Bundesanstalt für Materialforschung und -prüfung (BAM)

The certification of mass fractions of Pt, Pd, and Rh in used car catalyst

BAM-M504b

Certification report

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Abstract

This report describes the preparation and certification of reference material BAM-M504b, a used cordierithe car catalyst material, carried out in co-operation with the Committee of Chemists of GDMB. The certified mass fractions and additional determined data are listed below.

Parameter	Mass fraction	
	Certified Value [1)] in mg/kg	Uncertainty [2)] in mg/kg
Platinum	1159	8
Palladium	1128	9
Rhodium	314.2	2.6

1) Unweighted mean value of the means of accepted sets of data (consisting of at least 4 but usually 6 single results), each set being obtained by a different laboratory and/or a different method of measurement.
2) Estimated expanded uncertainty U with a coverage factor of $k = 2$, corresponding to a level of confidence of approx. 95 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).

Contents

List of abbreviations

(if not explained elsewhere)

ICP-OES	Inductively coupled plasma optical emission spectrometry
XRF	X-ray fluorescence spectrometry

M	mean of the laboratories' means
u_c	combined uncertainty of certified mass fraction
s_M	standard deviation of the accepted laboratory mean values of interlaboratory comparison for certification
n	number of accepted laboratory mean values of interlaboratory comparison for certification

I	ICP-OES (Tables 4 – 6)

1 Introduction

1.1 Scope

Catalysts containing the platinum group elements (PGEs) are employed for a variety of industrial and chemical uses. Since more than 40 years, catalytic converters have been widely implemented to reduce air pollution from automobile exhaust emissions. Today modern three-way catalysts are used to completely oxidize hydrocarbon species and carbon monoxide to carbon dioxide and water and also to reduce nitrogen oxides to molecular nitrogen. These catalysts consist of a ceramic base body made of aluminum magnesium and/or calcium aluminum silicates (usually cordierite) with a honeycomb structure that exposes a maximum surface area to the exhaust stream. The platinum group metals platinum (Pt), rhodium (Rh) and palladium (Pd) are the catalytically active components. These precious metals in different ratios are finely dispersed on the surface. Cerium and other rare earth elements are added to the washcoat during catalyst production. Cordierite-based catalytic converters have delivered an optimal perfomance in practice due to their favourable properties, such as low temperature coefficient of thermal expansion and excellent thermal resistance, along with reasonable mechanical properties [1]. The use of expensive platinum group elements in catalyst production fostered the development of recycling strategies for used car catalysts which today are well established and of high economical benefit. The high price of the precious metals platinum, palladium and rhodium is the reason why analytical methods with small uncertainty are necessary for their determination. The new certified reference material BAM-M504b replaces the CRMs ERM-EB504 and ERM-EB504a, which both were in good demand. The matrix composition of the three CRMs is quite similar, the precious metals contens vary depending on the precious metals composition of the used car catalysts taken as candidate material.

1.2 Certification procedure

Certification of reference material BAM-M504b was carried out in close cooperation with the working group „Precious Metals" of the Committee of Chemists of the Society of Metallurgists und Miners (GDMB). Since all the laboratories participating in this certification project are highly experienced with precious metals analysis and had already participated in earlier inter-laboratory comparisons, there was no preceding round robin for qualification necessary.
Certification was done on the basis of ISO 17034 [2] and the relevant ISO-Guides [3, 4].

1.3 Candidate material

200 kg of used cordierite-based car catalysts (Mairec Edelmetallgesellschaft mbH, Alzenau, Germany) were taken as candidate material. After annealing the material at 700 °C for 12 h, it was grinded to a particle size < 100 µm using a ball mill with stainless steel balls and a swing mill made of stainless steel. After removing particles with a size of > 100 µm by sieving, the material was mixed for 48 h in a drum hoop mixer and preliminary tested for homogeneity. After delivery to BAM the whole batch was devided into 10 subbatches.

2 Participating laboratories

2.1 Preparation of the material

- The material was prepared by Institut für Materialprüfung Glörfeld GmbH, Willich.
- The material was bottled by Bundesanstalt für Materialforschung und -prüfung (BAM).

2.2 Homogeneity testing

The analytical investigations and all statistical evaluations for the homogeneity testing were carried out by BAM.

2.3 Certification analysis

14 laboratories participated in the interlaboratory comparison for certification. Since all participating laboratories are highly experienced with precious metals analysis and participated in several interlaboratory comparisons organised within the working group "Precious Metals" within the Committee of Chemists of GDMB, there was no preceding round robin test for qualification.

- ALS Minerals Division | Inspection Services, Knowsley Business Park, Prescot (United Kingdom)
- Alfred Knight Int. Ltd, St. Helens (United Kingdom)
- Allgemeine Gold- und Silberscheideanstalt AG, Pforzheim (Germany)
- AnRec® GmbH & Co. KG, Gelnhausen (Germany)
- Aurubis AG, Hamburg (Germany)
- Bureau Veritas Commodities UK Ltd, Witham, Essex (United Kingdom)
- Forschungsinstitut Edelmetalle & Metallchemie, Schwäbisch Gmünd (Germany)
- Institut für Materialprüfung Glörfeld GmbH, Willich (Germany)
- Ledoux & Company, Teanec NJ (USA)
- ReMetall Deutschland AG, Drochow (Germany)
- Umicore AG & Co. KG, Hanau (Germany)
- Umicore Precious Metals, Hoboken (Belgium)
- W.C. Heraeus, Hanau (Germany)
- WRC World Resources Company GmbH, Wurzen (Germany)

3 Homogeneity investigation of the material

From each of the 10 subbatches two samples were taken and tested for homogeneity twice using wavelength dispersive X-ray fluorescence spectrometry (XRF, MagiX Pro, Panalytical, Almelo, Netherlands). XRF-measurements were carried out on pressed powder pellets. 6.5 g of test sample were taken and pressed in Al-cups on a 200 kN-press to pellets with a thickness of 5 mm and a diameter of 32 mm (pressing-time: 10 s). One of the pellets was randomly chosen as drift control sample. This sample was measured 10 times before and five times during the whole measurement sequence. XRF measuring conditions are given in Table 1.

Table 1: XRF measuring conditions

Element	Testing time	Background measuring time	Line
Pt	50 s	20 s	L_β
Pd	200 s	80 s	K_α with filter
Rh	200 s	80 s	K_α with filter

Spectrometer:	MagiX Pro Panalytical (wavelength dispersive) (Panalytical, Almelo, Netherlands)
X-ray tube:	Rhodium
Tube voltage:	60 kV
Tube current	65 mA
Collimator	150 µm lamella distance
Aperture:	30 mm
Crystal:	LiF200
Detector:	scintillation counter

The estimates of analyte-specific inhomogeneity contributions u_{bb} to be included into the total uncertainty budget were calculated according to ISO Guide 35 [4] using Eq. (1) and Eq. (2):

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

$$s_{bb\_min} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \qquad (2)$$

with:

MS_{among}	mean of squared deviations between bottles (from 1-way ANOVA)
MS_{within}	mean of squared deviations within bottles (from 1-way ANOVA)
n	number of replicate sub-samples per bottle
N	number of bottles selected for homogeneity study

s_{bb} signifies the between-bottle standard deviation, whereas s_{bb_min} denotes the maximum heterogeneity that can potentially be hidden by an insufficient repeatability of the applied measurement method (which has to be considered as the minimum uncertainty contribution). In any case the larger of the two values was used as u_{bb}. Eq. (1) does not apply if MS_{within} is larger than MS_{among}. The calculated relative values of s_{bb}, s_{bb_min}, and u_{bb} are given in the following Table 2.

Table 2: Relative uncertainty contributions due to possible sample inhomogeneity

Element	$s_{bb,r}$ (%)	$s_{bb\_min,r}$ (%)	$u_{bb,r}$ (%)
Pt	0.182	0.294	0.294
Pd	0.152	0.190	0.190
Rh	$MS_{among} < MS_{within}$	0.186	0.186

The results of the homogeneity tests are listed in the appendix.

4 Stability of the material

Due to its chemical composition cordierite-based material is very stable. It was annealed at 700 °C for 12 h under air. Because of its chemical inertness and its stability at high temperatures and the experience with ERM-EB504 and ERM-EB504a, both were stable over the whole period of availability, no specific stability test was performed for BAM-M504b.

5 Characterisation study

5.1 Analytical methods used for certification

14 laboratories participated in the certification interlaboratory comparison. For some elements part of the laboratories used more than one analytical method and therefore reported more than one dataset. The laboratories were asked to analyse six subsamples. They were free to choose any suitable method for analysis. Table 3 shows the analytical methods used by the participating laboratories.
All participating laboratories were instructed to use only calibrants prepared from pure metals or stoichiometric compounds or well checked commercial calibration solutions.

Table 3: Analytical procedures used by the participating laboratories

Lab-No.	Element.	Sample mass	Sample pretreatment/Calibration	Analytical method
1	Pt, Pd, Rh	7.5 g	Cu-collection	ICP-OES, calibration with Pd-metal, Pt-metal and Rh-metal
2	Pt, Pd, Rh	12.5 g	Cu-collection	XRF, calibration with pure metals
3*	Pt, Pd, Rh	2 g	Decomposition with sodium peroxide, precipitation with Te	ICP-OES, calibration with Pd-metal, Pt-metal and Rh-standard solution (NIST traceable)
4*	Pt, Pd, Rh	5 g	Cu-collection	ICP-OES, calibration with Pd-metal, Pt-metal and commercial Rh-standard solution (checked gravimetrically)
5	Pt, Pd, Rh	0.5 g	Decomposition with sodium peroxide, precipitation with Sn/Te	ICP-OES with interna standard, calibration with Pd-metal, Pt-metal and Rh-standard solution (checked gravimetrically)
6	Pt, Pd, Rh	1 g	Pb/Au-collection, dissolution in aqua regia	ICP-OES, calibration with Pd-metal, Pt-metal and $RhCl_3$, Sc as internal standard
7*	Pt, Pd, Rh	0.5 g	Decomposition with sodium peroxide, precipitation with Sn/Te	ICP-OES, calibration with Pd-metal, Pt-metal and Rh-standard solution (checked gravimetrically)
10*	Pt, Pd, Rh	0.5 g	Alkaline frit fusion, Te/Co-precipitation	ICP-OES, calibration with gravimetrically prepared standards
11*	Pt, Pd, Rh	1 g	Dissolution with Na_2O_2/HCl, separation of precious metals with Sn/Te-precipitation	ICP-OES, calibration with commercial certified standard solutions
15	Pt, Pd, Rh	2.5 g	Cu-collection	ICP-OES, calibration with pure metals
16	Pt, Pd, Rh	2 g	Cu-collection	ICP-OES, calibration with Pd-metal, Pt-metal and commercial Rh-standard solution (checked gravimetrically)
18*	Pt, Pd, Rh	3 g	Fire assay, acid solution	ICP-OES, calibration with standard solutions prepared from pure substances
19	Pt, Pd, Rh	1 g	Peroxide fusion	ICP-OES, calibration with standard solution prepared from pure substances
22	Pt, Pd, Rh	8-9 g	Cu-collection, dissolution with aqua regia	ICP-OES, calibration with pure chemicals, Y as int. standard

*accredited acc. to ISO IEC 17025

5.2 Analytical results and statistical evaluation

The analytical results of the certification inter-laboratory comparison are listed in Tables 4 to 6. These tables show the single results (M_i) of each laboratory, the respective laboratories' mean values (M), absolute and relative intra-laboratory standard deviation (s and s_{rel}, respectively), the standard deviation of laboratory means (s_M), and in addition the square root of mean of variances of data sets under repeatability conditions ($\bar{s}_i$). n is the number of accepted data sets. The continuous line marks the certified value (mean of the laboratories' means), the broken lines mark the standard deviation, calculated from the laboratories' means.
In the related figures for each laboratory its mean value and single standard deviation is given.

Table 4: results for Pt

Lab./Meth.	16/I	4/I	15/I	5/I	7/I-1	19/I	7/I-2	18/I	2/XRF	22/I	3/I	6/I	11/I	10/I	1/I		
M_i [mg/kg]	1146	1142	1156	1151	1144	1154	1164	1157	1161	1164	1162	1168	1166	1173	1162		*n*
	1151	1151	1141	1157	1160	1153	1153	1161	1161	1165	1164	1162	1168	1169	1167		15
	1121	1144	1154	1151	1146	1159	1156	1156	1162	1162	1170	1166	1167	1170	1166		
	1150	1150	1144	1156	1162	1163	1158	1156	1162	1163	1170	1171	1162	1164	1170		
	1138	1160	1157	1155	1152	1160	1156	1162	1162	1165	1163	1170	1172	1163	1173		
	1131	1143	1157	1153	1172		1161	1158	1163	1170	1166	1168	1173	1172	1173		
***M* [mg/kg]**	**1139.5**	**1148.3**	**1151.5**	**1153.8**	**1156.0**	**1157.8**	**1158.0**	**1158.2**	**1161.8**	**1164.8**	**1165.8**	**1167.4**	**1168.0**	**1168.3**	**1168.6**		**1159.2**
s [mg/kg]	11.84	6.83	7.12	2.56	10.66	4.21	3.95	2.56	0.75	2.79	3.49	3.16	4.05	4.04	4.10	s_M [mg/kg]	8.48
																$\bar{s_i}$ [mg/kg]	5.64
s_{rel}	0.010	0.006	0.006	0.002	0.009	0.004	0.003	0.002	0.001	0.002	0.003	0.003	0.003	0.003	0.004		0.0073

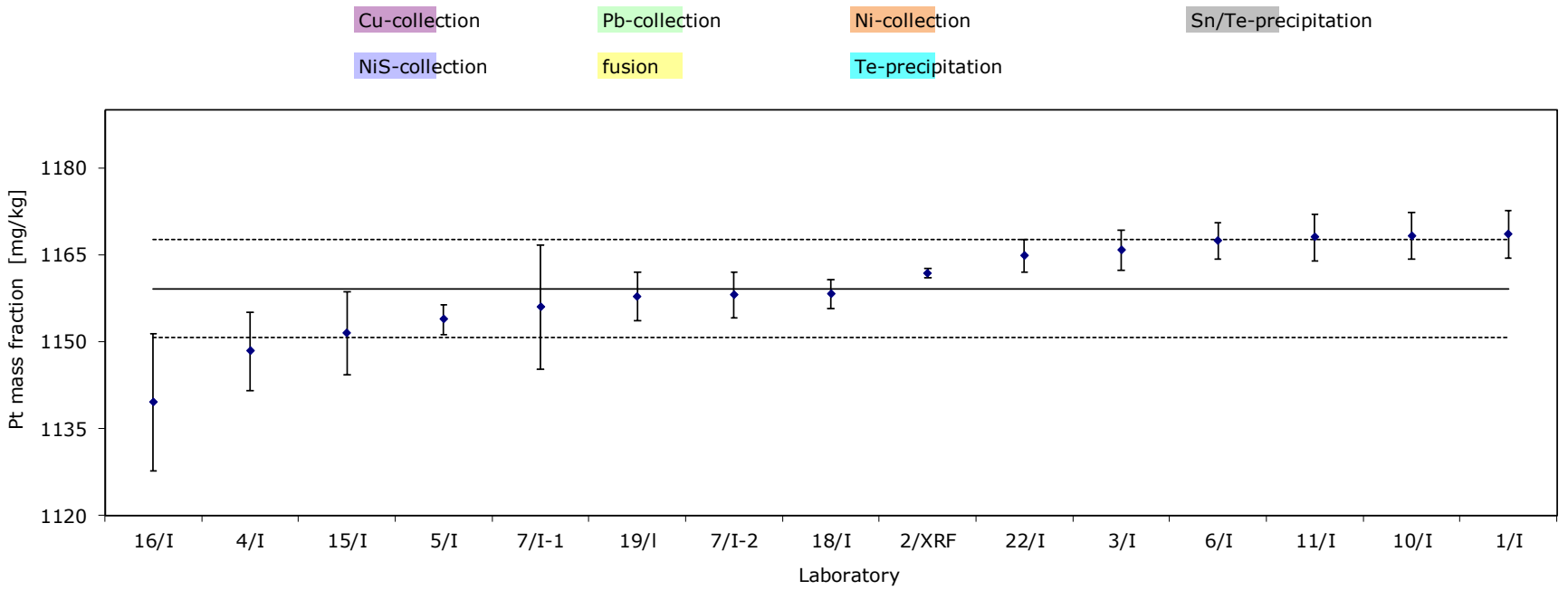


Table 5: results for Pd

Lab./Meth.	11/I	4/I	10/I(R)	18/I	19/I	22/I	15/I	16/I	7/I-2	2/XRF	7/I-1	1/I	6/I	3/I	5/I		
M_i [mg/kg]	1117	1124	1124	1122	1125	1128	1129	1133	1131	1127	1130	1126	1133.4	1142	1141		*n*
	1111	1113	1121	1125	1123	1124	1121	1126	1126	1131	1132	1128	1132.2	1143	1143		15
	1103	1123	1123	1125	1128	1126	1128	1118	1130	1129	1123	1129	1134.2	1146	1142		
	1105	1111	1123	1125	1118	1121	1115	1132	1125	1130	1133	1133	1136.6	1136	1141		
	1109	1126		1126	1129	1125	1143	1132	1129	1130	1130	1136	1138.2	1140	1138		
	1107	1124		1123		1130	1126	1125	1125	1128	1137	1139	1130.5	1141	1148		
***M* [mg/kg]**	**1108.7**	**1120.2**	**1123.0**	**1124.2**	**1124.6**	**1125.7**	**1127.0**	**1127.7**	**1127.7**	**1129.2**	**1130.8**	**1131.7**	**1134.2**	**1141.3**	**1142.2**		**1127.9**
s [mg/kg]	4.97	6.43	1.23	1.50	4.39	3.14	9.40	5.82	2.66	1.47	4.62	4.84	2.83	3.33	3.31	s_M [mg/kg]	8.16
																$\bar{s}_i$ [mg/kg]	4.51
s_{rel}	0.004	0.006	0.001	0.001	0.004	0.003	0.008	0.005	0.002	0.001	0.004	0.004	0.002	0.003	0.003		0.007

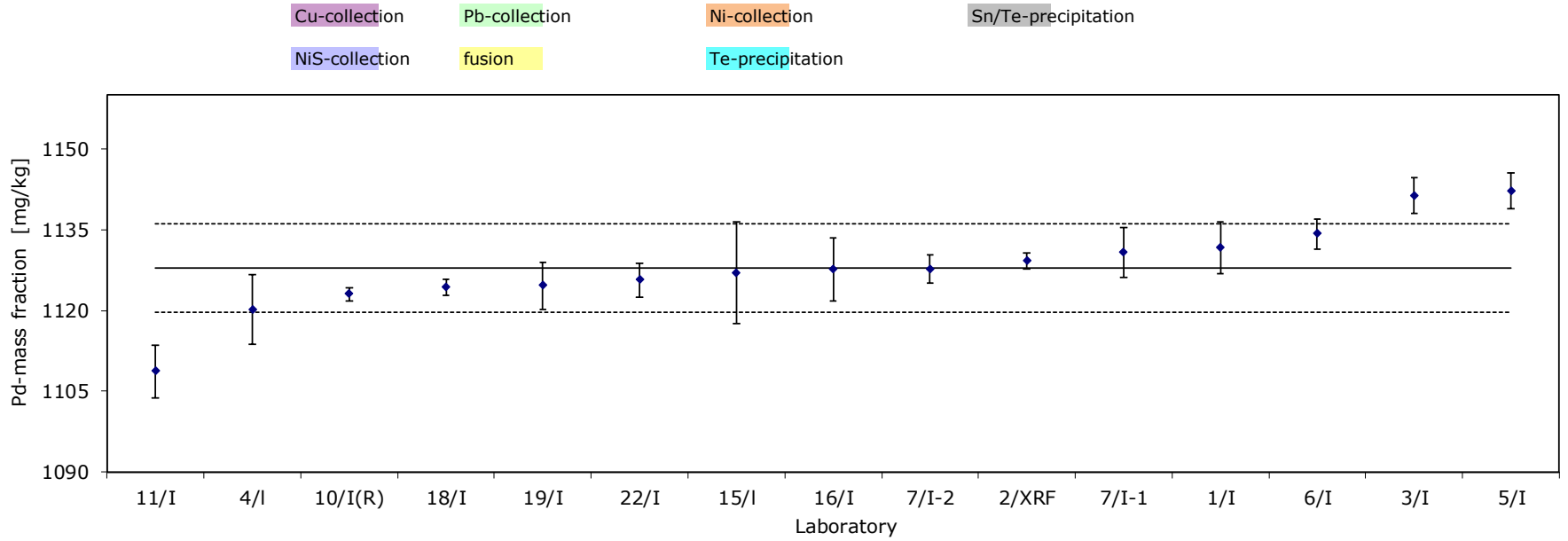
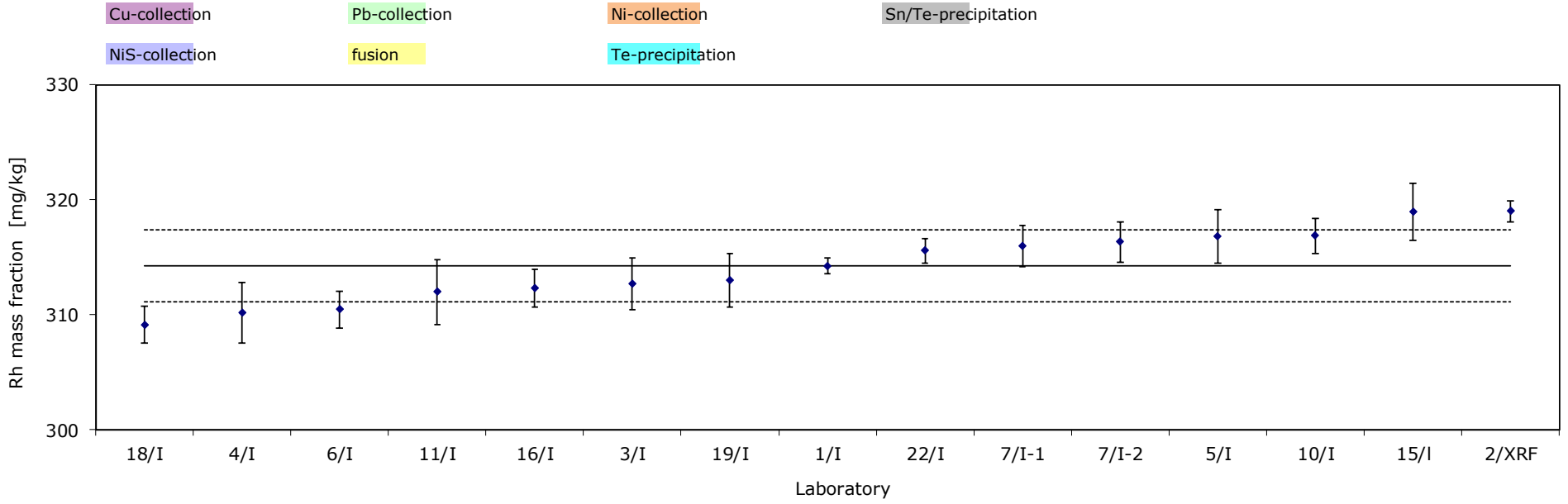


Table 6: results for Rh

Lab./Meth.	18/I	4/I	6/I	11/I	16/I	3/I	19/I	1/I	22/I	7/I-1	7/I-2	5/I	10/I	15/I	2/XRF		
M_i [mg/kg]	306.7	311.0	309.0	315.0	313.0	313.0	312.0	313.3	316.5	317.0	319.0	316	318.6	319.8	318.0		*n*
	308.7	309.0	308.7	309.0	312.0	316.0	311.0	314.2	315.5	316.0	316.0	315	318.4	318.2	319.0		15
	309.2	312.0	309.7	308.0	310.0	312.0	315.0	313.8	315.3	313.0	315.0	315	317.4	320.0	318.0		
	308.7	308.0	312.6	313.0	314.0	309.0	311.0	314.3	313.6	318.0	314.0	316	314.9	314.5	320.0		
	311.6	314.0	311.9	314.0	314.0	313.0	316.0	314.6	316.0	315.0	317.0	318	315.7	321.8	319.0		
	309.8	307.0	310.9	313.0	311.0	313.0		315.3	316.5	317.0	317.0	321	316.2	319.6	320.0		
M [mg/kg]	**309.1**	**310.2**	**310.5**	**312.0**	**312.3**	**312.7**	**313.0**	**314.3**	**315.6**	**316.0**	**316.3**	**316.8**	**316.9**	**319.0**	**319.0**		**314.2**
s [mg/kg]	1.60	2.64	1.59	2.83	1.63	2.25	2.35	0.68	1.08	1.79	1.75	2.32	1.50	2.48	0.89	s_M [mg/kg]	3.14
																$\bar{s}_i$ [mg/kg]	1.93
s_{rel}	0.005	0.009	0.005	0.009	0.005	0.007	0.007	0.002	0.003	0.006	0.006	0.007	0.005	0.008	0.003		0.010



The statistical evaluation of the data was performed using the software program eCerto [5]. The following results were obtained:

Tab. 7: Outcome of statistical tests on the results obtained for Pt

	1st run
Number of data sets	15
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	Laboratory 16
Nalimov (α = 0.01)	Laboratory 16
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	Laboratory 16
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal

The outlying result was not removed.

Tab. 8: Outcome of statistical tests on the results obtained for Pd

	1st run
Number of data sets	15
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	Laboratory 11
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	Laboratory 11
Nalimov (α = 0.01)	Laboratory 11
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	Laboratory 15
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal

The outlying result was not removed.

Tab. 9: Outcome of statistical tests on the results obtained for Rh

	1st run
Number of data sets	15
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	---
Nalimov (α = 0.01)	---
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	---
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal

The uncertainties of the certified mass fractions consist of three uncertainty contributions, one resulting from the possible inhomogeneity of the material (u_{bb}), one resulting from the certification inter-laboratory comparison (u_{ilc}) and one reflecting the average precision of accepted laboratory means (u_{prec}) which is calculated according to Eq. (3):

$$u_{\text{prec}} = \sqrt{\sum_{i=1}^{N} (SD_i)^2 / nN} \qquad (3)$$

where SD_i is the standard deviation of the results of an individual participant, N is the number of accepted individual data sets, and n is the number of replicate analyses performed by each participant.

The different contributions to the overall uncertainties of the certified mass fractions were combined using the following Eq. (4):

$$u_{\text{CRM}} = \sqrt{u_{\text{ILC}}^2 + u_{\text{bb}}^2 + u_{\text{prec}}^2} \qquad (4)$$

with

$u_{ilc} = \sqrt{\frac{s_M^2}{n}}$: uncertainty contribution resulting from inter-laboratory comparison

n : number of data sets used for calculating the certified mass fraction of each element

Table 10: Uncertainty calculation

	uncertainty contribution from									
	M	n	s_M	u_{ilc}	u_{prec}	u_{bb}	$u_{combined}$	U		u_{bb} (rel)
	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		
Pt	1159.2	15	8.4752	2.1883	2.3847	2.2060	3.9168	7.8337		0.1903
Pd	1127.9	15	8.1584	2.1065	1.9066	3.3139	4.3651	8.7302		0.2938
Rh	314.2	15	3.1369	0.8100	0.8149	0.5846	1.2891	2.5782		0.1861

The expanded uncertainties U are calculated by multiplication of $u_{combined}$ with a coverage factor of k = 2 using Equation 5.

$$U = k \cdot u_{\text{combined}} \quad (5)$$

The calculated mass fractions and their resp. expanded uncertainties are given on Page 2 of this report. Rounding was done according to DIN 1333 [6].

6 Instructions for use

6.1 Area of application

The main area of application is to check the trueness of results when one or more of the certified parameters in car catalyst materials are determined by a laboratory. Based on own results and on certified values the uncertainty of own measurements can be calculated.

6.2 Recommendations for correct sampling and sample preparation

To ensure a representative sub-sampling for the analysis the bottle containing the CRM should be shaken in different directions for about two minutes before taking the sub-sample. Each sub-sample has to be taken separately. According to the sub-sample masses taken for the homogeneity testing at least 5 g of powder has to be weighed. Before weighing, the material has to be dried for 8 h at 105 °C.

6.3 Recommendations for correct storage

The sample should be stored in a dust-free and dry environment avoiding contamination and moisture.

6.4 Safety guidelines

Used car catalyst powder is not known to be toxic. No hazardous effect is to be expected if the material is used under conditions usually adopted in analytical laboratories when handling finely dispersed powder materials.

7. Metrological Traceability

To ensure traceability of the certified mass fractions to the SI (Système International d'Unités) calibration was performed using standard solutions prepared from pure metals or stoichiometric compounds or traceable commercial calibration solutions.

8 References

[1] Kingon AI, and Davis RF, in Engineered Materials Handbook,Volume 4. Ceramics and Glasses, technical chairman Schneider SJ, ASM International, Metals Park, OH, 1991, pp. 758–761.

[2] DIN EN ISO 17034, General requirements for the competence of reference material producers, 2016

[3] ISO Guide 31, Reference materials - Contents of certificates, labels and accompanying documentation, 2015

[4] ISO Guide 35, Reference materials - Guidance for characterization and assessment of homogeneity and stability, 2017

[5] J. Lisec, eCerto Software, BAM 2021

[6] DIN 1333:1992-02 Zahlenangaben

9 Information on and purchase of the CRM

Certified reference material BAM-M504b is supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)
Fachbereich 1.6: Anorganische Referenzmaterialien
Richard-Willstätter-Str. 11, D-12489 Berlin, Germany
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 - 8104 72061
Email: sales.crm@bam.de
https://www.webshop.bam.de

Each unit will be distributed together with a detailed certificate containing the certified values and their uncertainties, the mean values and standard deviations of all accepted data sets and information on the analytical methods used and the names of the participating laboratories.
Information on certified reference materials can be obtained from BAM, https://www.bam.de.

Appendix: Homogeneity testing (mass fractions in %)

Platinum

	1	2
F1o	0.120	0.119
F1u	0.119	0.120
F2o	0.119	0.119
F2u	0.119	0.119
F3o	0.120	0.120
F3u	0.120	0.119
F4o	0.120	0.120
F4u	0.120	0.120
F5o	0.120	0.121
F5u	0.120	0.119
F6o	0.119	0.120
F6u	0.119	0.120
F7o	0.120	0.120
F7u	0.120	0.120
F8o	0.121	0.120
F8u	0.119	0.118
F9o	0.119	0.120
F9u	0.120	0.121
F10o	0.120	0.120
F10u	0.119	0.120

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.0000104	19	5.47368E-07	1.8245614	0.0954364	2.137009
Within groups	6E-06	20	3E-07			
Total	0.0000164	39				
within-sd	0.000547723			status:	homogeneous	
effective n	2.00					
s_bb	0.000351688					
s_bb_min	0.000217794					
u_bb	0.000351688					
u_bb(rel.)	0.293807569					

Palladium

	1	2
F1o	0.109	0.110
F1u	0.109	0.110
F2o	0.109	0.110
F2u	0.109	0.109
F3o	0.109	0.110
F3u	0.108	0.109
F4o	0.110	0.110
F4u	0.110	0.110
F5o	0.110	0.109
F5u	0.110	0.109
F6o	0.110	0.110
F6u	0.109	0.109
F7o	0.109	0.110
F7u	0.110	0.110
F8o	0.110	0.110
F8u	0.110	0.109
F9o	0.110	0.109
F9u	0.110	0.110
F10o	0.109	0.110
F10u	0.110	0.110

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	6.275E-06	19	3.30263E-07	1.200957	0.343485	2.137009
Within groups	5.5E-06	20	2.75E-07			
Total	1.1775E-05	39				
within-sd	0.0005244			status:	homogeneous	
effective n	2.00					
s_bb	0.00016623					
s_bb_min	0.00020852					
u_bb	0.00020852					
u_bb(rel.)	0.19030047					

Rhodium

	1	2
F1o	0.02995	0.03015
F1u	0.03010	0.02990
F2o	0.02995	0.02995
F2u	0.02980	0.02980
F3o	0.03005	0.02980
F3u	0.02995	0.03000
F4o	0.02990	0.02990
F4u	0.02980	0.03020
F5o	0.02990	0.02985
F5u	0.02995	0.03020
F6o	0.03000	0.02995
F6u	0.02985	0.03020
F7o	0.03020	0.03020
F7u	0.02985	0.03015
F8o	0.03010	0.02990
F8u	0.03005	0.02980
F9o	0.02990	0.03010
F9u	0.03000	0.03020
F10o	0.03010	0.03000
F10u	0.02985	0.02995

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	2.96188E-07	19	1.55888E-08	0.7918129	0.6927633	2.137009
Within groups	3.9375E-07	20	1.96875E-08			
Total	6.89937E-07	39				
within-sd	0.000140312			status:	homogeneous	
effective n	2.00					
s_bb	0					
s_bb_min	5.57931E-05					
u_bb	5.57931E-05					
u_bb(rel.)	0.186062191					