CCQM-K160: Platinum Group Elements in Automotive Catalyst

Key Comparison Final Report
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SUMMARY

The platinum group elements (PGEs) play an important role in reducing emissions from automotive vehicles through their use in catalytic convertors but also for catalysis in the pharmaceutical industry. The immense economic value of platinum (Pt), palladium (Pd) and rhodium (Rh) highlights the importance of highly accurate measurements. Therefore, there is a need for National Metrology Institutes (NMIs) and Designated Institutes (DIs) to demonstrate measurement capability in this space.

A pilot comparison (CCQM-P63) for precious metals in automotive catalyst took place in 2006, but with a limited number of institutes participating. Furthermore, this study was performed over 17 years ago. Therefore, there was a need to maintain existing capability and demonstrate new capability in a key comparison, in order to claim calibration and measurement capability claims (CMCs). With the core capability matrix, this study falls into the "Difficult to dissolve metals/metal oxides" which will support CMC categories 8 (Metal and metal alloys), 9 (Advanced materials) & 14 (Other materials).

Eleven NMIs and DIs participated in the Key Comparison CCQM-K160 Platinum Group Elements in Automotive Catalyst. Participants were requested to evaluate the mass fractions of Pt, Pd and Rh in mg/kg in an unused autocatalyst material (cordierite ceramic base). The Key Comparison Reference Values (KCRVs) and Degrees of Equivalence (DoEs) were calculated utilising the NIST Decision Tree for the measurands. The participants utilised a number of sample preparation and analytical methods including hot plate digestion, microwave digestion and sodium fusion, followed by either atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) detection. Several calibration techniques were used, namely external calibration, standard addition, isotope dilution mass spectrometry (IDMS) and an exact matching procedure. Additionally, one participant employed instrumental neutron activation analysis (INAA) with k_0 standardisation which is a direct solid analysis method. The majority of participants claimed traceability to NIST primary calibrants or their own CRMs. Furthermore, several matrix CRMs were included or spiked samples for quality control. All institutes were required to determine the dry mass fraction using the stipulated protocol.

The NIST decision tree was implemented for the calculation of the KCRVs and DoEs. The participant results overall showed good agreement with the KCRV, despite the variety of dissolution procedures and measurement techniques for this highly complex matrix and challenging measurands. Successful participation in CCQM-K160 demonstrated measurement capabilities for the determination of mass fraction of Pt, Pd and Rh in the mg/kg range and will support broad scope CMC claims for a wide range of challenging matrices.

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INTRODUCTION

Catalysts containing the platinum group elements (PGEs) are employed for a variety of industrial and chemical uses. Palladium (Pd), platinum (Pt) and rhodium (Rh) are the active components in automobile catalytic converters as well as catalysts used in pharmaceutical / biological applications and petroleum refining. The immense economic value of these elements highlights the importance of highly accurate measurements.

There has been one previous IAWG CCQM comparison in 2006 for precious metals in automotive catalyst, namely CCQM-P63: Platinum group elements in an automotive catalyst, however a limited number of institutes participated. Furthermore, this study was performed over 17 years ago. Therefore, there was the need for NMIs and DIs to demonstrate existing capability in a key comparison for such challenging measurands in order to claim calibration and measurement capability claims (CMCs).

Within the IAWG strategy, the sample matrix “Difficult to dissolve metals/metal oxides” was scheduled to support CMCs within categories 8 (Metal and metal alloys), 9 (Advanced materials) & 14 (Other materials). To fulfil this, CCQM-K160 was organised by LGC for Pd, Pt and Rh in an automotive catalyst material under the broad core capability approach. To address this need, in April 2019, the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) approved the Key Comparison (KC) CCQM-K160 “Platinum Group Elements in Automotive Catalyst”.

The ceramic matrix represents a significant challenge in terms of dissolution and/or full extraction of the PGMs. Additionally, the presence of matrix elements such as Zr, Nd and Hf may cause instrumental interferences which should be fully resolved. Successful participation in CCQM-K160 will demonstrate capability to measure “Difficult to dissolve metals” in a challenging matrix and will support CMCs for the analyte groups of “platinum group elements” (Pt, Pd, Rh, Ru, Ir), some “transition group elements” (Ag, Au) and some “rare earth elements” (La, Ce), all at the mg/kg level.

The following sections of this report document the timeline of CCQM-K160, the measurands, study material, participants, results, and the measurement capability claims that participation in CCQM-K160 can support. The Appendices reproduce the official communication materials, participant supplementary information and the NIST Decision Tree results.

TIMELINE

The timeline for CCQM-K160 is outlined in Table 1. There were significant delays and issues caused by the pandemic which affected the timeline.

Table 1: Timeline for CCQM-K160

Date	Action
April 2019	Proposed to CCQM
April 2019	Draft protocol presented to IAWG
April 2020	IAWG authorised CCQM-K160
August 2020	Call for participation to IAWG members
May – November 2021	Study samples shipped to participants. The range in shipping times reflects delays from shipping and customs.
6th May 2022	Reporting deadline
December 2023	Draft A report distributed to IAWG
January 2024	Draft B report distributed to IAWG
TBD	Final report approved by IAWG

MEASURANDS

The measurands were Pd, Pt and Rh, with the indicative ranges provided in Table 2.

Table 2: Measurands and expected mass fraction range

Element	Expected Range (mg/kg)
Pt	1000-4000
Pd	1000-4000
Rh	100-500

STUDY MATERIALS

The sample is an unused 3-way autocatalyst material, with a PGM coating on a cordierite base (MgO, alumina, SiO_2). The bulk material initially underwent pan milling, followed by pin milling. The material was passed through the pin mill a total of three times. Particle size analysis was performed using the Malvern Mastersizer 2000 analyser with sonication which indicated at least 95 % of the material was <45 µm. It was bottled in numbered amber glass bottles containing 100 g of powdered material. The material was shipped under ambient conditions and should be stored at ambient conditions (20 °C ± 5 °C). All participants received one bottle except for three institutes which requested 2 bottles.

The bottle should be thoroughly mixed before removing an aliquot and a minimum sample size of 200 mg was recommended. A **minimum of 5** independent replicates were required.

The material is hygroscopic; therefore, the moisture content should be determined by the predefined method provided and results submitted on a dry mass basis.

Homogeneity Assessment of Study Material

Homogeneity was undertaken by XRF on 10 bottles prepared in triplicate. The results were subjected to a one-way ANOVA test at the 95 % confidence level. Based on the F-test score in Table 3, the sample is suitably homogeneous for the study.

Table 3: Results of the homogeneity assessment.

Analyte	P Value	Significance level	F Value	F Critical	Result
Pt	0.63	0.05	0.79	2.39	Pass
Pd	0.22	0.05	1.49	2.39	Pass
Rh	0.61	0.05	0.81	2.39	Pass

Stability Assessment of Study Material

Based on historical data and the nature of the matrix, stability assessment of this material was deemed not necessary.

PARTICIPANTS, INSTRUCTIONS AND SAMPLE DISTRIBUTION

The call for participation was sent in August 2020 with the intent to distribute samples in September 2020 and a reporting deadline of 26th February 2021. However, several participants noted that they would be reliant on the NIST SRM 3144 primary calibration standard for Rh which was out of stock at that time. The pandemic and restrictions in the different countries also caused further issues. Therefore, it was agreed to delay the start of the study to enable NIST to release SRM 3144, and registration was reopened until February 2021. Table 4 lists the institutions that registered for CCQM-K160.

Table 4: List of participants

Lab ID	Institute	Country	Contact Name	Key	Pilot
1	UNIIM*	Russia	Egor Sobina	Pt, Pd, Rh	
2	JSI	Slovenia	Radojko Jacimovic	Pt, Pd, Rh	
3	NIS	Egypt	Randa Yamani	Pt, Pd	Pt, Pd
4	PTB	Germany	Olaf Rienitz	Pt	
5	NMISA	South Africa	Maré Linsky	Pt, Pd	
6	LGC	UK	Heidi Goenaga-Infante	Pt, Pd, Rh	
7	RISE	Sweden	Conny Haraldsson	Pt, Pd, Rh	
8	LNE	France	Paola Fisicaro	Pt, Pd, Rh	
9	NIM	China	Tongxiang Ren	Pt, Pd, Rh	
10	BAM	Germany	Jochen Vogl	Pt, Pd	
11	INTI	Argentina	Hernán Ezequiel Lozano & Mabel Puelles	Pt, Pd	

The samples were shipped on 19th May 2021. Ten of the participants received the sample within 2 weeks except for NIS which experienced significant issues with customs authorities and COVID related delays. The sample was eventually received on 22nd November 2021. As a result, the reporting deadline was extended to 18th February 2022. However, due to the ongoing impact of the pandemic, a number of laboratories requested extensions. The final reporting deadline was 6th May 2022.

RESULTS

Participants were requested to report a minimum of five independent replicates to determine the mass fraction as mg/kg on a dry weight basis. Additionally, participants were instructed to describe their analytical methods, traceability, and approach to uncertainty estimation. Appendix A reproduces the report form.

CCQM-K160 results were received from all eleven institutions that registered. One institute submitted results one day after the deadline. There were also some deviations from the registration information. These are summarised in

Table 5.

Table 5: List of deviations from the registration and deadlines

Lab ID	Institute	Deviation
2	JSI	Registered for Rh but could not report due to presence of large interference from Nd
3	NIS	Registered for Pt & Pd in both the key and pilot study but only reported results for the key
3	NIS	Reported on 7th May, one day after deadline of 6th May 2022
11	INTI	Registered for Pt & Pd but also submitted results for Rh

Methods Used by Participants

The majority of participants utilised ICP-MS as the measurement technique combined with acid assisted microwave digestion. A mixture of calibration approaches was implemented which included IDMS, external calibration and standard addition. One participant implemented INAA which is a direct analysis approach. Table 6 summarises the measurement methods used by the participating NMIs/DIs. A full description of the analytical methods, including sample preparation, analytical technique, quantification approach and uncertainty estimation, is provided in Appendix B.

Table 6: Summary of calibration methods and techniques used in CCQM-K160

Institute	Pt		Pd		Rh	
	Calibration	**Technique**	**Calibration**	**Technique**	**Calibration**	**Technique**
UNIIM	Standard Addition	ICP-MS	Standard Addition	ICP-MS	Standard Addition	ICP-MS
JSI	k_0 Standardisation	k_0-INAA	k_0 Standardisation	k_0-INAA	-	-
NIS	External Calibration	AAS	External Calibration	AAS	-	-
PTB	Standard Addition	ICP-OES	-	-	-	-
NMISA	External Calibration	ICP-MS	External Calibration	ICP-MS	-	-
LGC	IDMS	ICP-MS	IDMS	ICP-MS	Exact Matching	ICP-MS
RISE	External Calibration	ICP-MS	External Calibration	ICP-MS	External Calibration	ICP-MS
LNE	IDMS	ICP-MS	IDMS	ICP-MS	Standard Addition	ICP-MS
NIM	IDMS	ICP-MS	IDMS	ICP-MS	External Calibration	ICP-MS
BAM	IDMS	ICP-MS	IDMS	ICP-MS	-	-
INTI	External Calibration	ICP-OES	External Calibration	ICP-OES	External Calibration	ICP-OES

Calibration Materials Used by Participants

Participants were allowed to establish the metrological traceability of their results to the SI using a direct realisation via a primary method, certified reference materials (CRMs) from an NMI/DI having the required CMC claims, or by preparing their own calibration standards using commercially available high purity materials for which they determined the purity themselves. The calibrant choices are provided in Table 7, and Table 8 describes the quality control materials implemented by the participants.

Table 7: Summary of calibration materials used in CCQM-K160

Institute	Pt Calibrant	Pd Calibrant	Rh Calibrant
UNIIM	NIST SRM 3140	NIST SRM 3138	NIST SRM 3144
JSI	NIST SRM 3121 via ERM-EB530a (Al-0.1 % Au alloy)[#]	NIST SRM 3121 via ERM-EB530a (Al-0.1 % Au alloy)[#]	-
NIS	NIST SRM 3140*	NIST SRM 3138*	-
PTB	NIST SRM 3140	-	-
NMISA	NIST SRM 3140	NIST SRM 3138	-
LGC	NIST SRM 3140	NIST SRM 3138	NIST SRM 3144
RISE	NIST SRM 3140	NIST SRM 3138	NIST SRM 3144
LNE	NIST SRM 3140	NIST SRM 3138	NIST SRM 3144
NIM	GBW08693	GBW08696	NIST SRM 3144
BAM	ERM-AE141	ERM-AE140	-
INTI	NIST SRM 3140	NIST SRM 3138	NIST SRM 3144

[#]NIST SRM 3121 Au was used to validate ERM-EB530a – see further explanation below

*Majority of submitted values were calibrated with these standards – see further explanation below

The majority of participants utilised the NIST SRM 31XX series of primary calibrants. NIM and BAM employed certified reference materials produced by their own institutes. JSI obtained the mass fraction of Pd and Pt with k_0-INAA which uses Au as the calibration standard and a neutron flux monitor of an irradiation channel in a nuclear reactor. The CRM ERM-EB530a, Al-0.1 % Au alloy, produced by EC JRC with a mass fraction of 1005 mg/kg ± 7 mg/kg Au (k = 2), was employed. However due to CMC issues, JSI performed in-house validation of the CRM using NIST SRM 3121 to maintain SI traceability. For NIS, NIST SRM 3140 and SRM 3138 were utilised for all replicate results, but one sample replicate was additionally determined against a NIS CRM calibrant and averaged with the NIST SRM result.

Table 8: Summary of quality control measures

Institute	Pt Matrix QC	Pd Matrix QC	Rh Matrix QC
UNIIM	Spiked sample	Spiked sample	Spiked sample
JSI	ERM-EB504a	ERM-EB504a	-
NIS	Spiked sample	Spiked sample	-
PTB	Internal Standardisation	-	-
NMISA	NIST SRM 2556, NIST SRM 2557, ERM 504a	NIST SRM 2556, NIST SRM 2557, ERM 504a	-
LGC	ERM-EB504a, NIST SRM2557, spiked sample	ERM-EB504a, NIST SRM2557, spiked sample	ERM-EB504a, NIST SRM2557, spiked sample
RISE	NIST SRM 2557	NIST SRM 2557	NIST SRM 2557
LNE	NIST SRM 2557	NIST SRM 2557	NIST SRM 2557
NIM	NIST SRM 2557	NIST SRM 2556	NIST SRM 2557
BAM	BAM-M504b	BAM-M504b	-
INTI	Spiked sample	Spiked sample	Spiked sample

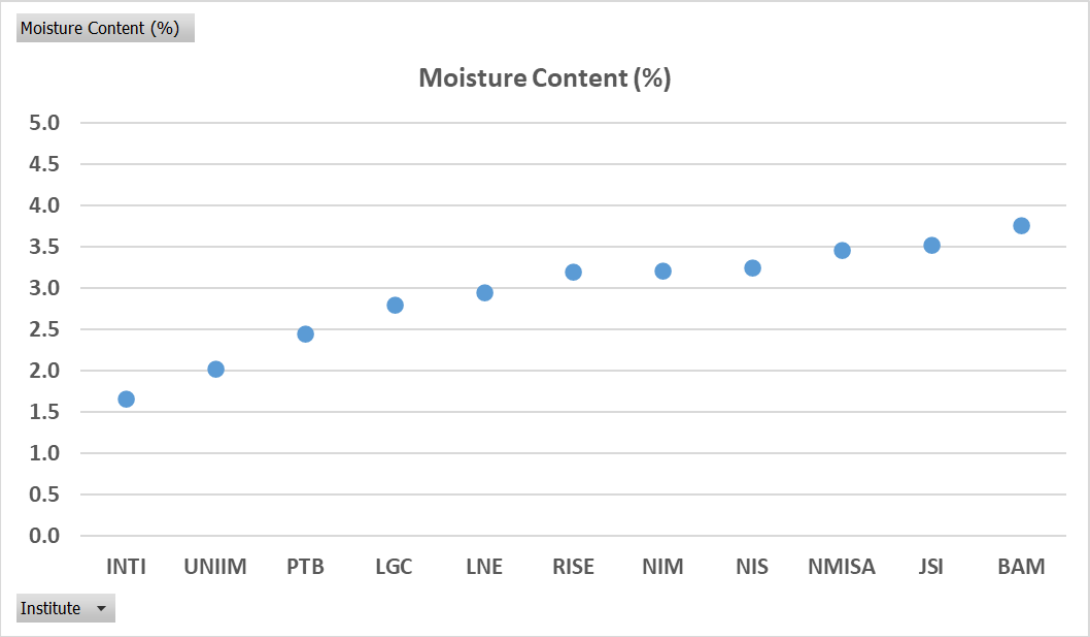
Dry Mass Determination

A protocol was provided for the determination of the moisture content which should be undertaken using separate sub-samples at the same time of sample preparation. A 2 g aliquot should be prepared in duplicate. The following temperature programme should be applied, either using a muffle furnace or TGA:

- Ramp temperature to 105 °C over 5 minutes (15 °C/min) and hold for 30 min
- Ramp temperature to 500 °C over 20 minutes (20 °C/min) and hold for 30 min
- If using a muffle furnace, allow to cool in a dry environment, e.g., desiccator, before re-weighing

All participants followed the protocol. The results are shown in Figure 1. As multiple readings were taken by each participant, each result and the mean were plotted. No discernible trends or anomalies were detected.

Figure 1: Results of the dry mass determination/moisture content.



Participant Results for CCQM-K160

The results for CCQM-K160 for the determination of Pt, Pd and Rh are detailed in Table 9-Table 11 and presented graphically in Figure 2-Figure 4. The error bars represent the standard uncertainty (k = 1).

Table 9: Reported results for Pt (number of significant figures and *k* as reported)

Institute	Mass Fraction (mg/kg)	Standard uncertainty	Expanded uncertainty	*k*	*n*
NIS	1798.119	56.550	113.100	2	6
JSI	1873	66	132	2	11
LGC	1878	7	14	2	9
RISE	1885	14	27	2	6
INTI	1886	61	122	2	11
LNE	1889	28	56	2	7
NIM	1898	7	14	2	6
BAM	1906.8	5.0	10.0	2	7
UNIIM	1907	28.5	57	2	14
NMISA	1942	36	72	2	6
PTB	2261	36	72	2	10

Figure 2: CCQM-K160 Submitted results for Pt (mg/kg)

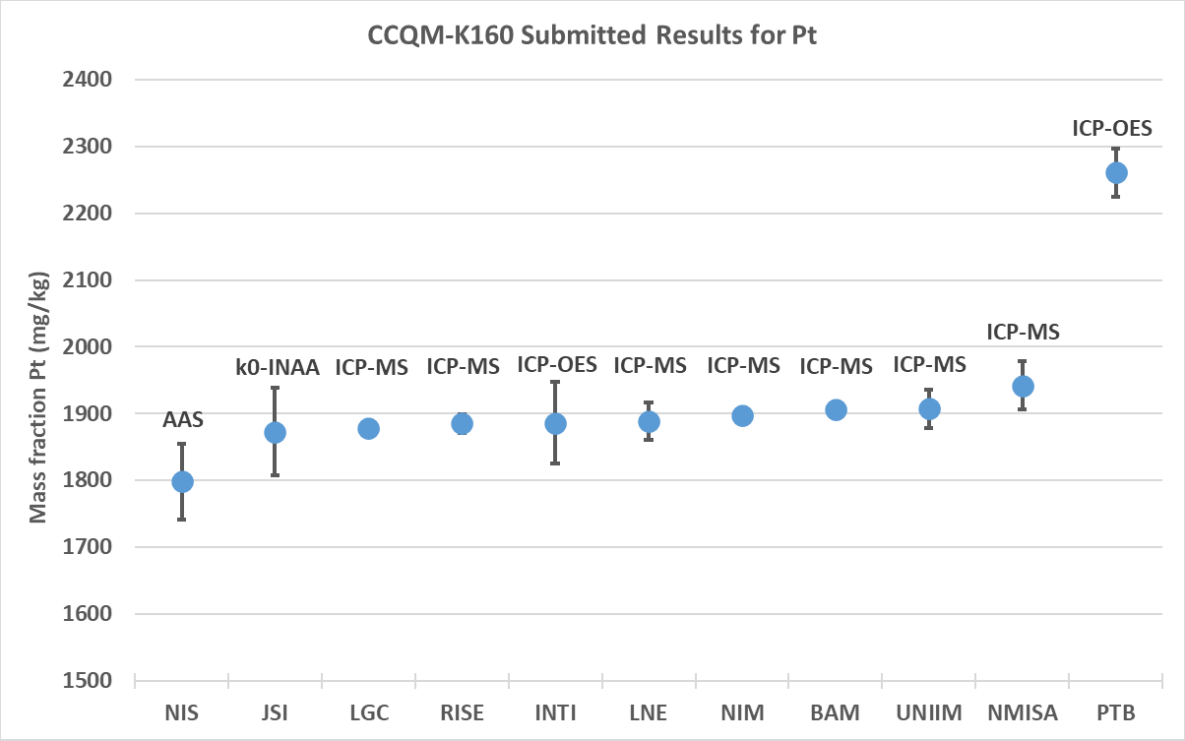


Table 10: Reported results for Pd (number of significant figures and *k* as reported)

Institute	Mass Fraction (mg/kg)	Standard uncertainty	Expanded uncertainty	*k*	*n*
UNIIM	2451	40	80	2	9
INTI	2735	55	110	2	11
NIS	2742.522	81.252	162.504	2	6
JSI	2823	106	212	2	9
LGC	2875	14	28	2	9
RISE	2933	27	53	2	6
LNE	2936	40	80	2	7
NIM	2945	14	28	2	6
BAM	2958	22	43	2	7
NMISA	3262	93	186	2	5

Figure 3: CCQM-K160 Submitted results for Pd (mg/kg)

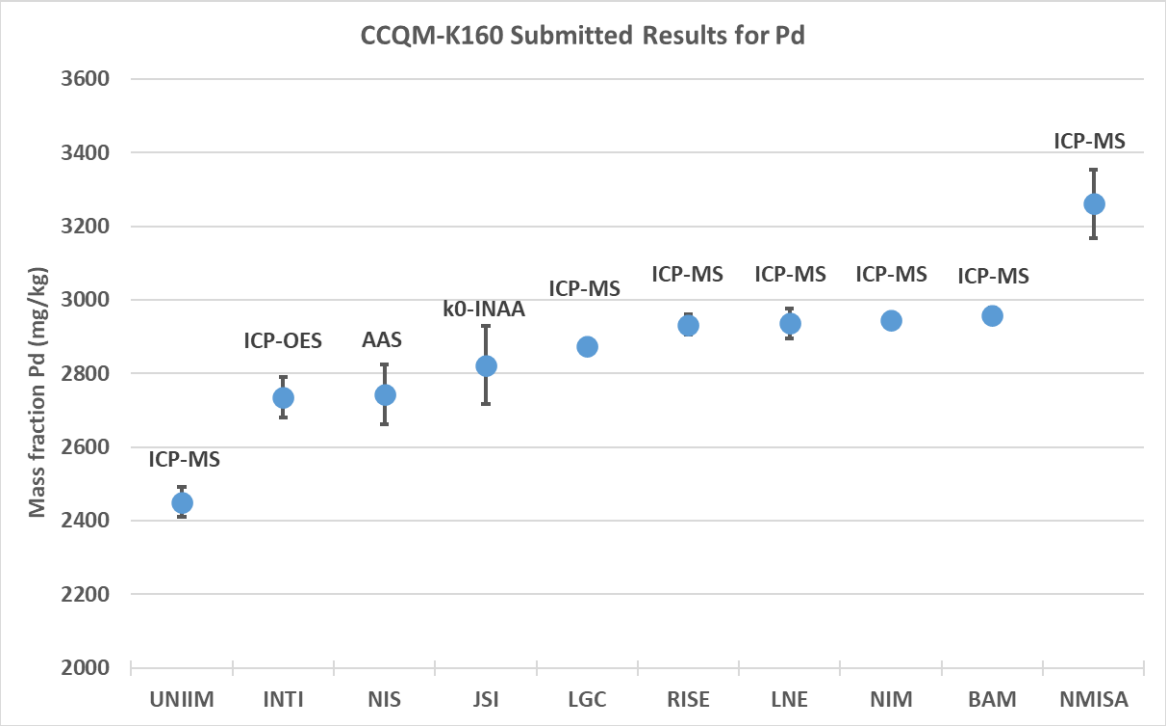
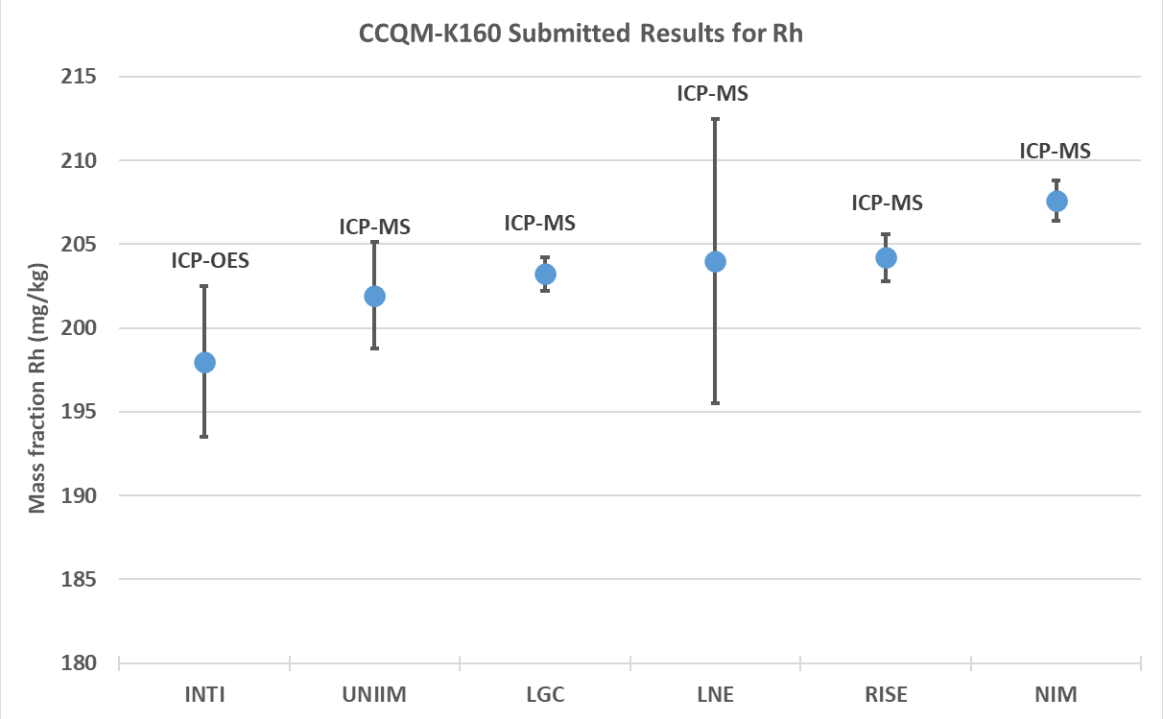


Table 11: Reported results for Rh (number of significant figures and *k* as reported)

Institute	Mass Fraction (mg/kg)	Standard uncertainty	Expanded uncertainty	*k*	*n*
INTI	198	4.5	9	2	11
UNIIM	202.0	3.2	6.4	2	9
LGC	203.2	1.0	2.0	2	9
LNE	204	8.5	17	2	7
RISE	204.2	1.4	2.8	2	6
NIM	207.6	1.2	2.4	2	6

Figure 4: CCQM-K160 Submitted results for Rh (mg/kg)



Discussion of Results

As noted in Table 5, JSI registered for Rh in the KC but did not report due an interference with INAA caused by the presence of Nd (≈ 6800 mg/kg). This contributed approximately 15 % to 17 % of the Rh signal, requiring an additional uncertainty component leading to a combined standard uncertainty of ≈ 10 %, which was considered too high for submission to the KC. However, the result obtained by JSI using k_0-INAA for Rh was 201 mg/kg ± 20 mg/kg (k = 1), (U = 40 mg/kg, k = 2, n = 8). Additionally, INTI were not registered for Rh in the KC but did submit results, which were accepted.

Following the initial release of the results, the participants were asked to review the data and investigate any anomalies. Following this, PTB thoroughly reviewed their calculations and experimental work for Pt but did not find any errors. Standard addition calibration with an internal standard (Au) was applied with ICP-OES detection, with 20 wavelength combinations available. The wavelengths selected for reporting were considered optimal. Additionally, the

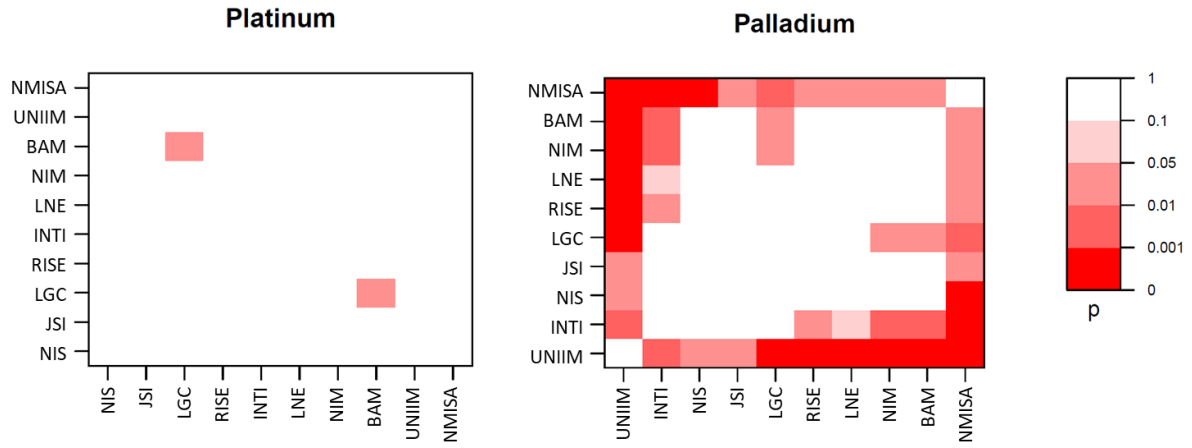
presence of the internal standard in the CCQM sample was checked beforehand and was shown not to be present. On review, other Pt/Au wavelength combinations did produce values close to the consensus value. It was also noted that the elements were not separated from the matrix so potentially an unknown interference could have played a role despite the standard addition calibration approach. Therefore, it was agreed to exclude the PTB Pt result from the KCRV calculations.

The data sets were subjected to statistical inspection using chi-squared and Shapiro-Wilk (Table 12), consistency plots (Figure 5) and median scaled differences (Figure 6). The Chi-squared values were above the critical value for 95 % confidence for all elements, suggesting that the laboratory results may be over-dispersed given their uncertainties and the presence of unexplained variation between laboratories (referred to as 'dark uncertainty'). The standardised results for normal distribution (Shapiro-Wilk) do not show strong evidence for a departure from normality but are borderline at 95 % confidence for two out of three elements. For Pd this is largely due to the low result submitted by UNIIM. For Rh, NIM has $z > 3$. This is consistent with the chi-squared values and the appearance of the submitted results plots.

Table 12: Chi-squared and Shapiro-Wilk results with the critical values

Element	χ^2	DF	Critical Value		Shapiro-Wilk (*p*-value)
			95 % Confidence	99 % Confidence	
Pt	24.41	9	16.92	21.67	0.33
Pd	177.91	9	16.92	21.67	0.06
Rh	13.14	5	11.07	15.09	0.10

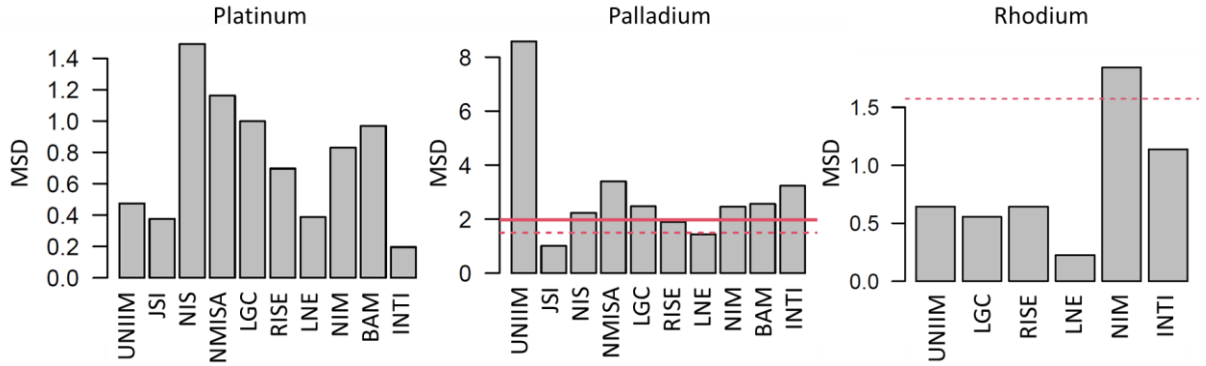
Figure 5: Consistency plot for Pt and Pd



The consistency plots (Figure 5) show that the Pt results were approximately symmetrically distributed with the PTB value excluded and largely consistent with each other given the uncertainties. Only LGC and BAM show a significant inconsistency at the 95 % level, but this is due to their small uncertainties rather than the results themselves. The Pd data also follow a symmetrical distribution, but with larger tails. This has resulted in some inconsistency between labs, particularly involving labs UNIIM and NMISA (which submitted the lowest and

highest results respectively). LGC is inconsistent with three participants as a consequence of the very small uncertainty associated with its result. Only six laboratories submitted results for Rh; the distribution is again symmetrical and there were no inconsistencies in the dataset.

Figure 6: Median scaled differences plot for Pt, Pd and Rh



Note: Dashed red line is 95 % quantile and full red line is 99 % quantile

The median scaled difference (MSD, Figure 6) provides an alternative indicator of anomalous values considering the laboratory's uncertainty without reliance on the choice of estimator for interlaboratory studies [1]. Generally, if the MSD is greater than 2, further inspection is warranted. For Pt, the MSD are below this threshold, matching to the conclusions of the Shapiro-Wilk test and consistency plot. For Pd, the MSD plot highlights the difference in magnitude for reported laboratory uncertainties, with seven participants above the 99 % quantile. For Rh, NIM is above the 95 % quantile, mirroring the observations from the chi-squared value and reported uncertainty.

KEY COMPARISON REFERENCE VALUE (KCRV)

The KCRVs for CCQM-K160 were calculated using the Decision Tree for Key Comparisons [2], following the guidance advice [3]. As noted in the previous discussion, the Pt result from PTB was not included in the KCRV calculations. Figure 7 shows the decision tree routes and Table 13 provides the statistical results with model selection. The full Decision Tree results are provided in Appendix C.

Figure 7: Decision Tree

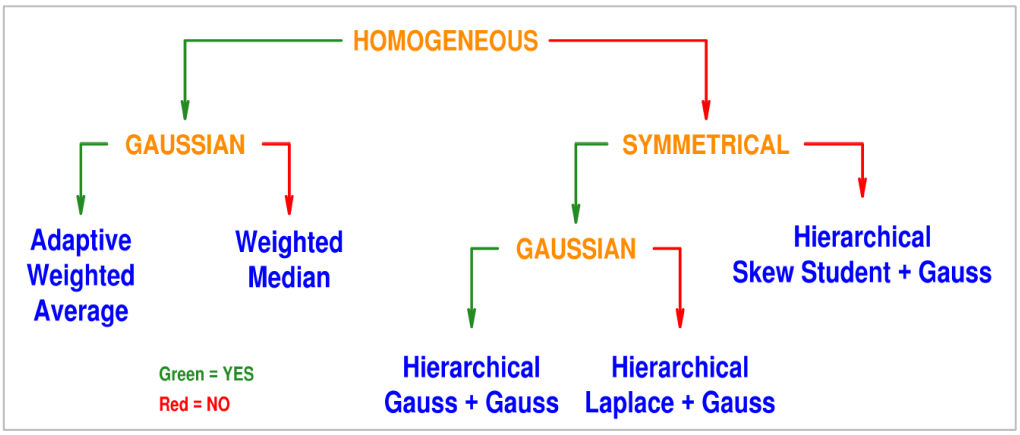


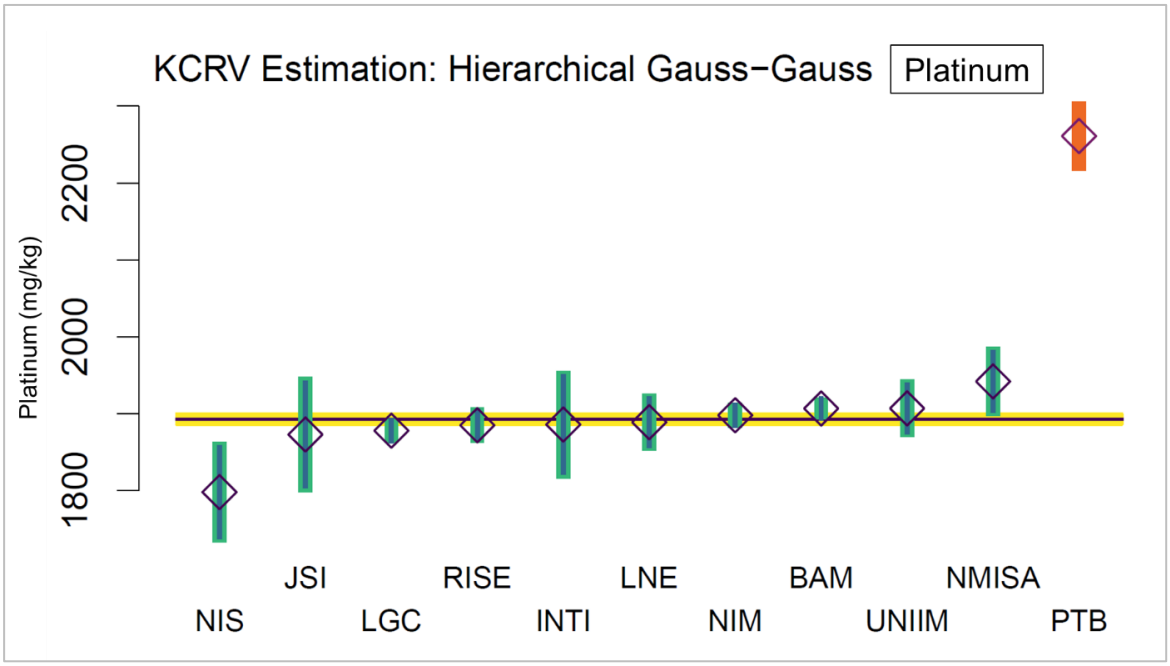
Table 13: Decision Tree results for Pt, Pd and Rh

	Pt	Pd	Rh
Selected Procedure	Hierarchical Gauss-Gauss	Hierarchical Gauss-Gauss	Hierarchical Gauss-Gauss
KCRV estimate	1893.0 mg/kg	2863 mg/kg	204.0 mg/kg
Standard uncertainty	6.8 mg/kg	57 mg/kg	1.1 mg/kg
Standard uncertainty, relative	0.4 %	2.0 %	0.5 %
Dark uncertainty	11.6 mg/kg	189 mg/kg	1.7 mg/kg
Dark uncertainty, relative	0.6 %	6.6 %	0.8 %

As the P values for Cochran's homogeneity for Pt and Rh were close to 0.05, the decision tree was applied again but accepting the homogeneity hypothesis, leading to the Adaptive Weighted Average model. However, very little difference was observed, with both consensus values affected by <0.1 %. For Pt, the standard uncertainty and dark uncertainty decreased from 6.8 mg/kg to 6.5 mg/kg and 11.6 mg/kg to 11.3 mg/kg, respectively. For Rh, the standard uncertainty and dark uncertainty very slightly increased from 1.1 mg/kg to 1.2 mg/kg and 1.7 mg/kg to 1.9 mg/kg, respectively. As the impact was minimal, the Hierarchical Gauss-Gauss model was retained in both cases.

The results from the participants compared to the KCRV are presented in Figure 8-Figure 10. The yellow band represents ± standard uncertainty, with the thick green line representing the participants standard uncertainty, the thin blue line includes the dark uncertainty component.

Figure 8: Participant results for Pt compared to the KCRV.



Note: Orange values were not included in the KCRV calculations.

Figure 9: Participant results for Pd compared to the KCRV.

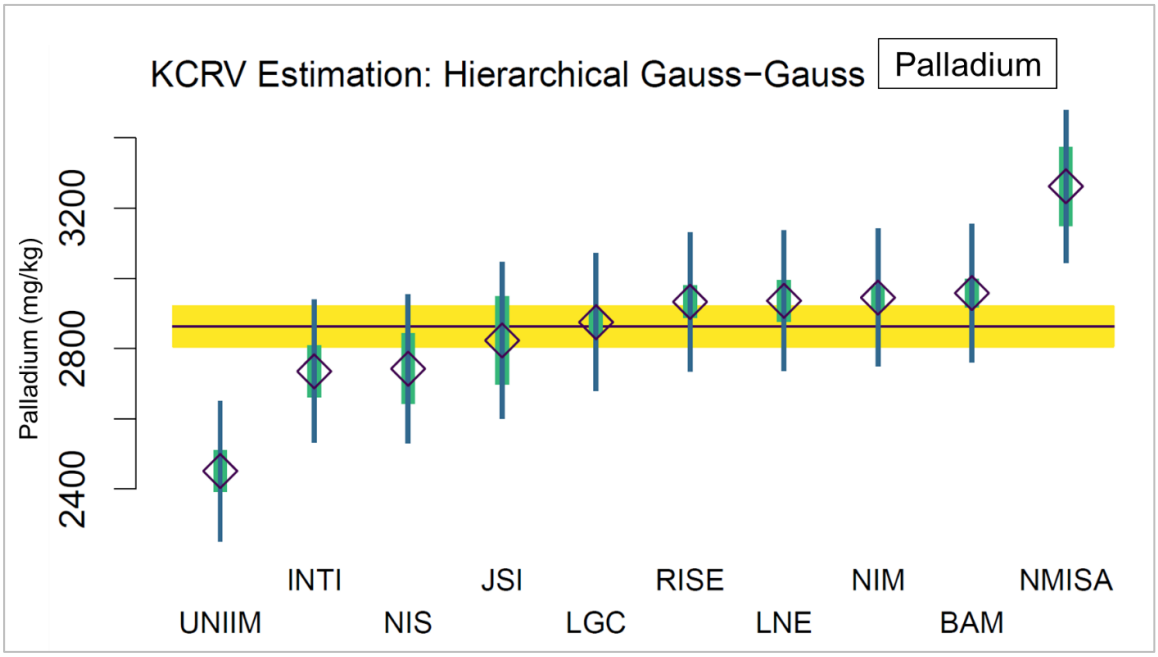
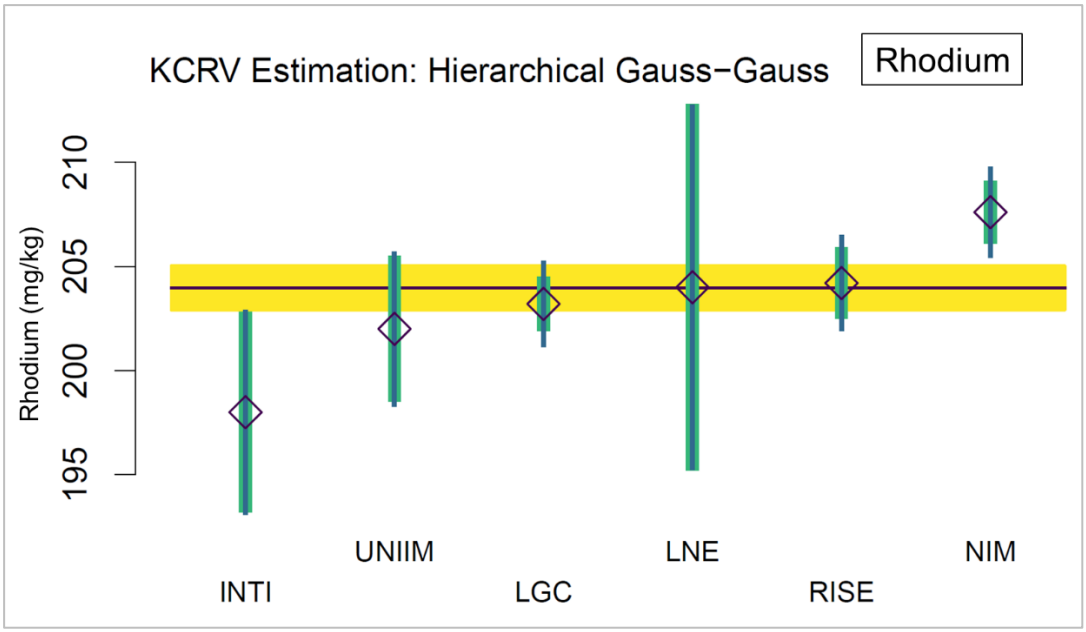


Figure 10: Participant results for Rh compared to the KCRV.



DEGREES OF EQUIVALENCE (DoE)

The degrees of equivalence were calculated using the NIST Decision Tree. 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. For the Bayesian procedure (Hierarchical Gauss Gauss) 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 posterior probability distribution.

The DoE results are provided in Table 14-Table 16 and shown graphically in Figure 11-Figure 13 in accordance with the guidance provided by the IAWG [3]. To enable comparison of the DoE estimates with other studies, it is convenient to express the d_i as relative to the KCRV: $\%d_i = 100 \cdot d_i/\text{KCRV}$.

Table 14: Degrees of equivalence for Pt in CCQM-K160

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	d_i (%)	$U(d_i)$	$d_i/U(d_i)$
NIS	1798.119	56.550	-94.9	-5.3 %	111	-0.86
JSI	1873	66	-20.1	-1.1 %	130	-0.15
LGC	1878	7	-15.1	-0.8 %	19.2	-0.78
RISE	1885	14	-8.0	-0.4 %	30.6	-0.26
INTI	1886	61	-7.0	-0.4 %	120	-0.06
LNE	1889	28	-4.0	-0.2 %	56.2	-0.07
NIM	1898	7	5.0	0.3 %	19.2	0.26
BAM	1906.8	5.0	13.8	0.7 %	16.7	0.82
UNIIM	1907	28.5	14.0	0.7 %	57.4	0.24
NMISA	1942	36	49.0	2.5 %	71.6	0.68
PTB[#]	2261	38*	368	16 %	77.1	4.77

[#]Data was not used in the calculation of the KCRV

*Column $u(x_i)$ as reported by participants (Table 9), unless accompanied by an asterisk (*) which are the reported values and tau (dark uncertainty associated with the KCRV) summed in quadrature.

Figure 11: Degrees of equivalence plot for Pt in CCQM-K160.

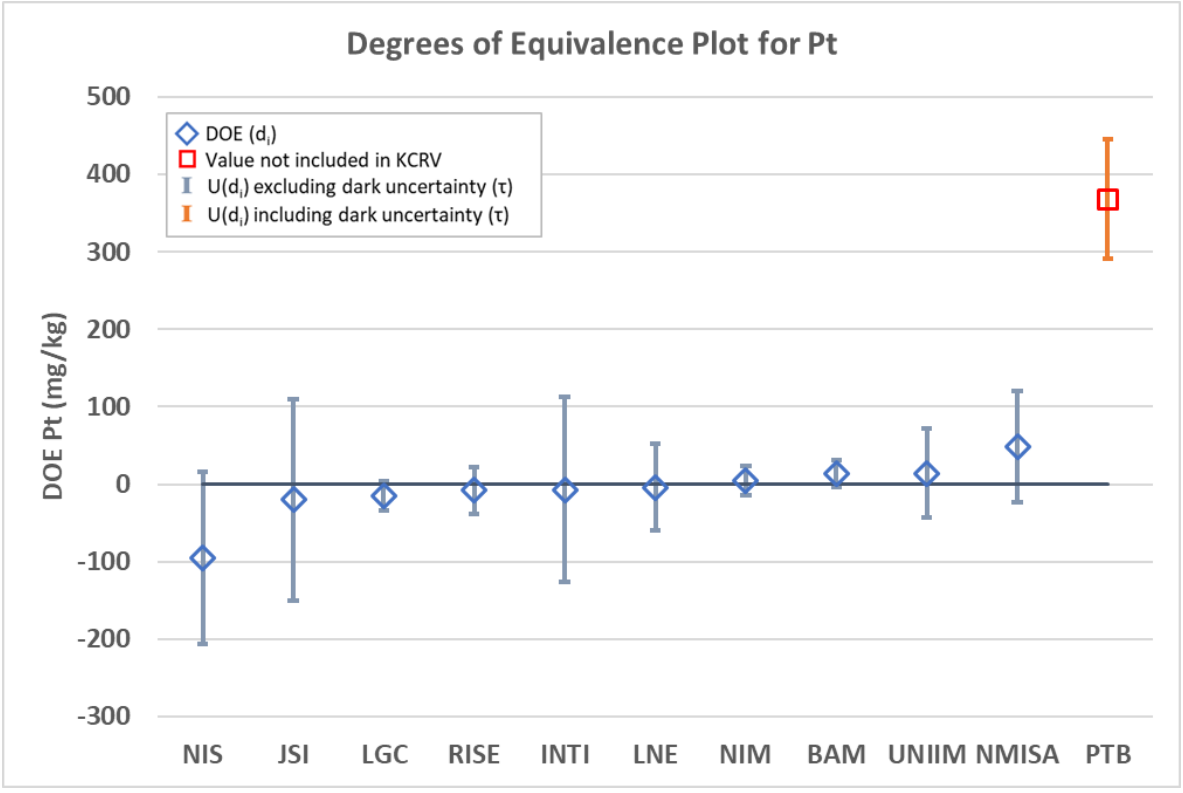


Table 15: Degrees of equivalence for Pd in CCQM-K160

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	d_i (%)	$U(d_i)$	$d_i/U(d_i)$
UNIIM	2451	194*	-412	-17%	434	-0.95
INTI	2735	55	-128	-4.7%	156	-0.83
NIS	2742.522	81.252	-121	-4.4%	196	-0.62
JSI	2823	106	-40.4	-1.4%	237	-0.17
LGC	2875	14	11.6	0.4%	117	0.10
RISE	2933	27	69.6	2.4%	124	0.56
LNE	2936	40	72.6	2.5%	138	0.52
NIM	2945	14	81.6	2.8%	116	0.70
BAM	2958	22	94.6	3.2%	122	0.78
NMISA	3262	211*	399	12%	464	0.86

*Column $u(x_i)$ as reported by participants (Table 10), unless accompanied by an asterisk (*) which are the reported values and tau (dark uncertainty associated with the KCRV) summed in quadrature

Figure 12: Degrees of equivalence plot for Pd in CCQM-K160.

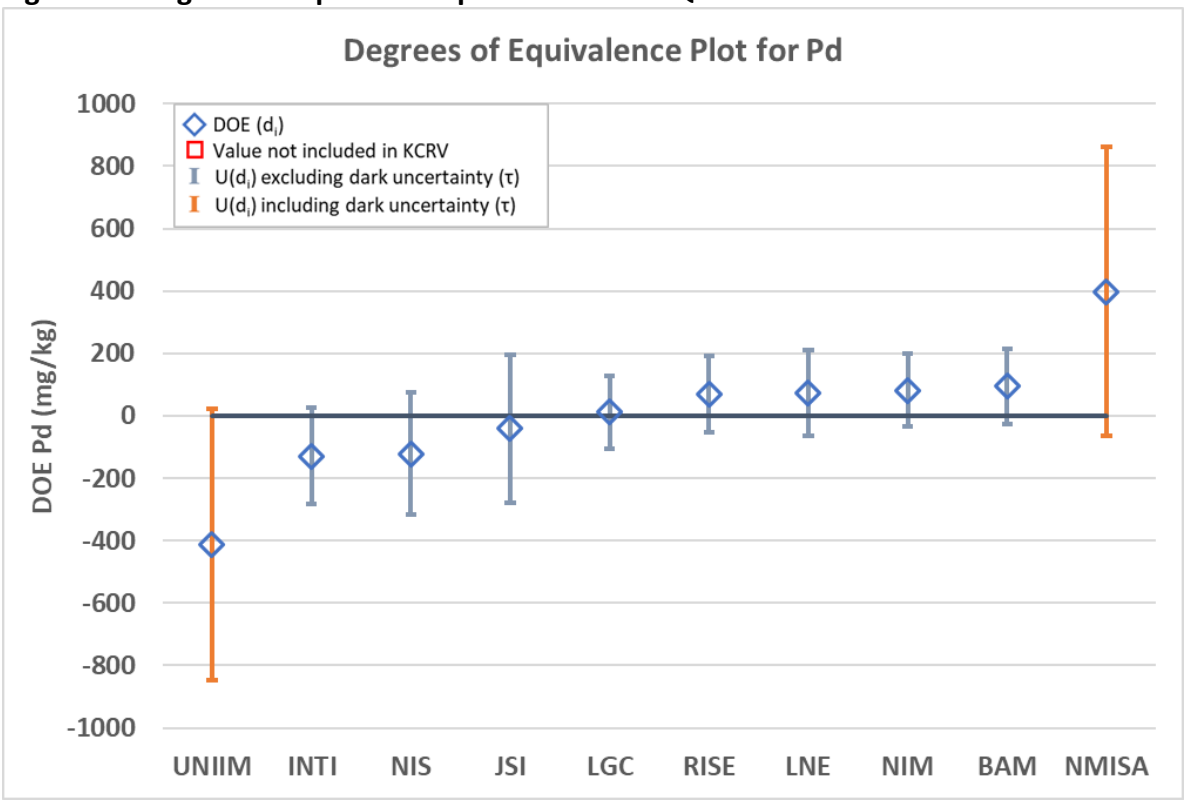
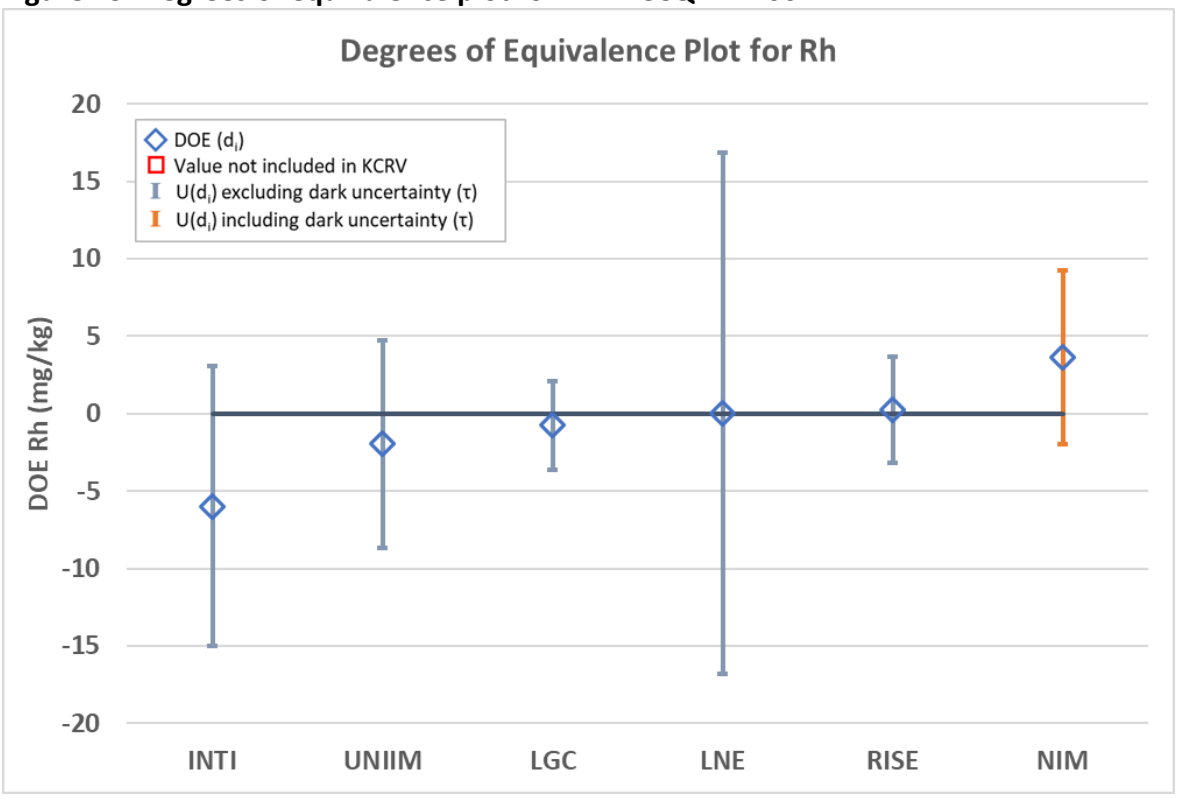


Table 16: Degrees of equivalence for Rh in CCQM-K160

Institute	x_i (mg/kg)	$u(x_i)$ (mg/kg)	d_i (mg/kg)	d_i (%)	$U(d_i)$	$d_i/U(d_i)$
INTI	198	4.5	-5.97	-3.0%	9.1	-0.66
UNIIM	202.0	3.2	-1.97	-1.0%	6.7	-0.30
LGC	203.2	1.0	-0.77	-0.4%	2.9	-0.27
LNE	204	8.5	0.03	0.0%	16.8	0.00
RISE	204.2	1.4	0.23	0.1%	3.4	0.07
NIM	207.6	2.1*	3.63	1.7%	5.6	0.64

*Column $u(x_i)$ as reported by participants (Table 11), unless accompanied by an asterisk (*) which are the reported values and tau (dark uncertainty associated with the KCRV) summed in quadrature

Figure 13: Degrees of equivalence plot for Rh in CCQM-K160.



USE OF CCQM-K160 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

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

In order to support the IAWG strategy with moving towards broad scope core capability claims, it is necessary to consider "how far does the light shine". Participation in CCQM-K160 has demonstrated capabilities for sample preparation (e.g. dissolution) and accurate analysis for challenging matrices and measurands. Considering the IAWG Core Capability Matrix, the material falls in the "Difficult to dissolve metals" matrix category and will support CMCs for the analyte groups of "platinum group elements" (Pt, Pd, Rh, Ru, Ir), some "transition group elements" (Ag, Au) and some "rare earth elements" (La, Ce), all at the mg/kg level. Successful participation within this study, as demonstrated through the DoE, will support broad scope claims for a wide range of challenging matrices within categories 8 (metal and metal alloys), 9 (advanced materials) and 14 (other materials).

As described in the IAWG Comparison Guide [3], the calculated DOE will use the uncertainty from either the reported result or incorporating tau (dark uncertainty). Those including tau in Table 14 to Table 16 are marked with an asterisk(*). For CMC claims, if the participant DOE was calculated using the reported uncertainty, the claim should use the reported uncertainty. If the DOE uncertainty was adjusted for tau, then the claim should use the adjusted uncertainty. If neither of these are consistent, then a CMC claim cannot be supported.

Core Capability Matrix

The measurement space covered by CCQM-K160 is shown in below.

Analyte groups	Matrix challenges					
	Water/aqueous	High Silica content (e.g. Soils, sediments, plants, ...)	High salts content (e.g. Seawater, urine, ...)	High organics content (e.g. high carbon) (e.g. Food, blood/serum, cosmetics, ...)	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)						
					K58 Silicon nitride (Ca) K144 Impurities in Alumina (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)						
					K58 Silicon nitride (Al, Fe, Ti) K144 Impurities in Alumina (Fe)	
Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt)						
		K75 Algae (Pt)			K160 Autocatalyst (Pt, Pd, Rh)	
Metalloids / Semi-metals (B, Si, Ge, As, Sb, Te, Se)						
					K144 Impurities in Alumina (Si)	
Non-metals (P, S, C, N, O)						
Halogens (F, Cl, Br, I)						
Rare Earth Elements (Lanthanides, Actinides)						

CONCLUSIONS

This study was very challenging due to the highly complex and refractory matrix, in addition to sample preparation challenges and measurement interferences. A variety of techniques and methods were implemented by the participants during the study, see Table 6 and Table 17 below. The majority of participants used IDMS and external calibration, with a smaller number opting for standard addition. Additionally, INAA was employed for 2 of the analytes which is a technique requiring no sample preparation. The results for INAA compare very well with the other methods.

Table 17: Summary of techniques used in CCQM-K160

Element	Calibration Technique				Measurement Technique			
	External Calibration	IDMS	Exact Matching	Standard Addition	AAS	ICP-MS	ICP-OES	k_0-INAA
Pt	4	4	-	2	1	7	2	1
Pd	4	4	-	1	1	7	1	1
Rh	3	-	1	2	-	5	1	-

The NIST Decision Tree [2] was utilised to generate the KCRV, DoEs and relevant uncertainties. Each step of the process was checked to ensure the correct decision was made for the KCRV and the uncertainty, which included a 'dark uncertainty' component. Additionally, alternative models were also tested which led to very similar results. For the DoEs, new guidance was provided [3] to standardise the implantation of the dark uncertainty for participants if the submitted uncertainty did not result in equivalence. This only applied to 4 institutes across the 3 elements.

Overall, the study results demonstrate the comparability and capabilities of the participants very well, especially considering the significant challenges from sample matrix, sample preparation and analysis. This study will enable participants to claim CMCs through the broad scope core capability approach for similar refractory matrices and elements.

ACKNOWLEDGEMENTS

The study coordinators wish to thank the participating laboratories for their efforts in providing the key comparison data and additional information used in this study. Further thanks are extended to Mike Winchester, Paola Fisicaro and Antonio Possolo for discussions regarding the KCRVs and Decision Tree process. Finally, thank you to the LGC Reference Materials Production Team for the logistical support and the LGC Statistics Team for the robust discussions regarding the data.

REFERENCES

[1] Ellison, SLR. (2018) An outlier-resistant indicator of anomalies among inter-laboratory comparison data with associated uncertainty. *Metrologia*, **55**, 840. DOI 10.1088/1681-7575/aae610

[2] 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, USA, [online], https://doi.org/10.6028/jres.126.007, (Accessed April 3, 2023).

[3] IAWG Guidance on Using NIST Decision Tree for Comparison Reporting. Mike Winchester (NIST), 30th June 2023, [published on the CCQM IAWG website 16th January 2024].

APPENDIX A: Call for Registration and Technical Protocol

CCQM-K160 & P203 Platinum Group Elements in Automotive Catalyst Registration Form

Rationale

Within the current IAWG 5 year plan, the sample matrix "Difficult to dissolve metals/metal oxides" was scheduled to support CMCs within categories 8, 9 & 14. To fulfil this, LGC is organising a key comparison and parallel pilot study for Pd, Pt and Rh in an automotive catalyst material under the broad core capability approach.

Sample and Measurands

The sample is an unused autocatalyst material supplied in amber glass bottles containing 100g of powdered material. If you require more than one bottle, please ensure this is indicated in the form. The sample matrix is a 3-way catalyst material on a cordierite base. The measurands are Pd, Pt and Rh.

Schedule

July 2020	Call for participation
31st August 2020	Registration deadline
September 2020	Sample distribution
26th February 2021	Deadline for reporting Results
April 2021	First presentation of the results at the CCQM IAWG meeting

Registration Form

Institute/ Laboratory:	
NMI/DI:	☐ National Metrology Institute (NMI) ☐ Designated Institute (DI)
Shipping address: (please include postcode/zip code and country)	
Name of contact person:	*Title / Given Name / Surname*
E-mail:	
Telephone no:	
Date:	
Number of bottles required:	
Any particular local customs / special permits required for samples shipment?	☐ Yes# ☐ No
# If yes, please provide further details:	

Please select the elements and study by checking the box

Analyte	CCQM-K160	CCQM-P203
Pd	☐	☐
Pt	☐	☐
Rh	☐	☐

Please return the completed form to Dr Sarah Hill by 31st August 2020.

Thank you very much for your participation!

Dr Sarah Hill
Science Leader | Inorganic Analysis | National Measurement Laboratory |
LGC | Queens Road | Teddington | Middlesex | TW11 0LY | UK
https://www.lgcgroup.com/nml

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CCQM-K160 & P203 Platinum Group Elements in Automotive Catalyst Technical Protocol

Rationale for the Comparison

Catalysts containing the platinum group elements (PGEs) are employed for a variety of industrial and chemical uses. Palladium (Pd), Platinum (Pt) and Rhodium (Rh) are the active components in automobile catalytic converters as well as catalysts used in pharmaceutical / biological applications and petroleum refining. The immense economic value of these elements highlights the importance of highly accurate measurements.

There has been one previous IAWG CCQM comparison in 2006 for precious metals in automotive catalyst, namely CCQM-P63: Platinum group elements in an automotive catalyst, however a limited number of NMIs participated. Furthermore, this study was performed over 12 years ago. Therefore, there is the need for NMIs/DIs to demonstrate existing capability in a key comparison for such challenging measurands in order to claim CMCs.

Within the current IAWG 5 year plan, the sample matrix "Difficult to dissolve metals/metal oxides" was scheduled to support CMCs within categories 8, 9 & 14. To fulfil this, LGC is organising a key comparison and parallel pilot study for Pd, Pt and Rh in an automotive catalyst material under the broad core capability approach.

Sample

The sample is an unused autocatalyst material and is a 3-way catalyst on a cordierite base (MgO, alumina, SiO_2). It will be supplied in a numbered amber glass bottles containing 100 g of powdered material (at least 95 % of the material is <45 µm). If you require more than one bottle, please ensure this is indicated in the form along with any specific customs requirements. The material will be shipped under ambient conditions. Every participant is asked to confirm the delivery of the samples by e-mail as soon as the samples have arrived. The sample should be stored at ambient conditions (20 °C ± 5 °C).

The bottle should be thoroughly mixed before removing an aliquot and a minimum sample size of 200 mg is recommended. The material is hygroscopic, therefore the moisture content should be determined by the predefined method provided and a correction factor should be applied to the measurement results. Homogeneity was undertaken by XRF for 10 bottles in triplicate with the % RSD calculated below. The results were subjected to an ANOVA test and based on the F-test score, the sample is suitably homogeneous for the study.

Element	%RSD (*n*=30)	%RSD Between bottle (*n*=10)	%RSD Within bottle (*n*=10)
Pt	0.34	0.18	0.30
Pd	0.36	0.23	0.31
Rh	0.62	0.33	0.57

Measurands

The measurands are Pd, Pt and Rh and the indicative ranges are shown below.

mg/kg	Expected Range
Pt	1000-4000
Pd	1000-4000
Rh	100-500

Schedule

May 2021	Sample distribution
30th November 2021	Deadline for reporting Results
April/May 2022	First presentation of the results at the CCQM IAWG meeting

Measurement Methods

The participants are free to choose any suitable method. Please include a full description of your method of analysis including the source of traceability to the SI. Furthermore, a full uncertainty budget should be reported as part of the results.

With regard to establishing traceability to the SI, please consider the requirements of CIPM 2009-24 if you plan to use the results of this key comparison to support CMC claims. Calibration standards sold by commercial entities often do not comply with the requirements of CIPM 2009-24.

Dry Mass Correction

The sample results should be reported on a dry mass basis using the moisture content procedure provided. This should be undertaken using separate sub-samples at the same time of sample preparation. A 2 g aliquot should be prepared in duplicate. The following temperature programme should be applied, either using a muffle furnace or TGA:

- Ramp temperature to 105 °C over 5 minutes (15 °C/min) and hold for 30 minutes
- Ramp temperature to 500 °C over 20 minutes (20 °C/min) and hold for 30 minutes
- If using a muffle furnace, allow to cool in a dry environment, e.g. desiccator, before re-weighing

Reporting

The final results, from a **minimum of 5** independent replicates, should be returned to the **Results Coordinator Gill Holcombe** **by 30th November 2021**, using the supplied reporting template. All participants must include:

- Final results and uncertainty budget, reported as mg/kg on a dry mass basis, from at least 5 independent replicate measurements
- A detailed description of the sample preparation methods, analytical techniques, calibration approach and any corrections applied
- Moisture content results and method of analysis
- Source of traceability

- Please note, only results from one technique/method per institute can be submitted for inclusion in the KCRV. However, institutes are welcome to report results from additional method(s) within the pilot study. The KC result must be clearly stated in the report if more than one will be provided.

Calibration and Measurement Capability Claims

In order to support the IAWG strategy and move towards broad scope core capability claims, it is necessary to consider "how far does the light shine" with this study and which matrices and elements could be grouped to support CMC claims.

Therefore, participation in CCQM K160 will help demonstrate capabilities for sample preparation (e.g. dissolution) and accurate analysis for challenging matrices and measurands. Considering the IAWG Core Capability Matrix, this material falls into the matrix category of "Difficult to dissolve metals" so will support CMCs for the analyte groups of "platinum group elements" (Pt, Pd, Rh, Ru, Ir), some "transition group elements" (Ag, Au) and some "rare earth elements" (La, Ce), all at the mg/kg level. Successful participation within this study will support broad scope claims for a wide range of challenging matrices within categories 8 (metal and metal alloys), 9 (advanced materials) and 14 (other materials).

Thank you very much for your participation!

Contact Details

Study Coordinator: Dr Sarah Hill (shipping issues, technical enquiries)

Results Coordinator: Gill Holcombe (results submission)

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APPENDIX B: Summary of Participants' Analytical Information

The following table summarises the detailed information about the analytical procedures each participant provided in the reporting template. The presentation of the information was consolidated and standardised.

Table B1: Detailed sample preparation information for CCQM-K160

Lab ID	Institute	Sample Mass (g)	Sample preparation information
1	**UNIIM**	0.1	Two approaches were applied. Process 1: 1:3 HNO_3:HCl, H_2O (deionized). Process 2: Fusion (melting) with Na_2O_2, melting point 800 °C, dissolving in HCl (1:1)
2	**JSI**	0.2	An aliquot of the sample was sealed into a pure polyethylene ampoule.
3	**NIS**	0.15-0.3	6 -10 mL of aqua regia (HCl:HNO_3, 3:1) and left to stand for 24 hours. Then the samples were heated at 130°C. After cooling, all samples were filtered and diluted to 50 mL with ultrapure water.
4	**PTB**	0.4	Au internal standard was added to the sample followed by 9 mL HCl and 3 mL HNO_3, 210°C in MLS Ethos Microwave, evaporated to near dryness using MLS Ethos evaporation kit. The residues were redissolved in 10.5 mL of HCl (0.01 g/g) on a hot plate at 120°C for 2 hrs. After leaving to stand overnight, 10 mL of the solution was transferred to a PFA bottle and the remaining residues treated again with 10 mL of HCl (0.01 g/g) on a hot plate as above. The process was performed one more time before making up the final solution to ≈ 100 g
5	**NMISA**	0.1	Two-step microwave digestion. Step 1: 10 mL UA-1 reagent (Inorganic Ventures) at 115 °C. Step 2: 50 mL UNS-1 reagent (Inorganic Ventures) at 105 °C. The final solution was made up to 100 mL gravimetrically.
6	**LGC**	0.2	The sample was mixed with ^{105}Pd and ^{196}Pt enriched spikes, plus Ru internal standard for Rh, followed by 4 mL HNO_3, 2 mL HCL, 2 mL HF, 190°C in Milestone Ethos UP. The final solutions were made up to 50 g with 1% HCl and subsequent dilutions with 1% HCl.
7	**RISE**	0.2	4 mL HNO_3, 12 mL HCl and 4 mL HF at 190 °C by microwave digestion. After cooling, 40 mL saturated $B(OH)_3$ was added to the microwave vessels and heated to 130°C. The final solutions were made up to 100 mL using water and subsequent dilution in 1% HNO_3 and 1% HCl.

Lab ID	Institute	Sample Mass (g)	Sample preparation information
8	**LNE**	0.2	The sample was mixed with ^{104}Pd and ^{196}Pt enriched spikes, followed by 2 mL HF, 1 mL H_2O_2, 2 mL HNO_3 and 8 mL HCl at 230°C in Milestone Ethos One. After cooling, 0.6 g H_3BO_3 was added to the microwave vessel and heated to 210°C.
9	**NIM**	0.2	The sample was mixed with ^{194}Pt and ^{108}Pd enriched isotopic spikes followed by 2 mL HNO_3, 6 mL HCl and 1 mL HF, 200°C in MARS7 microwave oven (CEM). After cooling, 6 mL of saturated boric acid solution was added to the microwave vessels 150°C for 10 minutes. The final solutions were made up to 50 g.
10	**BAM**	0.21	Two-step microwave digestion. 1st step: 6 mL HCl and 2 mL HNO_3 at 210 °C, samples centrifuged, solution removed, precipitate rinsed back into the vessel with 1 mL HNO_3, 3 mL HCl and 5 mL HF. 2nd step: 220 °C, solutions dried individually, residues dissolved in 30% HCl and combined with solution from 1st step. This was followed by a two-step analyte-matrix-separation with ion exchange resins. 1st step: AG 50W-X8: loading + eluting in 0.25 mol/L HCl. 2nd step: Triskem DGA resin, normal: loading in 3 mol/L HCl, eluting in 3 mol/L HNO_3
11	**INTI**	0.1-0.5g	10 mL aqua regia, 5 mL HF and 5 mL $HClO_4$ were added and heated on a hot plate until white fumes evolved. The sample was cooled and another 10 mL aqua regia and 5 mL HF added and heated again until white fumes. This was repeated twice further until complete dilution. The solution was made up with 10% HCl.

APPENDIX C: NIST Decision Tree Output

The following section includes the NIST Decision Tree outputs as generated for the KCRV, uncertainty and DoE calculations. This was performed on the 03/11/2023 with version 1.0.4. Pertinent information regarding the modelling parameters is provided in Table C1 below.

Table C1: NIST Decision Tree model parameters

Element	Model	Random seed number	Total MCMC steps	MCMC warm up steps	MCMC Draw steps
Pt	Hierarchical Gauss-Gauss	470	250000	125000	10
Pd	Hierarchical Gauss-Gauss	172	250000	125000	10
Rh	Hierarchical Gauss-Gauss	59	250000	125000	10

Figure C1: NIST Decision Tree report for Platinum

NIST Decision Tree Result – Platinum

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	NIS	1798.119	56.55	10000
TRUE	JSI	1873.000	66.00	10000
TRUE	LGC	1878.000	7.00	10000
TRUE	RISE	1885.000	14.00	10000
TRUE	INTI	1886.000	61.00	10000
TRUE	LNE	1889.000	28.00	10000
TRUE	NIM	1898.000	7.00	10000
TRUE	BAM	1906.800	5.00	10000
TRUE	UNIIM	1907.000	28.50	10000
TRUE	NMISA	1942.000	36.00	10000
FALSE	PTB	2261.000	36.00	10000

Date: 2023-11-03
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 470
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 1893
Standard uncertainty: 6.781
95% coverage interval: (1879, 1907)
Dark uncertainty (tau): 11.56
Tau posterior 0.025 and 0.975 quantiles: (2.831,30.1)

Decision Tree Hypothesis test results

Cochran's test for Homogeneity:
p-value: 0.05
Q = 16.94 (Reference Distribution: Chi-Square with 9 Degrees of Freedom)
tau est. = 11.26
tau/median(x) = 0.005963
tau/median(u) = 0.3984

Shapiro-Wilk test for Normality: p = 0.3281

Miao-Gel-Gastwirth test of Symmetry: p = 0.9514

DoE Table

Ignoring Dark Uncertainty

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
NIS	NIS	-94.930	111.00	-206.000	16.100
JSI	JSI	-20.050	130.10	-150.200	110.100
LGC	LGC	-15.050	19.21	-34.250	4.158
RISE	RISE	-8.048	30.55	-38.600	22.510
INTI	INTI	-7.048	119.50	-126.500	112.400
LNE	LNE	-4.048	56.22	-60.270	52.170
NIM	NIM	4.952	19.21	-14.260	24.160
BAM	BAM	13.750	16.68	-2.925	30.430
UNIIM	UNIIM	13.950	57.38	-43.420	71.330
NMISA	NMISA	48.950	71.62	-22.670	120.600
PTB	PTB	368.000	71.84	296.100	439.800

Including Dark Uncertainty

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
NIS	NIS	-94.930	114.70	-209.70	19.80
JSI	JSI	-20.050	134.10	-154.20	114.10
LGC	LGC	-15.050	35.59	-50.64	20.54
RISE	RISE	-8.048	42.21	-50.26	34.16
INTI	INTI	-7.048	123.40	-130.40	116.30
LNE	LNE	-4.048	63.43	-67.48	59.38
NIM	NIM	4.952	35.38	-30.42	40.33
BAM	BAM	13.750	34.29	-20.53	48.04
UNIIM	UNIIM	13.950	64.19	-50.24	78.14
NMISA	NMISA	48.950	77.62	-28.67	126.60
PTB	PTB	368.000	77.08	290.90	445.00

Lab Uncertainties Table

lab	x	u	nu	ut
NIS	1798	56.55	10000	57.72
JSI	1873	66.00	10000	67.00
LGC	1878	7.00	10000	13.51
RISE	1885	14.00	10000	18.15
INTI	1886	61.00	10000	62.08
LNE	1889	28.00	10000	30.29
NIM	1898	7.00	10000	13.51
BAM	1907	5.00	10000	12.59
UNIIM	1907	28.50	10000	30.75
NMISA	1942	36.00	10000	37.81
PTB	2261	36.00	10000	37.81

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
NIS	-94.930	58.62	114.70	-209.70	19.80	56.540	111.00	-206.000	16.100
JSI	-20.050	68.17	134.10	-154.20	114.10	66.160	130.10	-150.200	110.100
LGC	-15.050	17.54	35.59	-50.64	20.54	9.719	19.21	-34.250	4.158
RISE	-8.048	21.34	42.21	-50.26	34.16	15.570	30.55	-38.600	22.510
INTI	-7.048	62.84	123.40	-130.40	116.30	60.960	119.50	-126.500	112.400
LNE	-4.048	32.31	63.43	-67.48	59.38	28.780	56.22	-60.270	52.170
NIM	4.952	17.53	35.38	-30.42	40.33	9.751	19.21	-14.260	24.160
BAM	13.750	16.92	34.29	-20.53	48.04	8.422	16.68	-2.925	30.430
UNIIM	13.950	32.76	64.19	-50.24	78.14	29.290	57.38	-43.420	71.330
NMISA	48.950	39.38	77.62	-28.67	126.60	36.740	71.62	-22.670	120.600
PTB	368.000	39.44	77.08	290.90	445.00	36.670	71.84	296.100	439.800

Figure C2: NIST Decision Tree report for Palladium

NIST Decision Tree Result – Palladium

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	UNIIM	2451.000	40.000	10000
TRUE	INTI	2735.000	55.000	10000
TRUE	NIS	2742.522	81.252	10000
TRUE	JSI	2823.000	106.000	10000
TRUE	LGC	2875.000	14.000	10000
TRUE	RISE	2933.000	27.000	10000
TRUE	LNE	2936.000	40.000	10000
TRUE	NIM	2945.000	14.000	10000
TRUE	BAM	2958.000	22.000	10000
TRUE	NMISA	3262.000	93.000	10000

Date: 2023-11-03
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 172
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 2863
Standard uncertainty: 56.84
95% coverage interval: (2750, 2977)
Dark uncertainty (tau): 189.3
Tau posterior 0.025 and 0.975 quantiles: (120.4,326.6)

Decision Tree Hypothesis test results

Cochran's test for Homogeneity:
p-value: $p < 0.001$
$Q = 177.1$ (Reference Distribution: Chi-Square with 9 Degrees of Freedom)
tau est. = 119.5
tau/median(x) = 0.04114
tau/median(u) = 2.986

Shapiro-Wilk test for Normality: $p = 0.06456$

Miao-Gel-Gastwirth test of Symmetry: $p = 0.3812$

DoE Table

Ignoring Dark Uncertainty

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
UNIIM	UNIIM	-412.4	137.6	-550.00	-274.80
INTI	INTI	-128.4	155.5	-283.90	27.15
NIS	NIS	-120.9	195.9	-316.80	75.06
JSI	JSI	-40.4	236.7	-277.10	196.30
LGC	LGC	11.6	116.6	-105.00	128.20
RISE	RISE	69.6	124.0	-54.41	193.60
LNE	LNE	72.6	138.3	-65.65	210.90
NIM	NIM	81.6	116.4	-34.76	198.00
BAM	BAM	94.6	121.8	-27.18	216.40
NMISA	NMISA	398.6	214.3	184.30	612.90

Including Dark Uncertainty

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
UNIIM	UNIIM	-412.4	434.1	-846.50	21.73
INTI	INTI	-128.4	435.6	-564.00	307.20
NIS	NIS	-120.9	454.5	-575.30	333.60
JSI	JSI	-40.4	468.8	-509.20	428.40
LGC	LGC	11.6	428.2	-416.60	439.80
RISE	RISE	69.6	429.5	-359.90	499.10
LNE	LNE	72.6	429.3	-356.70	501.90
NIM	NIM	81.6	426.9	-345.30	508.50
BAM	BAM	94.6	427.4	-332.80	522.00
NMISA	NMISA	398.6	464.4	-65.82	863.00

Lab Uncertainties Table

lab	x	u	nu	ut
UNIIM	2451	40.00	10000	193.5
INTI	2735	55.00	10000	197.1
NIS	2743	81.25	10000	206.0
JSI	2823	106.00	10000	216.9
LGC	2875	14.00	10000	189.8
RISE	2933	27.00	10000	191.2
LNE	2936	40.00	10000	193.5
NIM	2945	14.00	10000	189.8
BAM	2958	22.00	10000	190.5
NMISA	3262	93.00	10000	210.9

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
UNIIM	-412.4	217.5	434.1	-846.50	21.73	69.47	137.6	-550.00	-274.80
INTI	-128.4	219.2	435.6	-564.00	307.20	79.34	155.5	-283.90	27.15
NIS	-120.9	227.8	454.5	-575.30	333.60	99.72	195.9	-316.80	75.06
JSI	-40.4	236.5	468.8	-509.20	428.40	120.30	236.7	-277.10	196.30
LGC	11.6	213.6	428.2	-416.60	439.80	58.62	116.6	-105.00	128.20
RISE	69.6	215.0	429.5	-359.90	499.10	62.77	124.0	-54.41	193.60
LNE	72.6	215.3	429.3	-356.70	501.90	69.81	138.3	-65.65	210.90
NIM	81.6	213.0	426.9	-345.30	508.50	58.52	116.4	-34.76	198.00
BAM	94.6	214.3	427.4	-332.80	522.00	60.87	121.8	-27.18	216.40
NMISA	398.6	232.6	464.4	-65.82	863.00	109.40	214.3	184.30	612.90

Figure C3: NIST Decision Tree report for Rhodium

NIST Decision Tree Result – Rhodium

Summary

Include	Laboratory	Result	Uncertainty	DegreesOfFreedom
TRUE	INTI	198.0	4.5	10000
TRUE	UNIIM	202.0	3.2	10000
TRUE	LGC	203.2	1.0	10000
TRUE	LNE	204.0	8.5	10000
TRUE	RISE	204.2	1.4	10000
TRUE	NIM	207.6	1.2	10000

Date: 2023-11-03
Version Number: 1.0.4
Type of DoE: Degrees of Equivalence Ignoring Dark Uncertainty
Random Seed: 59
Selected Procedure: Hierarchical Gauss-Gauss
Consensus estimate: 204
Standard uncertainty: 1.058
95% coverage interval: (201.9, 206.1)
Dark uncertainty (tau): 1.695
Tau posterior 0.025 and 0.975 quantiles: (0.1569,4.982)

Decision Tree Hypothesis test results

Cochran's test for Homogeneity:
p-value: 0.049
Q = 11.1 (Reference Distribution: Chi-Square with 5 Degrees of Freedom)
tau est. = 1.939
tau/median(x) = 0.009522
tau/median(u) = 0.8429

Shapiro-Wilk test for Normality: p = 0.09236

Miao-Gel-Gastwirth test of Symmetry: p = 0.5836

DoE Table

Ignoring Dark Uncertainty

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
INTI	INTI	-5.97000	9.065	-15.0400	3.095
UNIIM	UNIIM	-1.97000	6.677	-8.6470	4.707
LGC	LGC	-0.76990	2.862	-3.6320	2.092
LNE	LNE	0.03009	16.820	-16.7900	16.850
RISE	RISE	0.23010	3.445	-3.2150	3.675
NIM	NIM	3.63000	3.137	0.4928	6.767

Including Dark Uncertainty

	Lab	DoE.x	DoE.U95	DoE.Lwr	DoE.Upr
INTI	INTI	-5.97000	10.090	-16.060	4.123
UNIIM	UNIIM	-1.97000	7.983	-9.953	6.013
LGC	LGC	-0.76990	5.501	-6.271	4.731
LNE	LNE	0.03009	17.530	-17.500	17.560
RISE	RISE	0.23010	5.772	-5.541	6.002
NIM	NIM	3.63000	5.629	-1.999	9.259

Lab Uncertainties Table

lab	x	u	nu	ut
INTI	198.0	4.5	10000	4.809
UNIIM	202.0	3.2	10000	3.621
LGC	203.2	1.0	10000	1.968
LNE	204.0	8.5	10000	8.667
RISE	204.2	1.4	10000	2.198
NIM	207.6	1.2	10000	2.077

lab	D	uDR	UDR	LwrR	UprR	uDI	UDI	LwrI	UprI
INTI	-5.97000	5.153	10.090	-16.060	4.123	4.631	9.065	-15.0400	3.095
UNIIM	-1.97000	4.081	7.983	-9.953	6.013	3.385	6.677	-8.6470	4.707
LGC	-0.76990	2.726	5.501	-6.271	4.731	1.451	2.862	-3.6320	2.092
LNE	0.03009	8.930	17.530	-17.500	17.560	8.565	16.820	-16.7900	16.850
RISE	0.23010	2.883	5.772	-5.541	6.002	1.756	3.445	-3.2150	3.675
NIM	3.63000	2.807	5.629	-1.999	9.259	1.596	3.137	0.4928	6.767