CCQM-K144
Trace elements in alumina powder

Key Comparison

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SUMMARY

Aluminum oxide (Al_2O_3), commonly referred to as alumina, is extensively used in a variety of applications as a fundamental material for ceramics, catalyst substrates, ingredients in cosmetics, or media in chromatography. High purity alumina, in particular, plays a crucial role in the display and semiconductor industries. Trace elements such as iron (Fe), magnesium (Mg) and silicon (Si) in high-purity alumina can significantly affect the material's properties such as optical transparency and mechanical strength, potentially degrading the quality of final products. Therefore, the accurate measurements of trace elements in alumina are important for the relevant industries.

Despite the importance, there had been no CCQM (Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology) IAWG (Inorganic Analysis Working Group) comparison studies on such advanced materials since 2008. Thus, a Key Comparison was initiated to address the current and future CMCs (Calibration and Measurement Capabilities) for category "9. Advanced materials" in "List of Amount of Substance Categories" of CCQM CMCs particularly concerning "Difficult to dissolve metals" of "Matrix challenges" in the IAWG Core Capability table. Then, KRISS proposed a comparison for measurements of elemental impurities in alumina powder and CCQM IAWG approved the Key Comparison (KC), CCQM-K144 Trace elements in alumina powder, in parallel with CCQM-P182.

There are four participants, JSI (Slovenia), KRISS (Republic of Korea), NIM (China), UNIIM (Russia), in CCQM-K144. Participants measured the mass fractions, expressed in mg/kg, of iron (Fe), magnesium (Mg), and silicon (Si) in high purity alumina powder. Participants were free to choose any appropriate methods based on their measurement procedures, considering complete dissolution of the alumina powder, if required. Various measurement procedures including Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with standard addition (SA) or isotope dilution (ID) calibration approaches, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with standard addition (SA) following sample dissolution were employed by the participants. Additionally, Instrumental Neutron Activation Analysis with k_0-method (k_0-INAA) was also implemented for Fe without needing to dissolve the alumina by one participant demonstrating equivalence between measurement results regardless of sample dissolution.

After extensive discussions in the IAWG, the Key Comparison Reference Values (KCRVs) and Degrees of Equivalence (DoEs) for all three measurands were calculated using the NIST Decision Tree (NDT) for Key Comparisons (https://decisiontree.nist.gov). The consensus estimates and standard uncertainties for mass fractions of Fe, Mg, and Si were calculated based on the statistical model, "Hierarchical Gauss-Gauss", recommended in the NDT application and were then selected as the candidate KCRVs and their standard uncertainties. The values were w(Fe)=2.332 mg/kg (u(Fe)=0.109 mg/kg), w(Mg)=2.341 mg/kg (u(Mg)=0.307 mg/kg) and w(Si)=12.22 mg/kg (u(Si)=0.83 mg/kg), respectively.

Successful participation in CCQM-K144 directly demonstrates each participant's measurement capabilities in determining mass fraction of iron (Fe), magnesium (Mg) and silicon (Si), in mass fraction range more than 0.05 mg/kg in an alumina powder and similar matrices. All participants' DoE values were statistically indistinguishable from zero at 95 % confidence, demonstrating their competence within their respective levels of uncertainty. Therefore, CMCs that align with the "How Far the Light Shines" (HFTLS) statement can be supported by this CCQM-K144.

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INTRODUCTION

Aluminum oxide (Al_2O_3), commonly known as alumina, is a fundamental material used in a variety of applications including ceramics, catalyst substrates, cosmetic ingredients, and chromatographic media. In recent high-tech industries, high-purity alumina is crucial as it serves as advanced material in the manufacture of sapphire glasses for displays, capping and dielectric layers in semiconductors, ceramic components for electric vehicles, nanoparticles, and more. Trace elements, such as iron (Fe), magnesium (Mg) and silicon (Si), present in high-purity alumina can significantly impact the material's properties such as optical transparency and mechanical strength. High levels of these elemental impurities can adversely affect the quality and yield of the final products. Therefore, the accurate measurements of trace elements in alumina are important for the relevant industries.

Despite the importance, there have been no CCQM (Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology) IAWG (Inorganic Analysis Working Group) comparison studies on advanced materials since 2008. Therefore, in October 2016, the CCQM IAWG approved the Key Comparison (KC) CCQM-K144, titled 'Trace elements in alumina powder'. The purpose of this KC is to evaluate the participants' capabilities for measuring the mass fractions of impurities, specifically Fe, Mg and Si, in high-purity alumina powder. This KC is particularly challenging due to the difficulty associated with dissolving alumina powder during sample preparation.

Successful participation in CCQM-K144 directly demonstrates a participant's measurement capabilities to determine the mass fractions of iron (Fe), magnesium (Mg) and silicon (Si) in alumina powder and similar matrices. This capability is aligned with the '9. Advanced materials' category in the 'List of Amount of Substance Categories' within CCQM Calibration and Measurement Capabilities (CMCs). In the IAWG Core Capability table, magnesium is classified under 'Group I and II: Alkali and Alkaline earth', iron under 'Transition elements', and silicon under 'Metalloids/Semi-metals'. This is specifically relevant for mass fraction range of more than 0.05 mg/kg for all three elements, categorized under 'Difficult to dissolve metals' of 'Matrix challenges.

The following sections of this report document the timeline of CCQM-K144, the measurands, study material, participants, results, and how participation in CCQM-K144 supports CMC claims including "How Far the Light Shines" statement. The Appendices contain official communication materials and summaries of information about the results provided by the participants.

TIMELINE

Table 1: Timeline for CCQM-K144

Date	Action
Apr. 2016	Proposal presented in CCQM IAWG
Oct. 2016	IAWG approval as CCQM-K144
Apr. 2018	Draft protocol presented to IAWG
Oct. 2018	Call for participation to IAWG members
Dec. 2018	Sample distribution to participants.
Aug. 2019	Result submission
Sep. 2019	First discussion on the results
Nov. 2020	Second discussion on the results
May. 2021	Discussion on the candidate KCRVs and DoEs using Decision Tree approach
Jun. 2023	Distribution of "IAWG Guidance on Using NIST Decision Tree for Comparison Reporting"
Nov. 2023	Confirmation of the KCRVs and DoEs
Apr. 2024	Circulation of Draft A report
Nov. 2024	Circulation of Draft B report
Feb. 2025	Final report approved by IAWG

MEASURANDS

The measurands are the mass fractions (on a dry mass basis), mg/kg, of the elements, iron (Fe), magnesium (Mg), and silicon (Si) in alumina powder. The expected mass fractions are listed in the following table:

Table 2: Expected range of measurands for CCQM-K144

Element	Expected mass fraction (mg/kg)
Fe	1~20
Mg	1~20
Si	1~20

STUDY MATERIALS

Each participant received two PFA bottles and each bottle sealed in a polymer bag contained about 30 g of alumina powder. It was required to report the measurement results obtained only from one sample bottle. The sample in the other bottle was recommended to use for preliminary analysis.

The sample of alumina powder for CCQM-K144 was produced by KRISS in accordance with ISO 17034 and ISO Guide 35 from a single batch of high-purity alumina powder (with nominal purity of 99.999 % provided by a commercial company). The raw material was carefully selected after particle size analysis using field-emission scanning electron microscopy (FE-SEM) and preliminary analysis by ICP-MS. The particle size distribution was in the range from 0.3 μm to 0.8 μm. To obtain appropriate homogeneity as a reference material, the alumina powder batch in a polypropylene bottle was thoroughly mixed using cylinder roller. Then, the homogenized powder was bottled into 50 mL PFA bottles. All sample handling processes were carried out in a clean environment with filtered air through PTFE HEPA filter. All bottles and sample handling tools contacting with sample were sequentially cleaned by using 6 % mass fraction hydrochloric acid, 10 % mass fraction nitric acid, 5 % mass fraction hydrofluoric acid, and deionized water (18 MΩ·cm resistivity).

The recommended minimum sample amount for analysis was at least 1 g. Measurement results were to be reported on a dry-mass basis.

Dry Mass Determination

Dry mass correction of the sample masses was to be carried out to obtain the equivalence among the participants' reported results. All participants were required to follow the method outlined in the protocol. Samples of about 1 g taken in weighing bottles were to be dried at 110 °C for 2 hours by using a drying oven. Samplings for both dry mass correction and analysis were recommended to be weighed out at the same time to minimize any change in moisture content during sampling. The true mass changes before and after drying had to be evaluated for dry mass correction of the measurement results.

Homogeneity Assessment of Study Material

The homogeneities were evaluated by ICP-MS and ICP-OES measurements. The standard deviations of measurement results of Fe, Mg, and Si in subsamples taken from 12 bottles were used to estimate between-bottle homogeneity. The between-bottle standard deviations were 1.92 %, 2.55 %, 3.52 % for Fe, Mg, and Si, respectively. For the estimation of within-bottle homogeneity, three subsamples in each bottle were taken and the mean of the standard deviations of measurement results were used. The within-bottle standard deviations were less than 2.9 %, 1.6 %, and 2.5 % for Fe, Mg, and Si, respectively. The mass of subsamples taken was about 1 g. After the alumina powder samples were dissolved by pressurized microwave-assisted acid digestion with 25 % volume fraction hydrochloric acid, the sample solutions were centrifuged to observe if any undissolved particles were present. In addition, the sample solutions were also investigated by dynamic light scattering and optical microscopy. No particles in sample solutions were observed after sample dissolution.

Table 3: Results of the homogeneity assessment for Fe, Mg and Si in alumina powder sample for CCQM-K144

Element	Fe	Mg	Si
Within-bottle standard deviation*, s_{wth}:	1.92 %	2.55 %	3.52 %
Between-bottle standard deviation, s_{btw}:	2.9 %	1.6 %	2.5 %

* Within-bottle standard deviations were obtained by ICP-OES

Stability Assessment of Study Material

Since the alumina powder was well known to be stable, the mass fractions of Fe, Mg and Si in the study material are stable. The mass fractions of Fe, Mg and Si in the study material measured in 2018 and 2019 were in good agreement with each other.

PARTICIPANTS, INSTRUCTIONS AND SAMPLE DISTRIBUTION

The call for participation was distributed in October 2018 with the intent to distribute samples in December 2018, receive results in August 2019, and discuss results, firstly, at the Ekaterinburg IAWG meeting, September 2019. See Table 1 for study timeline. Appendix A reproduces the Call for Participation; Appendix B reproduces the study Protocol. Table 4 lists the institutions that registered for CCQM-K144.

Table 4: Institutes registered for CCQM-K144

NMI or DI	Code	Country	Contact
Jožef Stefan Institute	JSI	Slovenia	Radojko Jaćimović
Korea Research Institute of Standards and Science	KRISS	Republic of Korea	Kyoung-Seok Lee
National Institute of Metrology	NIM	China	Tao Zhou
Ural Research Institute for metrology – Affiliated Branch of the D.I. Mendeleev Institute for Metrology	VNIIM-UNIIM	Russian Federation	Egor Sobina

Each participant received two PFA bottles of alumina powder. It was requested to report the measurement results obtained only from one sample bottle. The sample in the other bottle was recommended to use for preliminary analysis. When each participant received the sample bottles, it was required to return “Sample Receipt Form” to the pilot laboratory, KRISS, for confirmation of package and its content.

A Report Form of Results was provided to the participants by e-mail. Participants were required to report their results as mass fraction, mg/kg, obtained from measurements of at least five sub-samples of 1 g in a single sample bottle with dry mass correction. Participants confirmed one result for each measurand for the KCRV calculation in CCQM-K144. The completed Report Form of Results was submitted to KRISS on the scheduled deadline by e-mail. It was recommended to provide detailed information about the applied procedure for the measurement:

- Final results with standard and expanded uncertainties for each measurand.

- If the final result has been calculated from more than two measurement methods,it was requested that the individual results are combined to report one final result.
- Additional results obtained from more than two measurement methods were encouraged to be submitted to CCQM-P182.
- Information about sample preparation: sample dissolution method (apparatus, reagents with their quantities and concentration, temperature, pressure, time, etc.) or direct sampling procedures.
- Information about instrumental analysis: Instrument and experimental conditions used for the measurement.
- Information about the calibration method including reference material used for calibration or other materials in the analytical procedure.
- Details of the uncertainty evaluation: all uncertainty sources and their typical values.

RESULTS

Participants were requested to report a single estimate of the mass fraction, mg/kg, for Fe, Mg, and Si from only one sample bottle, respectively. In addition to the quantitative results, participants were instructed to describe their analytical methods and approach to uncertainty estimation. Appendix B reproduces the report form.

CCQM-K144 results were received from 4 institutions for Fe and 3 institutions for Mg and Si that received samples.

Methods Used by Participants

For CCQM-K144, participants used various measurement procedures which are summarized in Table 5. For Fe and Si, both NIM and VNIIM-UNIIM used Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with standard addition calibration method. For Mg, VNIIM-UNIIM applied the isotope dilution mass spectrometry (IDMS) to ICP-MS. KRISS combined Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with standard addition (SA) for all three measurands. When participants used ICP-MS and ICP-OES, sample dissolutions with concentrated acids by microwave digestion and autoclave heating were employed. For Fe measurements, JSI used Instrumental Neutron Activation Analysis with k_0-method (k_0-INAA) without alumina dissolution. There was no clear trend or discrepancy between measurement results depending on whether sample dissolutions were employed or not, except NIM's result.

Table 5: Summary of measurement methods used by participating NMI/DI

Participating NMI/DI	Measurand: *w*(element), (mg/kg)	Sample preparation method	Calibration method	Analytical instrument
JSI	*w*(Fe)	No treatment	k_0-method	INAA (TRIGA Mark II reactor, HPGe detectors)
KRISS	*w*(Fe), *w*(Mg), *w*(Si)	Microwave digestion	Standard addition (SA)	ICP-OES
NIM	*w*(Fe), *w*(Mg), *w*(Si)	Microwave digestion	Standard addition (SA)	ICP-MS (high resolution)
VNIIM-UNIIM	*w*(Fe), *w*(Mg), *w*(Si)	Autoclave acid dissolution	Mg: Isotope dilution mass spectrometry (IDMS) Fe and Si: Standard addition (SA)	ICP-MS

Calibration Materials Used by Participants

Participants established the metrological traceability of their results using certified reference materials (CRMs) with stated traceability and/or commercially available high-purity materials for which they determined the purity. In Table 6, reference materials for calibration and the traceability sources used by participants were summarized.

Table 6: Summary of calibration materials used by participants

Participating NMI/DI	Measurand: *w*(element), (mg/kg)	Reference material used for calibration (traceability)
JSI	*w*(Fe)	Fe: IRMM-530R (Al-0.1 %Au alloy); JRC, IRMM, $w(\mathrm{Au}) = (1.003 \pm 0.012)$ g/kg, $k = 2$
KRISS	*w*(Fe), *w*(Mg), *w*(Si)	KRISS mono-elemental standard solution CRM of Fe, Mg, and Si (Traceable to the SI by in-house purity assessment)

NIM	*w*(Fe), *w*(Mg), *w*(Si)	Fe: GBW08616 calibration solution of Fe, *w*(Fe) = (1000 ± 2) μg/mL Mg: GBW(E)080126 calibration solution of Mg Si: GBW(E)080272 calibration solution of Si
VNIIM-UNIIM	*w*(Fe), *w*(Mg), *w*(Si)	Fe: PRM-1.3-176-003-2016-Fe (99.9636±0.0093) % Traceable to in-house purity measurement procedure Mg: PRM № 3158 Mg^{24} (atomic fraction of 24Mg is (99.846 ± 0.002) %, atomic fraction of 25Mg is (0.090 ± 0.002) %) Traceable to in-house isotope ratio measurement procedure Si: PRM Si № 5213B (99.98 ± 0.02) % Traceable to in-house purity measurement procedure

Participant Results for mass fraction of iron (Fe)

The results for CCQM-K144 for the determination of iron are detailed in Table 7 and presented graphically in Figure 1.

Table 7: Reported results for mass fraction of iron, *w*(Fe)

Participating NMI/DI	Reported *w*(Fe) (mg/kg)	Reported combined standard uncertainty, u_c (mg/kg)	Coverage factor, *k* (95 % level of confidence)	Expanded uncertainty, *U* (mg/kg)	Number of replicates, *n*
KRISS	2.14	0.096	2.36	0.23	7
VNIIM-UNIIM	2.24	0.205	2	0.41	6
JSI	2.25	0.09	2	0.18	7
NIM	2.9	0.2	2	0.4	6

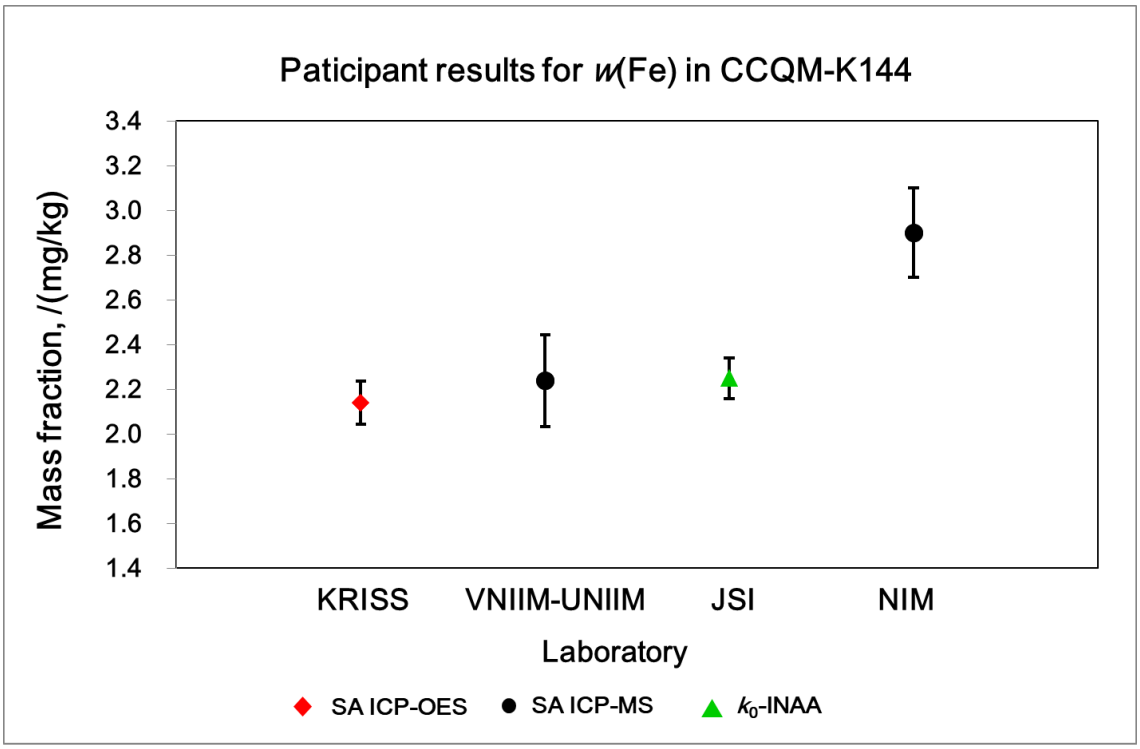

Figure 1: Illustrated Reported Results for the mass fraction of iron, *w*(Fe), (mg/kg). Error bars are u_c.

Participant Results for mass fraction of magnesium (Mg)

The results for CCQM-K144 for the determination of magnesium is detailed in Table 8 and presented graphically in Figure 2.

Table 8: Reported results for mass fraction of magnesium, *w*(Mg)

Participating NMI/DI	Reported *w*(Mg) (mg/kg)	Reported combined standard uncertainty, u_c (mg/kg)	Coverage factor, *k* (95 % level of confidence)	Expanded uncertainty, *U* (mg/kg)	Number of replicates, *n*
KRISS	1.95	0.09	2.36	0.20	7
VNIIM-UNIIM	2.08	0.12	2	0.24	6
NIM	3.5	0.43	2	0.9	6

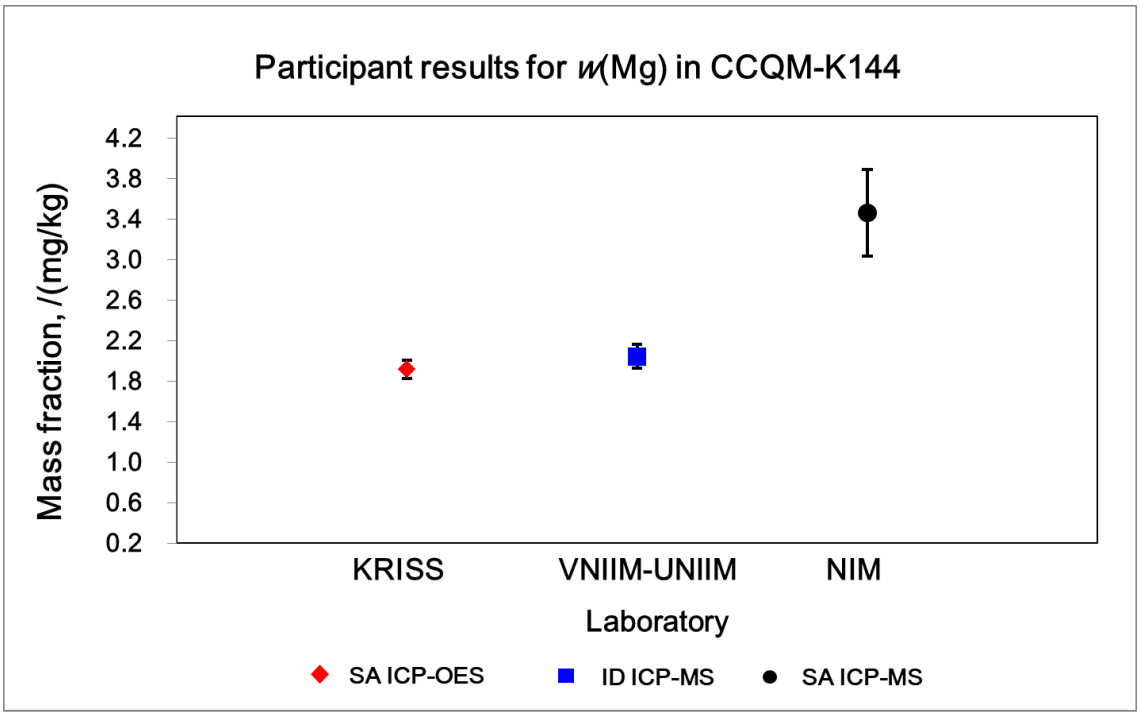

Figure 2: Illustrated Reported Results for the mass fraction of magnesium, *w*(Mg), (mg/kg). Error bars are u_c.

Participant Results for mass fraction of silicon (Si)

The results for CCQM-K144 for the determination of silicon (Si) is detailed in Table 9 and presented graphically in Figure 3.

Table 9: Reported results for mass fraction of silicon, *w*(Si)

Participating NMI/DI	Reported *w*(Si) (mg/kg)	Reported combined standard uncertainty, u_c (mg/kg)	Coverage factor, *k* (95 % level of confidence)	Expanded uncertainty, *U* (mg/kg)	Number of replicates, *n*
VNIIM-UNIIM	10.28	0.97	2	1.94	6
KRISS	12.2	0.1	2.36	0.21	7
NIM	14.6	1.5	2	3.0	6

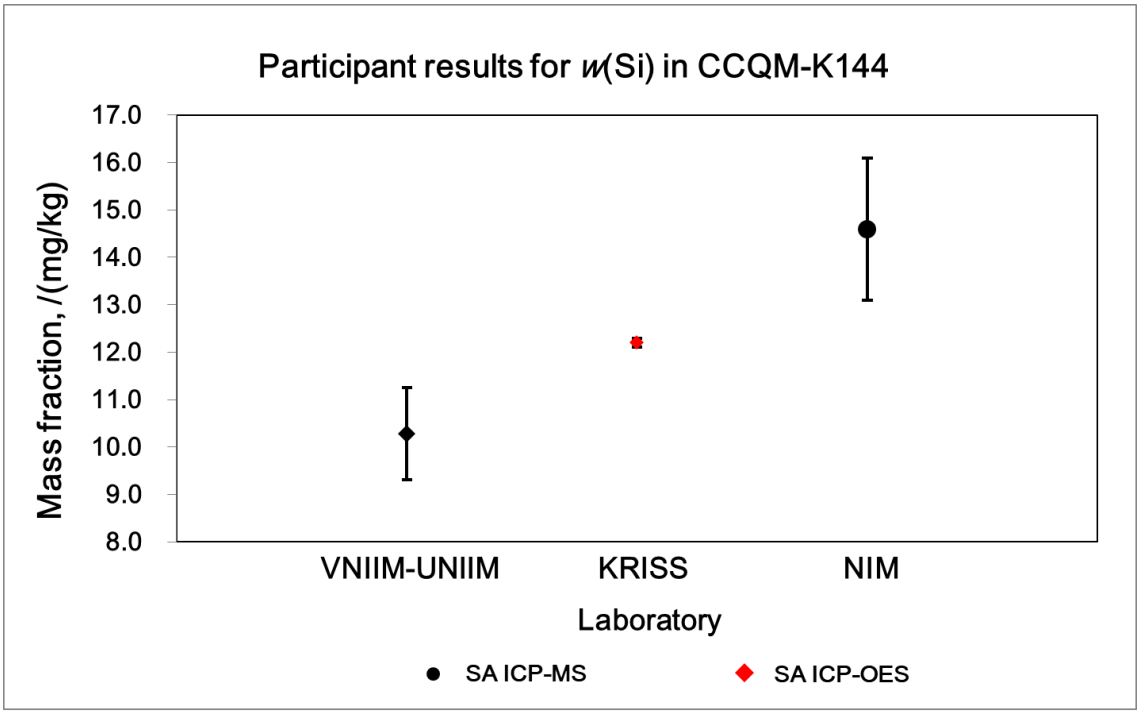

Figure 3: Illustrated Reported Results for the mass fraction of silicon, *w*(Si), (mg/kg). Error bars are u_c.

KEY COMPARISON REFERENCE VALUE (KCRV) ESTIMATION

As per the agreement made by the IAWG, the NIST Decision Tree (NDT, (Version 1.0.4)) was used to calculate the KCRVs 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. When a participant did not report the DoF value, it has been estimated based on the reported coverage factor. Following a series of hypothesis tests related to homogeneity, symmetry, and normality (Gaussian shape) of the set of data, the NDT recommends the best statistical model for calculating the KCRV and DoE. The recommendation of the NDT has been followed, unless otherwise noted.

From the results reported by the participants, three different statistical tests were conducted, and the 'Hierarchical Gauss-Gauss' model was recommended for all three elements, as shown in Figure 4. While the power of the statistical tests is not high with small data sets, the selected model appears reasonable from a visual inspection of the data. The results of these tests for each measurand as reported by the participants are summarized in In Table 10.

Table 10: The NIST Decision Tree test results for participants' reported results of Fe, Mg, and Si

Steps (Statistical test)	Element	Test results	Suggestion	Recommendation
Step 1. Homogeneity (Cochran's Q-test)	Fe	p-value = 0.0080 Q = 11.82	Heterogeneous (overdispersion)	Hierarchical Gauss-Gauss (HGG)
	Mg	p-value = 0.0018 Q = 12.64	Heterogeneous (overdispersion)	
	Si	p-value = 0.039 Q = 6.47	Heterogeneous (overdispersion)	
Step 2. Symmetry (Miao-Gel-Gastwirth test)	Fe	p-value = 0.128	Symmetrical	
	Mg	p-value = 0.2532	Symmetrical	
	Si	p-value = 0.7492	Symmetrical	
Step 3. Normality (Shapiro-Wilk test)	Fe	p-value = 0.226	Gaussian	
	Mg	p-value = 0.5755	Gaussian	
	Si	p-value = 0.8833	Gaussian	

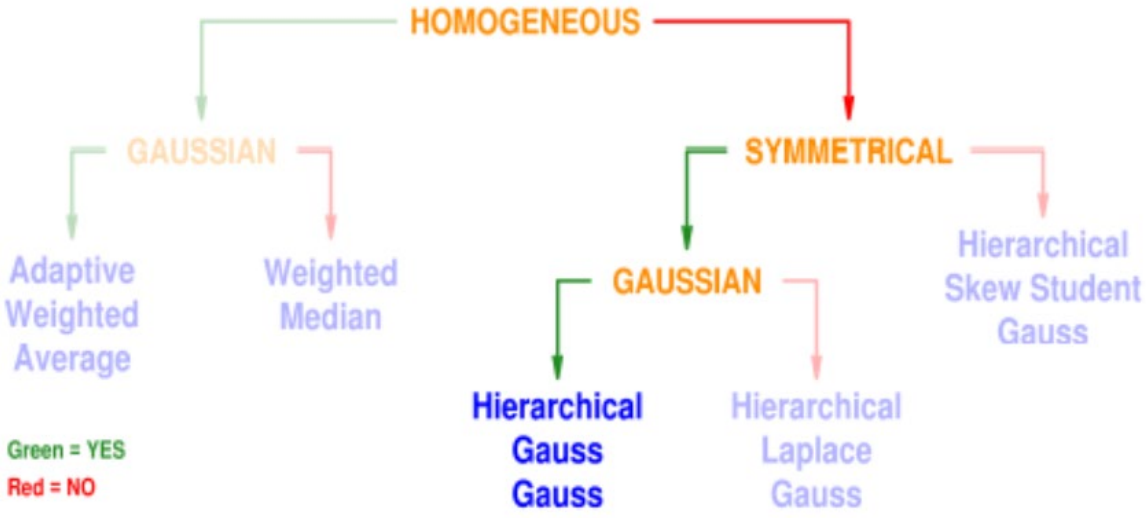

Figure 4: Decision Tree recommendation of Hierarchical Gauss-Gauss for participants' reported results of Fe, Mg, and Si in CCQM-K144

The NDT provides dark uncertainty, τ (tau), from dispersion of the participants' reported results, as well as the consensus estimate of the mass fraction, w, and its standard uncertainty, u. Thus, the contribution from the dark uncertainty to each participant's reported result was represented by the square root of $(u_i^2+\tau^2)$, where u_i is the participant's reported uncertainty, when comparing the participants' results with respect to the candidate KCRV and its standard uncertainty. Detailed in Table 11 to 13 are the consensus estimates of mass fractions of Fe, Mg and Si and their standard uncertainties, 95 % coverage intervals (expanded uncertainties), dark uncertainties, and the models used for their estimation. Figures 5 to 10 illustrate the participants' results, considering the contribution of dark uncertainty.

Table 11: Consensus estimate of the candidate KCRV for iron (Fe) and its standard uncertainty, 95 % coverage interval, and dark uncertainty with the model for the estimation.

Consensus estimate of w(Fe) (mg/kg)	Standard uncertainty, u (mg/kg)	95 % coverage interval (mg/kg)	Dark uncertainty, τ (mg/kg)	Model used for the estimation
2.332	0.109	2.11-2.55	0.153	HGG

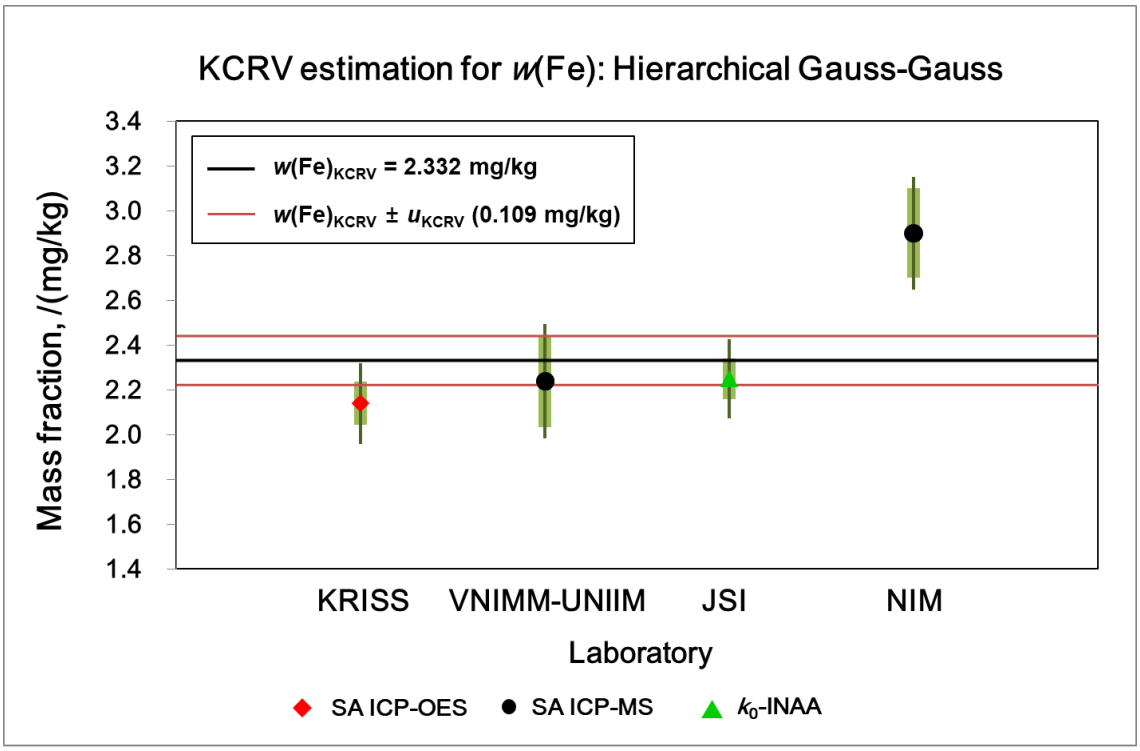

Figure 5: Participants' results for the mass fraction of iron, w(Fe), with respect to the candidate KCRV, $w(\text{Fe})_{\text{KCRV}}$ (represented by a thick black line), and its associated standard uncertainty, u_{KCRV} (shown as red lines) in CCQM-K144. The thick error bars indicate the standard uncertainty of each participant's result, u_i, while the thin error bars incorporate the dark uncertainty, τ (i.e., $\pm\sqrt{(u_i^2+\tau^2)}$).

Table 12: Consensus estimate of the candidate KCRV for magnesium (Mg) and its standard uncertainty, 95 % coverage interval, and dark uncertainty with the model for the estimation.

Consensus estimate of w(Mg) (mg/kg)	Standard uncertainty, u (mg/kg)	95 % coverage interval (mg/kg)	Dark uncertainty, τ (mg/kg)	Model used for the estimation
2.341	0.307	1.742-2.94	0.448	HGG

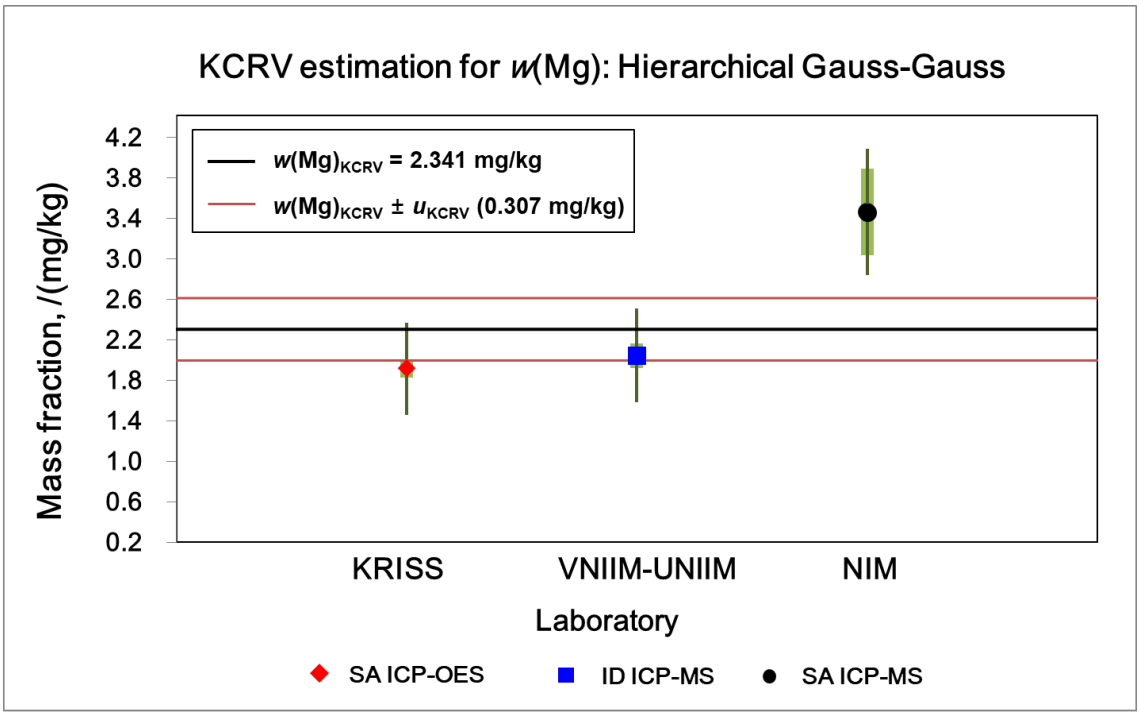

Figure 6: Participants' results for the mass fraction of magnesium, w(Mg) with respect to the candidate KCRV, $w(\mathrm{Mg})_{\mathrm{KCRV}}$ (represented by a thick black line), and its associated standard uncertainty, u_{KCRV} (shown as red lines) in CCQM-K144. The thick error bars indicate the standard uncertainty of each participant's result, u_i, while the thin error bars incorporate the dark uncertainty, τ (i.e., $\pm\sqrt{(u_i^2+\tau^2)}$).

Table 13: Consensus estimate of the candidate KCRV for silicon (Si) and its standard uncertainty, 95 % coverage interval, and dark uncertainty with the model for the estimation.

Consensus estimate of w(Si) (mg/kg)	Standard uncertainty, u (mg/kg)	95 % coverage interval (mg/kg)	Dark uncertainty, τ (mg/kg)	Model used for the estimation
12.22	0.83	10.5-13.95	1.40	HGG

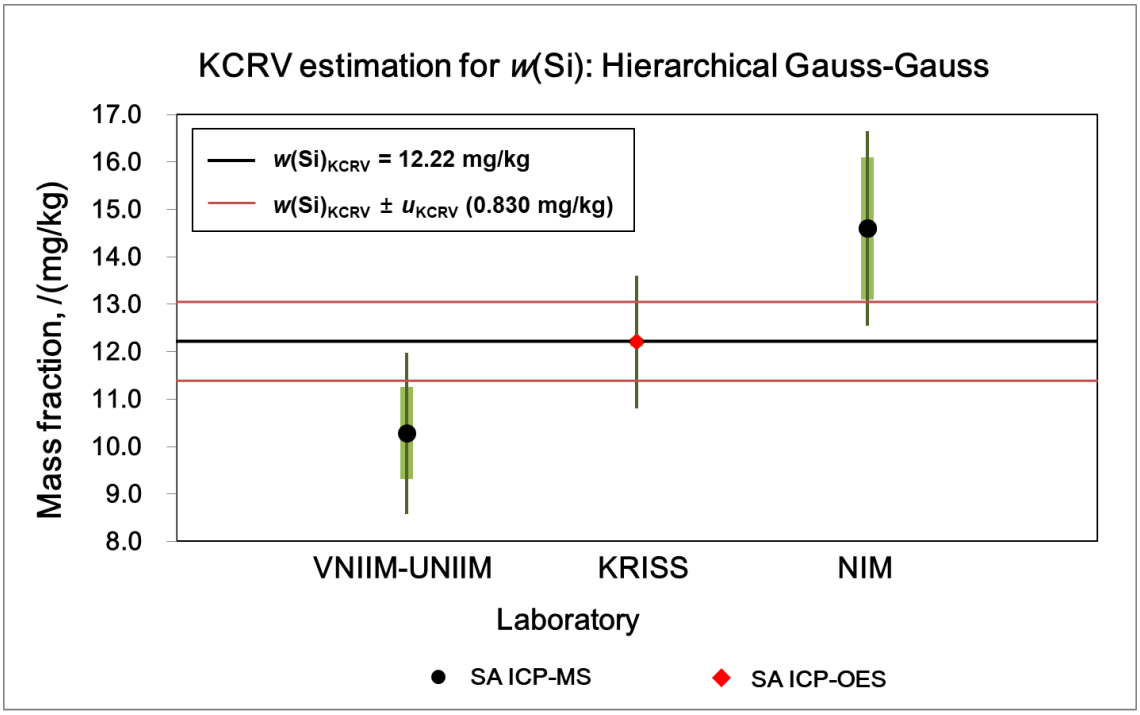

Figure 7: Participants' results for the mass fraction of silicon, w(Si) with respect to the candidate KCRV, $w(\mathrm{Si})_{\mathrm{KCRV}}$ (represented by a thick black line), and its associated standard uncertainty, u_{KCRV} (shown as red lines) in CCQM-K144. The thick error bars indicate the standard uncertainty of each participant's result, u_i, while the thin error bars incorporate the dark uncertainty, τ (i.e., $\pm\sqrt{(u_i^2+\tau^2)}$).

DEGREES OF EQUIVALENCE (DoE)

The degrees of equivalence in CCQM-K144 were evaluated using the NIST Decision Tree (https://decisiontree.nist.gov). The DoE value for a given measurand and for the i^{th} participant, D_i, is the reported measurement value, x_i, minus the KCRV ($D_i = x_i - \text{KCRV}$). They are listed in Tables 14-16 and graphically shown in Figures 8-10. For the NDT procedures used to estimate each of the KCRVs in this comparison, the expanded uncertainty of D_i, $U(D_i)$, is half the shortest interval centered on D_i that is believed to encompass the true value with 95 % probability, where the endpoints of the interval are derived directly from a large sample drawn from the corresponding probability distribution. Therefore, the error bars in the plots represent the expanded uncertainties of D_i at 95 % confidence level, $U(D_i)$. In these figures, the horizontal line denotes perfect agreement with the KCRV, the black dot represents the D_i value, and the uncertainty bars represent $U(D_i)$.

All participants in CCQM-K144 demonstrated equivalence. In the third column in each table, the uncertainties with symbol * are the participant's reported uncertainty and the dark uncertainty added in quadrature, $\sqrt{(\tau^2+u^2(x_i))}$. For participants without an asterisk (*), the value is just their reported standard uncertainty $u(x_i)$.

Table 14: Degrees of Equivalence, *Di*, and the expanded uncertainty, *U*(*Di*), for the mass fraction of iron (Fe) in CCQM-K144. Those values accompanied by an asterisk (*) are the participant's reported uncertainty and dark uncertainty added in quadrature, $\sqrt{(\tau^2+u^2(x_i))}$, while those without an asterisk are the reported uncertainty, $u(x_i)$.

Participating NMI/DI	Reported mass fraction, x_i (mg/kg)	Standard uncertainty, $u(x_i)$ (mg/kg)	Difference from KCRV, D_i (mg/kg)	Expanded uncertainty of the difference, $U(D_i)$ (mg/kg)	D_i / $U(D_i)$
KRISS	2.14	0.096	-0.190	0.285	-0.667
VNIIM-UNIIM	2.24	0.205	-0.090	0.454	-0.198
JSI	2.25	0.09	-0.080	0.280	-0.286
NIM	2.9	0.25*	0.570	0.646*	0.882

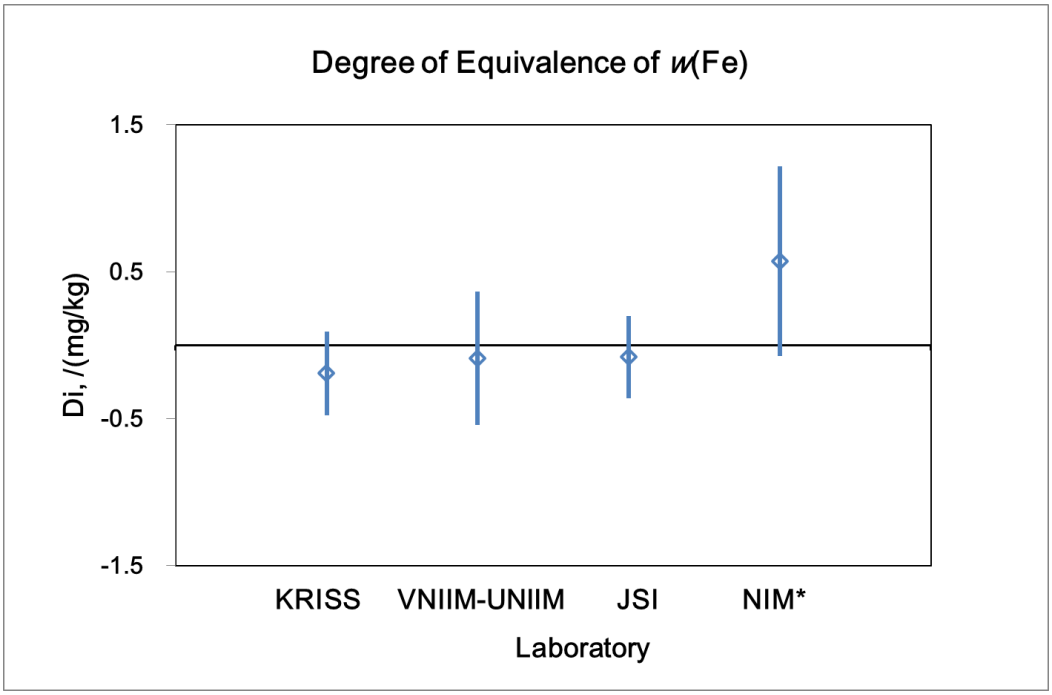

Figure 8: Degrees of Equivalence, *Di*, and the expanded uncertainty, *U*(*Di*), for the mass fraction of iron (Fe) in CCQM-K144. Those values accompanied by an asterisk (*) are estimated using the participant's reported uncertainty and dark uncertainty added in quadrature, $\sqrt{(\tau^2+u^2(x_i))}$, while those without an asterisk are estimated using just the reported uncertainty, $u(x_i)$.

Table 15: Degrees of Equivalence, *Di*, and the expanded uncertainty, *U*(*Di*), for the mass fraction of magnesium (Mg) in CCQM-K144. Those values accompanied by an asterisk (*) are the participant's reported uncertainty and dark uncertainty added in quadrature, $\sqrt{(\tau^2+u^2(x_i))}$, while those without an asterisk are the reported uncertainty, $u(x_i)$.

Participating NMI/DI	Reported mass fraction, x_i (mg/kg)	Standard uncertainty, $u(x_i)$ (mg/kg)	Difference from KCRV, D_i (mg/kg)	Expanded uncertainty of the difference, $U(D_i)$(mg/kg)	D_i / $U(D_i)$
KRISS	1.95	0.09	-0.391	0.625	-0.626
VNIIM-UNIIM	2.08	0.12	-0.261	0.645	-0.404
NIM	3.5	0.62*	1.159	1.701*	0.681

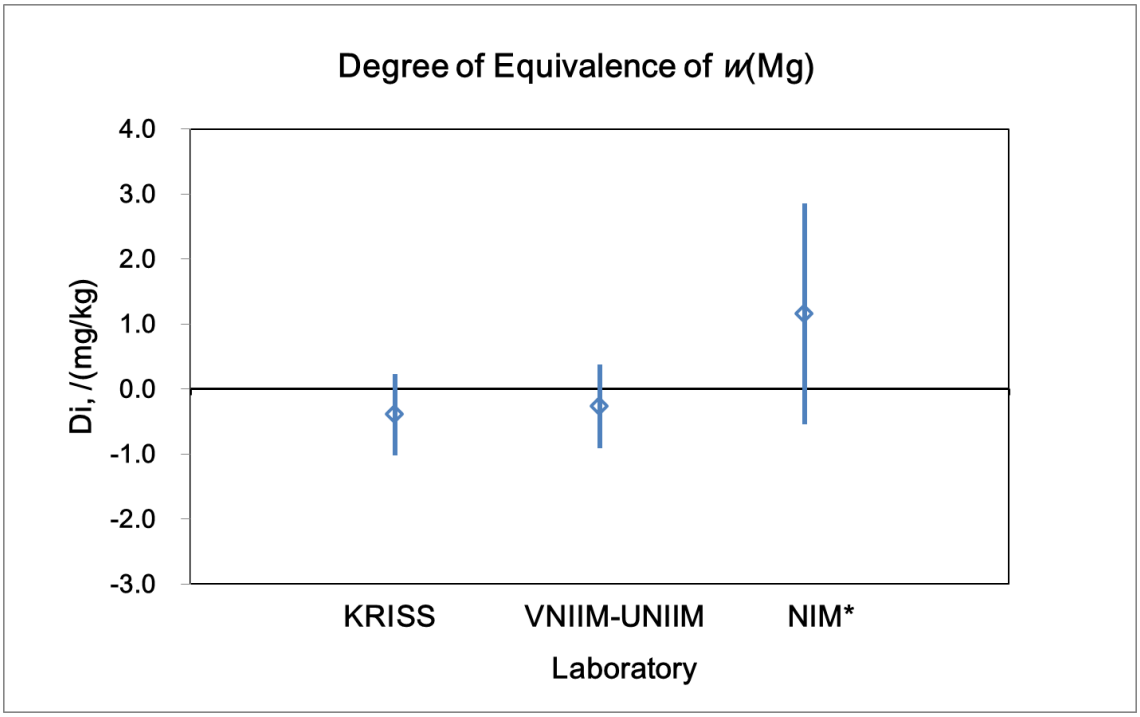

Figure 9: Degrees of Equivalence, *Di*, and the expanded uncertainty, *U*(*Di*), for the mass fraction of magnesium (Mg) in CCQM-K144. Those values accompanied by an asterisk (*) are the participant's reported uncertainty and dark uncertainty added in quadrature, $\sqrt{(\tau^2+u^2(x_i))}$, while those without an asterisk are the reported uncertainty, $u(x_i)$.

Table 16: Degrees of Equivalence, *Di*, and the expanded uncertainty, *U*(*Di*), for the mass fraction of silicon (Si) in CCQM-K144.

Participating NMI/DI	Reported mass fraction, x_i (mg/kg)	Standard uncertainty, $u(x_i)$ (mg/kg)	Difference from KCRV, D_i (mg/kg)	Expanded uncertainty of the difference, $U(D_i)$ (mg/kg)	D_i / $U(D_i)$
VNIIM-UNIIM	10.28	0.97	-1.942	2.529	-0.768
KRISS	12.2	0.1	-0.02199	1.733	-0.013
NIM	14.6	1.5	2.378	3.374	0.705

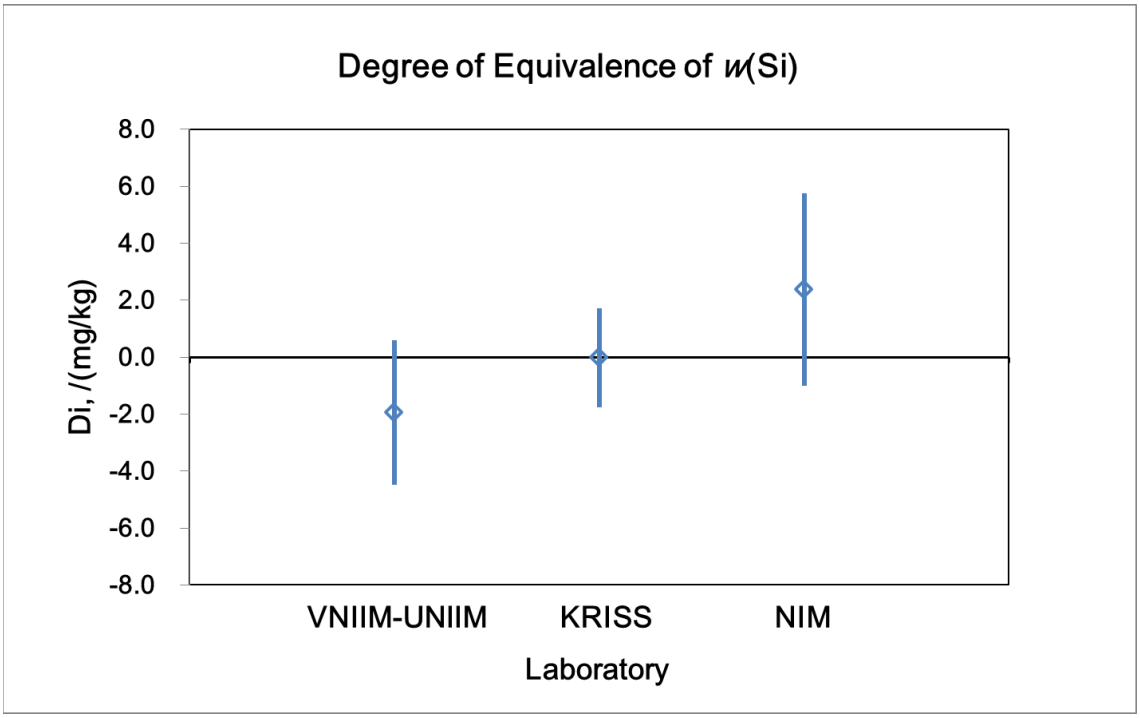

Figure 10: Degrees of Equivalence, *Di*, and the expanded uncertainty, *U*(*Di*), for the mass fraction of silicon (Si) in CCQM-K144.

USE OF CCQM-K144 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

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

Successful participation in CCQM-K144 demonstrates the following measurement capabilities in determining mass fraction of alkali and alkaline earth elements, transition metals (except Hg), and metalloids in mass fraction range more than 0.05 mg/kg in alumina powder or other metal or metal oxide matrices that are difficult to dissolve.

All participants' DoE cross zero, meaning that everyone has demonstrated their competency within the level of uncertainty used to calculate their DoE values. Consequently, CMCs that align with the HFTLS and with uncertainties aligned with the DoE are supported.

Core Capability Table

Analyte groups	Matrix challenges					
	Water	High Silica content (e.g. Soils, sediments, plants, ...)	High salts content (e.g. Seawater, urine, ...)	High organics content (e.g. high carbon) (e.g. Food, blood/serum, cosmetics, ...)	Difficult to dissolve metals (Autocatalysts, ...)	High volatile matrices (e.g. solvents, fuels, ...)
Group I and II: Alkali and Alkaline earth (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba)						
					K144 (Mg)	
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)						
					K144 (Fe)	
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)						
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)						
					K144 (Si)	
Non-metals (P, S, C, N, O)						
Halogens (F, Cl, Br, I)						
Rare Earth Elements (Lanthanides, Actinides)						

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

CONCLUSIONS

CCQM-K144 Trace elements in alumina powder has been successfully conducted demonstrating measurement capabilities of all participants. This KC directly evaluates the ability to accurately determine the mass fractions of iron (Fe), magnesium (Mg) and silicon (Si), in range more than 0.05 mg/kg in an alumina powder and similar matrices. For Fe measurement, four NMIs/DIs, JSI (Slovenia), KRISS (Republic of Korea), NIM (China), and VNIIM-UNIIM (Russia) participated in CCQM-K144. For Mg and Si, three participants, KRISS, NIM, and VNIIM-UNIIM, reported their measurement results. Various measurement procedures were employed, including Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with standard addition (SA) or isotope dilution (ID) calibration approaches, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with standard addition (SA) following sample dissolution. Additionally, one participant used the Instrumental Neutron Activation Analysis with k_0-method (k_0-INAA) for Fe without needing to dissolve the alumina, demonstrating equivalence can be achieved regardless of sample dissolution.

The consensus estimates for the mass fractions of Fe, Mg, and Si were calculated using the 'Hierarchical Gauss-Gauss' model recommended by the NIST Decision Tree (NDT) for Key Comparisons. These values were subsequently approved as the KCRVs in CCQM IAWG. Following the procedures in the "IAWG Guidance on Using the NIST Decision Tree for Comparison Reporting", an assessment was conducted to determine the incorporation of dark uncertainty into the uncertainties. This evaluation resulted in the final DoE tables. All participants' results complied with the KCRVs, although a few participants required their reported measurement uncertainty to be expanded by dark uncertainty to agree with the KCRV. Remarkably, all participants' DoEs crossed zero, and the absolute values of D_i / $U(D_i)$ remained below one, demonstrating their competence within their respective levels of uncertainties. Therefore, participants can use this KC as supporting evidence for claiming the CMCs that align with the HFTLS.

ACKNOWLEDGEMENTS

The study coordinator sincerely thanks the participating laboratories for participating in the Key Comparison, CCQM-K144, and providing the requested information used in this study. Additionally, the coordinator acknowledges the contributions of the following colleagues from each participating laboratory:

Hyungsik Min, Enwha Kim, and Seunghee Kim
Korea Research Institute of Standards and Science (KRISS), Republic of Korea

Gao Tianheng, Tang Yiming and Zhou Yuanjing
National Institute of Metrology of China (NIM), China

Tatyana Tabatchikova, Pavel Migal and Anton Zasukhin
Ural Research Institute for metrology – Affiliated Branch of the D.I.Mendeleev Institute for Metrology (VNIIM-UNIIM), Russia

Special thanks to Michael R. Winchester and Antonio Possolo for help in estimating the KCRVs and DoEs, as well as their development of the 'IAWG Guidance on Using the NIST Decision Tree for Comparison Reporting'.

REFERENCES

1. Possolo A, Koepke A, Newton D, Winchester MR, Comparisons, J. Res. Natl. Inst. Stan. Decision Tree for Key 126:126007(2021). https://doi.org/10.6028/jres.126.007
2. NIST Decision Tree for Key Comparisons (https://decisiontree.nist.gov/)
3. Possolo A, Koepke A, Newton D, Winchester MR, NIST Decision Tree User's Manual, May 20, 2022, NIST. file:///C:/Users/admin/Downloads/NDT_Manual.pdf

APPENDIX A: Call for Participation

Date: Nov. 6, 2018

E-mail title: Registration for CCQM-K144/P182: Mg, Fe and Si in Alumina

Dear Colleagues,

Please find attached documents prepared by KRISS for CCQM-K144/P182: Mg, Fe and Si in Alumina. The registration form should be returned to Dr. Kyoung-Seok Lee (E-mail: kslee@kriss.re.kr) and Dr. Yong-Hyeon Yim (E-mail: yhyim@kriss.re.kr) by 24 November 2018.

Please note that only participation in the key comparison will allow support of CMCs. Also if results from more than one method are submitted for CCQM-K144 only the method used for the result designated for the KCRV is directly approved for CMCs. The registration is open to NMIs/DIs in accordance with the CIPM MRA. Any proposed participation in CCQM-P182 by an expert laboratory should first be discussed with the coordinating laboratory (KRISS) and myself as it will be necessary to complete an additional BIPM form for approval by the CCQM President.

Best regards,

Mike Sargent

APPENDIX B: Protocol

CCQM-K144/CCQM-P182
"Trace elements in alumina powder"

Technical Protocol

1. Introduction

Aluminium oxide (Al_2O_3), commonly called alumina, has been widely used in various industries as a basic material for ceramics, a catalyst for chemical reactions, an ingredient for cosmetics, and a medium for chromatography. In recent industries, high purity alumina is essential as one of the advanced materials from raw material of sapphire glasses with excellent mechanical strength and high transparency to nanoparticles. Trace elements such as iron (Fe), magnesium (Mg), and silicon (Si) in high purity alumina may influence the material properties such as optical transparency and mechanical strength. If there are higher levels of these elements as impurities in high purity alumina, qualities and yields of final product can be severely reduced. Therefore, the accurate measurements of trace elements in alumina are important for the relevant industries.

Recent advances in high-end display and semiconductors require more robust quality control of advanced materials and the demands on relevant measurement standards are increasing. However, there were no CCQM IAWG studies on the advanced materials since 2008. Therefore, a Key Comparison was included in the IAWG's five-year plan of 2018 to cover current and future CMCs for these area ("9. Advance materials" and "14. Other materials" in "List of Amount of Substance Categories" of CMCs of Chemistry) which are related to the IAWG Core Capability table on "Difficult to dissolve metals" of "Matrix challenges." In 2016, KRISS proposed the comparison for the determination of trace elements in alumina powder and IAWG approved it as the Key Comparison, CCQM-K144 in parallel with CCQM-P182.

2. Sample

Each participant will receive two PFA bottles and each bottle sealed in a polymer bag containing about 30 g of the alumina powder. It is required to report the measurement results obtained only from one sample bottle for exclusion of consideration of between-bottle homogeneity in a participating laboratory. The sample in the other bottle can be used for preliminary analysis. Please confirm the delivery of the sealed samples by e-mail with the receipt as soon as the sample bottles have arrived.

The sample of alumina powder for CCQM-K144/P162 was produced by KRISS in accordance with ISO 17034 and ISO Guide 35 from a single batch of high purity alumina powder (≥ 99.999 %) which was synthesized by a commercial company, MiCo, Ltd., Korea. The raw material was carefully selected after particle size analysis using field-emission scanning electron microscopy (FE-SEM) and ICP-MS screening of Fe, Mg, and Si. The particle size distribution was in range of 0.3 μm to 0.8 μm. The alumina powder was put in a 50 L pre-cleaned polypropylene bottle. To obtain appropriate homogeneity as a reference material, alumina powder in the bottle was thoroughly mixed using cylinder roller. Then, the homogenized powder was bottled into 50 mL PFA bottle. Each bottle contains around 30 g of high purity alumina powder. All sample handling processes were carried out in a clean environment with filtered air through PTFE HEPA filter. All bottles and sample handling tools whose surfaces were contacted with sample were sequentially cleaned by using 6 % hydrochloric acid, 10 % nitric acid, 5 % hydrofluoric acid, and deionized water (18 MΩ·cm resistivity).

The homogeneities were evaluated by ICP-MS and ICP-OES measurements. The standard deviations of measurement results of iron (Fe), magnesium (Mg), and silicon (Si) in subsamples taken from 12 bottles were used to estimate between-bottle homogeneity. The between-bottle standard deviations were 1.92 %, 2.55 %, 3.52 % for Fe, Mg, and Si, respectively. For the estimation of within-bottle homogeneity, three subsamples in each bottle were taken and the mean of the standard deviations of measurement results were used. The within-bottle standard deviations were less than 2.9 %, 1.6 %, and 2.5 % for Fe, Mg, and Si, respectively. The amount of subsamples taken was about 1 g. After the sampled alumina powder was dissolved by pressurized microwave-assisted acid digestion with 25 % hydrochloric acid, the sample solution

was centrifuged to observe if any undissolved particles were present. In addition, the sample solution was also investigated by dynamic light scattering and optical microscopy. No particles in sample solutions were observed after sample dissolution.

3. Measurands

The measurands are the mass fractions, mg/kg, of the elements, iron (Fe), magnesium (Mg), and silicon (Si) in alumina powder. The expected mass fractions are listed in the following table:

Element	**Expected mass fraction (mg/kg)**
Fe	1~20
Mg	1~20
Si	1~20

4. Core Capabilities

The measurands with the expected range in alumina powder sample agreed in IAWG for this Key Comparison can be used to support CMCs based on the following core capability (CC) matrix table:

Analyte groups	Matrix challenges					
	Water	High Silica content (e.g. Soils, sediments, plants, ...)	High salts content (e.g. Seawater, urine, ...)	High organics content (e.g. high carbon) (e.g. Food, blood/serum, cosmetics, ...)	Difficult to dissolve metals (Autocatalysts, ...)	High volatile matrices (e.g. solvents, fuels, ...)
Group I and II: Alkali and Alkaline earth (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba)						
					K144 (Mg)	
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)						
					K144 (Fe)	
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)						
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)						
					K144 (Si)	
Non-metals (P, S, C, N, O)						
Halogens (F, Cl, Br, I)						
Rare Earth Elements (Lanthanides, Actinides)						

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

4. Sample storage and handling

The sample should be kept in its original package without exposure to direct light in a place at room temperature and with low humidity. The sample bottle should be shaken vigorously before opening to ensure re-homogenization of the content. Then, it opened only after being in equilibration at room temperature to prevent condensation of moisture from the air and a drift during weighing in mass measurements. To minimize silicon contamination, use of quartz or glass materials should be avoided.

5. Measurement method

Participants are free to choose any appropriate methods (e.g. ICP-MS, GDMS, ICP-OES, LA-ICP-MS, etc.) based on their own standard procedures for the measurement values and the evaluation of measurement uncertainties. In case of using more than two measurement methods, participants are required to submit only one result to CCQM-K144 for the KCRV calculation although participants are encouraged to submit all additional results to CCQM-P182. It is suggested that the measurement results are obtained from at least five sub-samples for each

measurand with a minimum sub-sample mass of 1 g. If sample dissolution procedures are necessary, it is recommended to check the absence of residual particles in sample solutions by centrifugation around 20,000 rpm for 10 min. to ensure complete dissolution of the alumina powder.

6. Dry mass correction

Dry mass correction of the sample masses should be carried out to obtain the equivalence among the participants' reported results. Samples of about 1 g taken in weighing bottles are dried at 110 °C for 2 hours by using a drying oven. Samplings for both dry mass correction and analysis are recommended to be carried out at the same time to minimize any change in moisture content during sampling. The true mass changes before and after drying should be evaluated for dry mass correction of the measurement results.

7. Reporting

A Report Form of Results will be provided to the participants by e-mail. ***Participants are required to report their results as mass fraction, mg/kg, obtained from measurements of at least five sub-samples of 1 g in a single sample bottle with dry mass correction.*** Participants confirm one result for each measurand for the KCRV calculation in CCQM-K144. The completed Report Form of Results should be submitted to KRISS on the scheduled dead line by e-mail. It is recommended to provide detailed information about the applied procedure for the measurement:

- Final results with standard and expanded uncertainties for each measurand.
- If the final result has been calculated from more than two measurement methods, please, report the individual results with the combined final results.
- Additional results obtained from more than two measurement methods are encouraged to submit to CCQM-P182.
- Information about sample preparation: sample dissolution method (apparatus, reagents w ith their quantities and concentration, temperature, pressure, time, etc.) or direct samplin g procedures
- Information about instrumental analysis: Instrument and experimental conditions used fo

r the measurement

- Information about the calibration method including reference material used for calibratio n or other materials in the analytical procedure
- Details of the uncertainty evaluation: all uncertainty sources and their typical values

8. Time schedule

- Sample dispatch: Dec. 2018
- Reporting: End of Aug. 2019
- Draft report: CCQM IAWG meeting in Sep. 2019

8. Contact:

Dr. Kyoung-Seok Lee

Korea Research Institute of Standards and Science (KRISS)

267 Gajeong-ro, Yuseong-gu, Daejeon 305-340, Republic of Korea

E-mail: kslee@kriss.re.kr

Tel: +82-42-868-5841

Fax: +82-42-868-5801

APPENDIX C: Registration Form

CCQM-K144/CCQM-P182 "Trace elements in alumina powder"

Registration Form

Institute	**Full Name:**
	Abbreviated Name:
Address*	**City:** **State:** **Country:** **Postcode:**
Contact Name	
E-mail	
Telephone/Fax	

*** The sample will be delivered to this address. Please fill it in detail.**

Measurand (as mass fraction)	CCQM-K144 (Yes/No)	CCQM-P182 (Yes/No)
Mg		
Fe		
Si		

Signature: _____ Date:

Please return the completed form via e-mail no later than 24th Nov. 2018 to

Dr. Kyoung-Seok Lee (E-mail: kslee@kriss.re.kr) and Dr. Yong-Hyeon Yim (E-mail: yhyim@kriss.re.kr)

Korea Research Institute of Standards and Science (KRISS)

Address: 267 Gajeong-ro, Yuseong-gu, Daejeon 305-340, Republic of Korea

Telephone: +82-42-868-5841 Fax: +82-42-868-5801

APPENDIX D: Sample Receipt Form

CCQM-K144/CCQM-P182 "Trace elements in alumina powder"

Sample Receipt Form

Institute	**National Institute of Metrology, China**
Contact Name	**Tao ZHOU**
Email	zhoutao@nim.ac.cn
Sample No. for 2 bottles	**126, 127**
Receipt date	**2018-12-17**

Confirmation of package content

State	1st bottle	2nd bottle
Intact	√	√
Broken	-	-
Other thing (please report)	-	-

Please return this form after receipt of the samples via e-mail to

Dr. Kyoung-Seok Lee (E-mail: kslee@kriss.re.kr**) and Dr. Yong-Hyeon Yim (E-mail:** yhyim@kriss.re.kr**)**

Korea Research Institute of Standards and Science (KRISS)

Address: 267 Gajeong-ro, Yuseong-gu, Daejeon 305-340, Republic of Korea

Telephone: +82-42-868-5841 Fax: +82-42-868-5801

APPENDIX E: Reporting Form

Report of Results

KRISS Korea Research Institute of Standards and Science

CCQM-K144/CCQM-P182 Trace elements in alumina powder

Participant Information

Institute Name	
Contact Name	
E-mail	
Analyst Name(s)	
Date	
Bottle No. used for analysis	

Measurand	CCQM-K144	CCQM-P182
Mg		
Fe		
Si		

Signature	

Report of Results

CCQM-K144 Trace elements in alumina powder

Summary of Results for CCQM-K144

Measurand	Mg	Fe	Si
Overall mean of measurement result (mg/kg)			
Number of subsamples (n)			
Standard deviation of the mean (mg/kg)			
Combined standard uncertainty, u_c (mg/kg)			
Coverage factor, k, of 95 % Confidence level			
Expanded uncertainty, U (mg/kg)			

Report of Results

CCQM-K144 Trace elements in alumina powder

Measurand: Magnesium (Mg)

		Sample mass (g)	Mass fraction (mg/kg)
Measurement for each subsample	1		
	2		
	3		
	4		
	5		
	6		
Mean (mg/kg)			
Standard deviation of the mean (mg/kg)			
Combined standard uncertainty, u_c (mg/kg)			
Coverage factor, k, of 95 % Confidence level			
Expanded uncertainty, U (mg/kg)			

Dry mass correction

		Sample mass (g)	Relative moisture content (%)
Measurement for each subsample	1		
	2		
	3		
Mean (%)			
Standard deviation of the mean (%)			

Sample treatment method (Please give details of sample preparation procedure)

Type of sample treatment	
Apparatus (if any)	
Procedure with operating parameters including reagents, target materials, temperature, time, pressure, power, etc.	

Measurement and Calibration method

Measurement method (ICP-OES, ICP-MS, GDMS, INAA, etc.)	
Calibration method (ID, Standard addition, direct comparator, k_0, external standard, etc.)	
Instrument with operating conditions	
Typical signal intensities of procedure blank, reagent blank, etc.	
Reactor and detector with operating conditions incluidng data analysis software	
Reference materials used for calibration (traceability, value, standard uncerainty, isotope ratios, etc.)	
Reference materials used for internal standard (provider, traceability, value, standard uncerainty, isotope ratios, etc.)	
Reference materials for quality control (provider, value, standard uncerainty, isotope ratios, etc.)	

Uncertainty budget

Measurement Model for the measurand and description of the input quantities

Input quantities	Unit	Uncertainty sources	Typical value	Standard uncertainty	Type

APPENDIX F: NIST Decision Tree Reports

For Fe,

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	A	2.14	0.096	10000
TRUE	B	2.24	0.205	10000
TRUE	C	2.25	0.090	10000
TRUE	D	2.90	0.200	10000

Date: 2023-11-05
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 100
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 2.33
Standard uncertainty: 0.109
95% coverage interval: (2.11, 2.55)
Dark uncertainty (tau): 0.153
Tau posterior 0.025 and 0.975 quantiles: (0.0075,0.543)

Decision Tree Hypothesis test results

Cochran's test for Homogeneity:
p-value: 0.008
Q = 11.82 (Reference Distribution: Chi-Square with 3 Degrees of Freedom)
tau est. = 0.2212
tau/median(x) = 0.09851
tau/median(u) = 1.494

Shapiro-Wilk test for Normality: p = 0.226

Miao-Gel-Gastwirth test of Symmetry: p = 0.128

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
A	A	-0.1900	0.563	-0.7530	0.373
B	B	-0.0901	0.645	-0.7360	0.555
C	C	-0.0801	0.563	-0.6430	0.483
D	D	0.5700	0.646	-0.0764	1.220

Lab Uncertainties Table

lab	x	u	nu	ut
A	2.14	0.096	10000	0.180
B	2.24	0.205	10000	0.256
C	2.25	0.090	10000	0.177
D	2.90	0.200	10000	0.252

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
A	-0.1900	0.276	0.563	-0.7530	0.373	0.145	0.285	-0.475	0.0951
B	-0.0901	0.329	0.645	-0.7360	0.555	0.231	0.454	-0.544	0.3640
C	-0.0801	0.276	0.563	-0.6430	0.483	0.142	0.280	-0.360	0.2000
D	0.5700	0.328	0.646	-0.0764	1.220	0.228	0.445	0.125	1.0100

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	17000
lambda[1]	1.001	50000
lambda[2]	1.001	50000
lambda[3]	1.001	50000
lambda[4]	1.001	9400
mu	1.001	33000
sigma[1]	1.001	50000
sigma[2]	1.001	50000
sigma[3]	1.001	29000
sigma[4]	1.001	49000
tau	1.001	5500

For Mg,

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	A	1.95	0.09	10000
TRUE	B	2.08	0.12	10000
TRUE	C	3.50	0.43	10000

Date: 2023-11-05
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 670
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 2.341
Standard uncertainty: 0.3074
95% coverage interval: (1.742, 2.94)
Dark uncertainty (tau): 0.4484
Tau posterior 0.025 and 0.975 quantiles: (0.03168,1.575)

Decision Tree Hypothesis test results

Cochran's test for Homogeneity:
p-value: 0.0018
Q = 12.64 (Reference Distribution: Chi-Square with 2 Degrees of Freedom)
tau est. = 0.3312
tau/median(x) = 0.1592
tau/median(u) = 2.76

Shapiro-Wilk test for Normality: p = 0.5755

Miao-Gel-Gastwirth test of Symmetry: p = 0.2532

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
A	A	-0.3909	1.523	-1.9140	1.132
B	B	-0.2609	1.521	-1.7820	1.260
C	C	1.1590	1.701	-0.5419	2.860

Lab Uncertainties Table

lab	x	u	nu	ut
A	1.95	0.09	10000	0.4573
B	2.08	0.12	10000	0.4642
C	3.50	0.43	10000	0.6212

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
A	-0.3909	0.7653	1.523	-1.9140	1.132	0.3209	0.6245	-1.0150	0.2336
B	-0.2609	0.7590	1.521	-1.7820	1.260	0.3303	0.6451	-0.9060	0.3842
C	1.1590	0.8687	1.701	-0.5419	2.860	0.5289	1.0360	0.1228	2.1950

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	36000
lambda[2]	1.001	50000
lambda[3]	1.001	50000
mu	1.001	50000
sigma[1]	1.001	50000
sigma[2]	1.001	50000
sigma[3]	1.001	50000
tau	1.001	50000

For Si,

NIST Decision Tree Report

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	A	10.28	0.97	10000
TRUE	B	12.20	0.10	10000
TRUE	C	14.60	1.50	10000

Date: 2023-11-05
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Recognizing Dark Uncertainty
Random Seed: 192
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 12.22
Standard uncertainty: 0.8299
95% coverage interval: (10.5, 13.95)
Dark uncertainty (tau): 1.401
Tau posterior 0.025 and 0.975 quantiles: (0.0871,5.397)

Decision Tree Hypothesis test results

Cochran's test for Homogeneity:
p-value: 0.039
Q = 6.469 (Reference Distribution: Chi-Square with 2 Degrees of Freedom)
tau est. = 1.225
tau/median(x) = 0.1004
tau/median(u) = 1.263

Shapiro-Wilk test for Normality: p = 0.8833

Miao-Gel-Gastwirth test of Symmetry: p = 0.7492

DoE Table

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
A	A	-1.94200	5.151	-7.093	3.209
B	B	-0.02199	4.914	-4.936	4.893
C	C	2.37800	5.604	-3.226	7.982

Lab Uncertainties Table

lab	x	u	nu	ut
A	10.28	0.97	10000	1.704
B	12.20	0.10	10000	1.404
C	14.60	1.50	10000	2.052

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
A	-1.94200	2.608	5.151	-7.093	3.209	1.282	2.529	-4.4700	0.5865
B	-0.02199	2.421	4.914	-4.936	4.893	0.836	1.733	-1.7550	1.7110
C	2.37800	2.863	5.604	-3.226	7.982	1.713	3.374	-0.9963	5.7520

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	26000
mu	1.001	50000
sigma[1]	1.001	28000
sigma[2]	1.001	50000
sigma[3]	1.001	16000
tau	1.001	18000