
9
10
12
14
RISE
KRISS
NMIJ
UME
NRC
UNIIM
NIM
VNIIFTRI*
GUM*


Unilateral DoE (Ignoring Dark Uncertainty)
0
2
4
6
RISE
KRISS
NMIJ
UME
NRC
UNIIM
NIM
VNIIFTRI*
GUM*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
RISE	RISE	-0.43990	0.67680	-1.11700	0.23690
KRISS	KRISS	-0.23990	0.87670	-1.11700	0.63680
NMIJ	NMIJ	-0.22990	0.27270	-0.50270	0.04280
UME	UME	-0.01894	0.06421	-0.08315	0.04527
NRC	NRC	0.03206	0.05962	-0.02756	0.09169
UNIIM	UNIIM	0.06006	0.95500	-0.89490	1.01500
NIM	NIM	0.22410	0.29790	-0.07379	0.52190
VNIIFTRI*	VNIIFTRI*	5.00000	1.88200	3.11800	6.88200
GUM*	GUM*	0.67010	1.94100	-1.27100	2.61100

Lab Uncertainties Table

lab	x	u	nu	ut
RISE	8.100	0.350	60	0.35190
KRISS	8.300	0.450	200	0.45150
NMIJ	8.310	0.150	60	0.15440
UME	8.521	0.038	60	0.05288
NRC	8.572	0.034	60	0.05009
UNIIM	8.600	0.500	60	0.50140
NIM	8.764	0.162	60	0.16610
VNIIFTRI*	13.540	0.960	60	0.96070
GUM*	9.210	0.990	60	0.99070

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
RISE	-0.43990	0.35010	0.6785	-1.11800	0.23860	0.34590	0.67680	-1.11700	0.23690
KRISS	-0.23990	0.45100	0.8788	-1.11900	0.63880	0.44880	0.87670	-1.11700	0.63680
NMIJ	-0.22990	0.15020	0.2921	-0.52210	0.06221	0.14220	0.27270	-0.50270	0.04280
UME	-0.01894	0.05061	0.1059	-0.12490	0.08701	0.03216	0.06421	-0.08315	0.04527
NRC	0.03206	0.05128	0.1058	-0.07378	0.13790	0.02884	0.05962	-0.02756	0.09169
UNIIM	0.06006	0.49960	0.9708	-0.91070	1.03100	0.49680	0.95500	-0.89490	1.01500
NIM	0.22410	0.16220	0.3132	-0.08912	0.53720	0.15460	0.29790	-0.07379	0.52190
VNIIFTRI*	5.00000	0.96160	1.8850	3.11500	6.88500	0.96040	1.88200	3.11800	6.88200
GUM*	0.67010	0.99150	1.9430	-1.27300	2.61400	0.99040	1.94100	-1.27100	2.61100

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

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	RISE	8.100	0.350	60
TRUE	KRISS	8.300	0.450	200
TRUE	NMIJ	8.310	0.150	60
TRUE	UME	8.521	0.038	60
TRUE	NRC	8.572	0.034	60
TRUE	UNIIM	8.600	0.500	60
TRUE	NIM	8.764	0.162	60
FALSE	VNIIFTRI*	13.540	0.960	60
FALSE	GUM*	9.210	0.990	60

Date: 2023-11-04
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 1000
Selected Procedure: Adaptive Weighted Average
Consensus estimate: 8.54
Standard uncertainty: 0.03427
Standard uncertainty (using parametric bootstrap): 0.04163
95% coverage interval: (8.473, 8.607)
95% coverage interval (using parametric bootstrap): (8.454, 8.625)
Dark uncertainty (tau): 0.03678

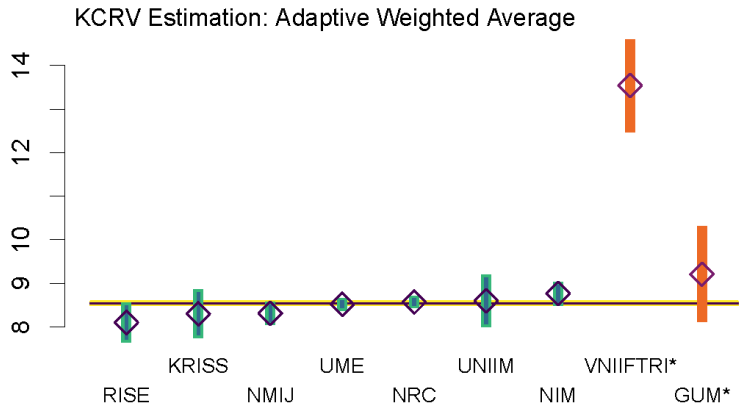
Decision Tree Hypothesis test results

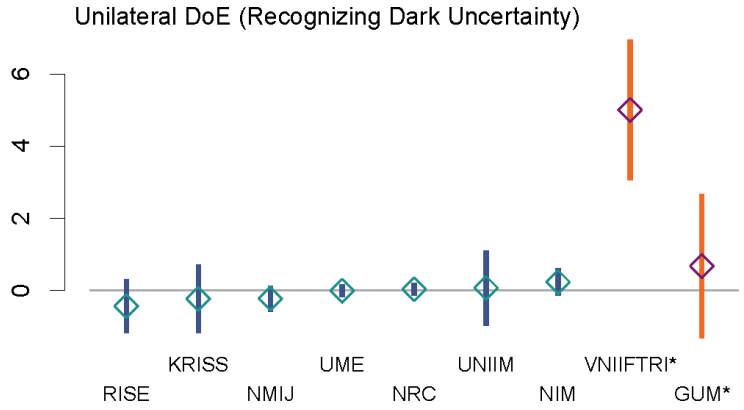
Cochran's test for Homogeneity:
p-value: 0.3
Q = 7.237 (Reference Distribution: Chi-Square with 6 Degrees of Freedom)
tau est. = 0.03678
tau/median(x) = 0.004316
tau/median(u) = 0.227

Shapiro-Wilk test for Normality: p = 0.3584

Miao-Gel-Gastwirth test of Symmetry: p = 0.4542

Plots


KCRV Estimation: Adaptive Weighted Average
8
9
10
12
14
RISE
KRISS
NMIJ
UME
NRC
UNIIM
NIM
VNIIFTRI*
GUM*


Unilateral DoE (Recognizing Dark Uncertainty)
0
2
4
6
RISE
KRISS
NMIJ
UME
NRC
UNIIM
NIM
VNIIFTRI*
GUM*

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
RISE	RISE	-0.43990	0.6785	-1.11800	0.23860
KRISS	KRISS	-0.23990	0.8788	-1.11900	0.63880
NMIJ	NMIJ	-0.22990	0.2921	-0.52210	0.06221
UME	UME	-0.01894	0.1059	-0.12490	0.08701
NRC	NRC	0.03206	0.1058	-0.07378	0.13790
UNIIM	UNIIM	0.06006	0.9708	-0.91070	1.03100
NIM	NIM	0.22410	0.3132	-0.08912	0.53720
VNIIFTRI*	VNIIFTRI*	5.00000	1.8850	3.11500	6.88500
GUM*	GUM*	0.67010	1.9430	-1.27300	2.61400

Lab Uncertainties Table

lab	x	u	nu	ut
RISE	8.100	0.350	60	0.35190
KRISS	8.300	0.450	200	0.45150
NMIJ	8.310	0.150	60	0.15440
UME	8.521	0.038	60	0.05288
NRC	8.572	0.034	60	0.05009
UNIIM	8.600	0.500	60	0.50140
NIM	8.764	0.162	60	0.16610
VNIIFTRI*	13.540	0.960	60	0.96070
GUM*	9.210	0.990	60	0.99070

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
RISE	-0.43990	0.35010	0.6785	-1.11800	0.23860	0.34590	0.67680	-1.11700	0.23690
KRISS	-0.23990	0.45100	0.8788	-1.11900	0.63880	0.44880	0.87670	-1.11700	0.63680
NMIJ	-0.22990	0.15020	0.2921	-0.52210	0.06221	0.14220	0.27270	-0.50270	0.04280
UME	-0.01894	0.05061	0.1059	-0.12490	0.08701	0.03216	0.06421	-0.08315	0.04527
NRC	0.03206	0.05128	0.1058	-0.07378	0.13790	0.02884	0.05962	-0.02756	0.09169
UNIIM	0.06006	0.49960	0.9708	-0.91070	1.03100	0.49680	0.95500	-0.89490	1.01500
NIM	0.22410	0.16220	0.3132	-0.08912	0.53720	0.15460	0.29790	-0.07379	0.52190
VNIIFTRI*	5.00000	0.96160	1.8850	3.11500	6.88500	0.96040	1.88200	3.11800	6.88200
GUM*	0.67010	0.99150	1.9430	-1.27300	2.61400	0.99040	1.94100	-1.27100	2.61100

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.

Tributyltin

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	VNIIM	4.10	0.70	60
TRUE	JSI	6.29	0.25	60
TRUE	UME	7.81	0.33	60
TRUE	NIM	7.96	0.81	60
TRUE	LNE	8.02	0.61	60

Date: 2023-11-04
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 1000
Selected Procedure: Hierarchical Laplace-Gauss
Consensus estimate: 7.02
Standard uncertainty: 0.5572
95% coverage interval: (5.928, 8.111)
Dark uncertainty (tau): 1.318
Tau posterior 0.025 and 0.975 quantiles: (0.5055,3.735)

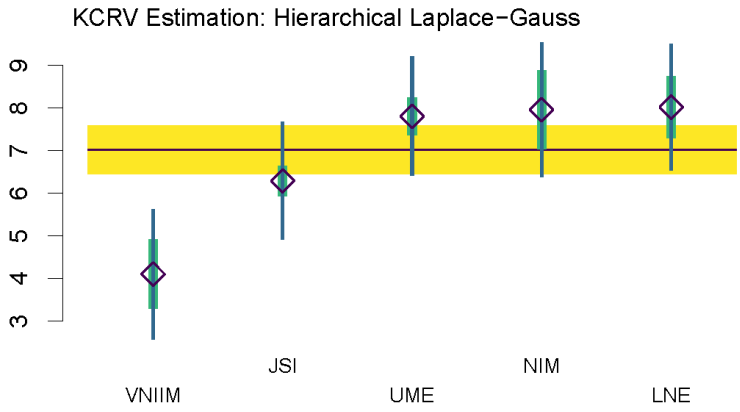
Decision Tree Hypothesis test results

Cochran's test for Homogeneity:
p-value: $p < 0.001$
$Q = 34.44$ (Reference Distribution: Chi-Square with 4 Degrees of Freedom)
tau est. = 1.228
tau/median(x) = 0.1573
tau/median(u) = 2.014

Shapiro-Wilk test for Normality: $p = 0.03042$

Miao-Gel-Gastwirth test of Symmetry: $p = 0.0648$

Plots


KCRV Estimation: Hierarchical Laplace−Gauss
3
4
5
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7
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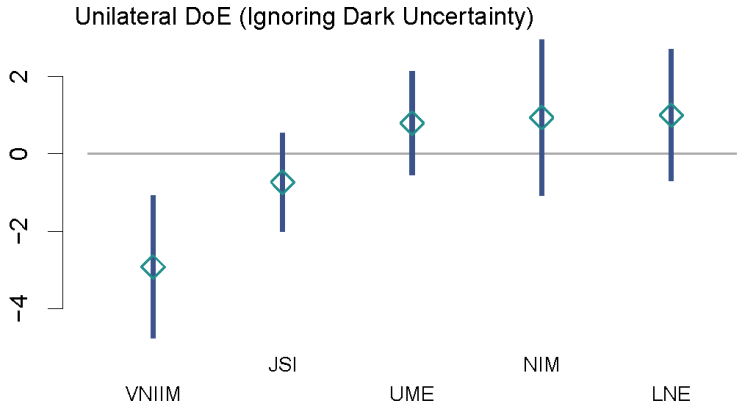
VNIIM
JSI
UME
NIM
LNE


Unilateral DoE (Ignoring Dark Uncertainty)
−4
−2
0
2
VNIIM
JSI
UME
NIM
LNE

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
VNIIM	VNIIM	-2.9200	1.783	-4.7020	-1.1370
JSI	JSI	-0.7296	1.207	-1.9370	0.4776
UME	UME	0.7904	1.280	-0.4894	2.0700
NIM	NIM	0.9404	1.947	-1.0070	2.8870
LNE	LNE	1.0000	1.645	-0.6442	2.6450

Lab Uncertainties Table

lab	x	u	nu	ut
VNIIM	4.10	0.70	60	1.493
JSI	6.29	0.25	60	1.342
UME	7.81	0.33	60	1.359
NIM	7.96	0.81	60	1.547
LNE	8.02	0.61	60	1.453

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
VNIIM	-2.9200	1.969	3.939	-6.859	1.020	0.9069	1.783	-4.7020	-1.1370
JSI	-0.7296	1.859	3.774	-4.504	3.044	0.6137	1.207	-1.9370	0.4776
UME	0.7904	1.884	3.747	-2.956	4.537	0.6504	1.280	-0.4894	2.0700
NIM	0.9404	2.029	4.001	-3.060	4.941	0.9930	1.947	-1.0070	2.8870
LNE	1.0000	1.936	3.845	-2.845	4.846	0.8368	1.645	-0.6442	2.6450

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	Rhat	n.eff
deviance	1.001	22000
lambda[1]	1.001	50000
lambda[2]	1.001	50000
lambda[3]	1.001	19000
lambda[4]	1.001	50000
lambda[5]	1.001	50000
mu	1.001	50000
sigma[1]	1.001	50000
sigma[2]	1.001	50000
sigma[3]	1.001	18000
sigma[4]	1.001	20000
sigma[5]	1.001	50000
tau	1.001	50000

NIST Decision Tree Report

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TRUE	LNE	8.02	0.61	60

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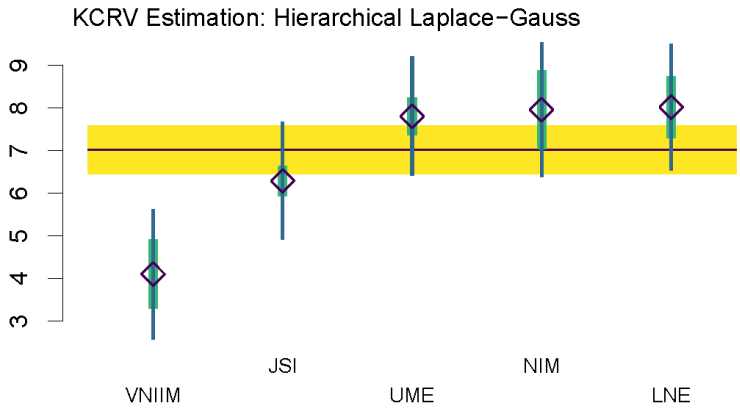
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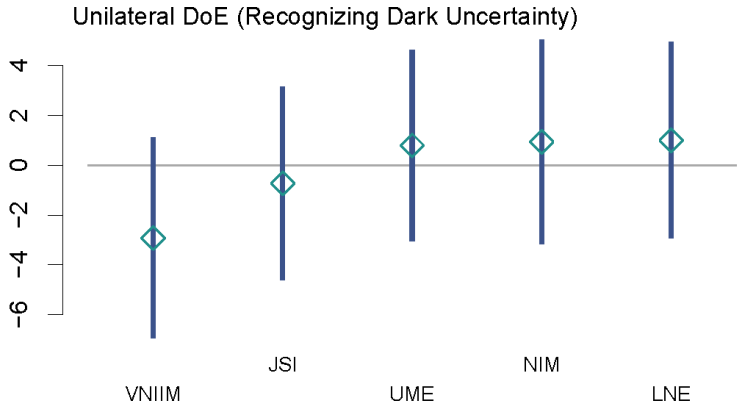
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−6
−4
−2
0
2
4
VNIIM
JSI
UME
NIM
LNE

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sigma[5]	1.001	50000
tau	1.001	50000