Bundesanstalt für Materialforschung und -prüfung (BAM)

in co-operation with the

Committee of Chemists of GDMB
Gesellschaft der Metallurgen und Bergleute e.V.

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

ERM®-EB504a

Certification report

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Abstract

This report describes the preparation and certification of reference material ERM®-EB504a, a used cordierite car catalyst material, carried out in co-operation with the Committee of Chemists of GDMB. The certified mass fractions are listed below.

Parameter	Mass fraction	
	Certified Value [1] in mg/kg	Uncertainty [2] in mg/kg
Platinum	1414	9
Palladium	1596	11
Rhodium	210.0	2.2

1) The certified values are the means of 22-25 series of results (depending on the parameter) obtained by different laboratories. Up to 9 different analytical methods were used for the measurement of one parameter. The methods applied for determination of element mass fractions were calibrated using pure substances of definite stoichiometry or solutions prepared from them, thus achieving traceability to the International System of Units (SI).

2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM) with a coverage factor k = 2. It includes contributions from sample inhomogeneity.

Contents

List of abbreviations

(if not explained elsewhere)

ICP-OES	Inductively coupled plasma optical emission spectrometry
SOES	Spark 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 inter-laboratory comparison for certification
n	number of accepted laboratory mean values of inter-laboratory comparison for certification

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 30 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.

1.2 Certification procedure

Certification of reference material ERM®-EB504a was carried out on the basis of the relevant ISO-Guides [2-4], the „Guidelines for the development and production of BAM Reference Materials“ [5] and the “Technical Guidelines for the Production and Acceptance of a European Reference Material” [6].

The statistical evaluation of all analytical results was performed using the software program SoftCRM 1.2.2. [7]. The certified values were calculated as means of the laboratory means reported from the participating laboratories of the inter-laboratory comparison. The certified uncertainties were calculated taking into account the contributions from inter-laboratory comparison and from inhomogeneity of the material.

1.3 Candidate material

150 kg of used cordierite based car catalysts 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. The whole batch was devided into 10 sub-batches using a sample splitter. From each sub-batch two samples were taken and tested for homogeneity using wavelength dispersive X-ray fluorescence spectrometry (XRF, MagiX Pro, Panalytical, Almelo, Netherlands). Since the material was sufficiently homogeneous it was bottled without any further homogenization steps. In total 734 bottles were filled with 200 g of powder each.

2 Participating laboratories

2.1 Allocation and preparation of the material

- The material was prepared by G + S Gesellschaft für Labortechnik und Probenaufbereitung mbH, Willich, Germany
- 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

21 laboratories from four different countries participated in the inter-laboratory comparison for certification. Since all participating laboratories are highly experienced with precious metals analysis and participated in several inter-laboratory 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)
- Aurubis AG, Hamburg (Germany)
- BASF Corporation, Union (USA)
- Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin (Germany)
- Bureau Veritas Commodities Division Inspectorate (Shanghai) Ltd, Shanghai (China)
- Clariant Produkte GmbH, Bruckmühl/Heufeld (Germany)
- Dorfner Analysenzentrum und Anlagenplanungsgesellschaft mbH (ANZAPLAN), Hirschau (Germany)
- Heraeus Deutschland GmbH & Co. KG, Hanau (Germany)
- Inspectorate America Corporation, Bureau Veritas Commodities Division, Sparks, NV (USA)
- Forschungsinstitut Edelmetalle & Metallchemie, Schwäbisch Gmünd (Germany)
- Institut für Materialprüfung Glörfeld GmbH, Willich (Germany)
- JSC "Krastsvetmet" Krasnoyarsk (Russian Federation)
- Ledoux & Company, Teanec NJ (USA)
- Nickelhütte Aue GmbH, Aue (Germany)
- ReMetall Deutschland AG, Drochow (Germany)
- Saxonia Edelmetalle GmbH, Halsbrücke (Germany)
- Umicore AG, Hanau (Germany)
- Umicore Precious Metals, Hoboken (Belgium)
- WRC World Resources Company GmbH, Wurzen (Germany)

3 Homogeneity investigation of the material

For homogeneity testing 19 bottles were randomly taken from a total of 734 bottles (see Table 1). From each of the N = 19 bottles four sub-samples were taken for analysis.

Tab. 1: Selected bottles analysed for homogeneity of ERM®-EB504a

25	28	56	57	130	198	281	315	321	370
487	491	521	583	628	642	667	678	734	

From each bottle 4 x 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). XRF measuring conditions are given in Table 2. One of the pellets was randomly chosen as drift control sample. This sample was measured 10 times during the whole measurement sequence.

Table 2: 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 [3] using Eq. (1) and Eq. (2):

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

$$u^*_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \qquad (2)$$

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 u^*_{bb} 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}, u^*_{bb} , and u_{bb} are given in the following Table 3.

Table 3: Relative uncertainty contributions due to possible sample inhomogeneity

Element	$s_{bb,r}$ (%)	$u^*_{bb,r}$ (%)	$u_{bb,r}$ (%)
Pt	0.190	0.140	0.190
Pd	$MS_{among} < MS_{within}$	0.153	0.153
Rh	0.034	0.184	0.184

The results of the homogeneity testing are listed in Appendix 1.

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 no specific stability test was performed for ERM®-EB504a.

5 Characterisation study

5.1 Analytical methods used for certification

21 laboratories participated in the certification inter-laboratory 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 sub-samples. They were free to choose any suitable method for analysis. Table 4 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 4: Analytical procedures used by the participating laboratories

Lab-No.	Element.	Sample mass	Sample pretreatment/Calibration	Analytical method
2	Pt, Pd, Rh	12.5 g	Cu-collection	XRF, calibration with pure metals
3	Pt, Pd, Rh	5 g	Cu-collection	ICP-OES, calibration with Pd-metal, Pt-metal and commercial Rh-standard solution (checked gravimetrically)
3	Pt, Pd, Rh	5 g	Pb-collection	ICP-OES
4	Pt, Pd, Rh	2 g	Sodium Peroxide fusion. Collection of precious metals with tellurium, $SnCl_2$-reduction	ICP-OES, calibration with Pd-metal, Pt-metal and $RhCl_3$, Y as int. standard
5	Pt, Pd, Rh	5 g	Cu-collection	ICP-OES, commercial standard solutions, Sc as internal standard
6	Pt, Pd, Rh	1 g	Pb/Au-collection, dissolution in aqua regia	ICP-OES, calibration with Pd-metal, Pt-metal and commercial Rh-standard solution, Sc as internal standard
6	Pt, Pd, Rh	1 g	NiS-collection, dissolution in HCl/aqua regia	ICP-OES, calibration with Pd-metal, Pt-metal and commercial Rh-standard solution, Sc as internal standard
7	Pt, Pd, Rh	10 g	NiS-collection, dissolution in HCl/aqua regia	ICP-OES, calibration with Pd-metal, Pt-metal and Rh-standard solution (checked gravimetrically), bracketing
8	Pt, Pd, Rh	0.5 g	Dissolution with Na_2O_2/HCl, separation of precious metals with SnTe-precipitation	ICP-OES, calibration with pure metals
8	Pt, Pd, Rh	2 g	NiS-collection, dissolution in HCl, separation of precious metals with SnTe-precipitation	ICP-OES, calibration with pure metals

Lab-No.	Element.	Sample mass	Sample pretreatment/Calibration	Analytical method
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 SnTe-precipitation	ICP-OES, calibration with commercial standard solutions
12	Pt, Pd, Rh	5 g	Cu_2O-collection, dissolution in HCl/aqua regia	ICP-OES, calibration with pure metals, Y as int. standard
14	Pt, Pd, Rh	5 g	Cu_2O-collection, dissolution in HCl/aqua regia	ICP-OES, calibration with pure metals (Pt, Pd) and Rh-standard solution (checked gravimetrically), Y as int. standard
15	Pt, Pd, Rh	2.5 g	Cu-collection	ICP-OES, calibration with pure metals
16	Pt, Pd, Rh	2 g	Cu-collection, dissolution with aqua regia	ICP-OES, calibration with pure metals (Pt, Pd) and commercial Rh-standard solution
17	Pt, Pd, Rh	1.5 g	Alkaline fusion, Te-collection	ICP-OES, calibration with gravimetrically prepared standards (pure metals or salts)
18	Pt, Pd, Rh	3-5 g	NiS-collection, dissolution in HCl. Separation of precious metals with SnTe-precipitation	ICP-OES, calibration with commercial standard solutions
19	Pt, Pd, Rh	2.5 g	Pb-collection, preparation of a Pb-beat	FOES, preparation of standards using pure Pb and pure precious metal powder
19	Pt, Pd, Rh	5 g	Pb-collection, dissolution in acid	ICP-OES, calibration with pure metals (Pt, Pd) and Rh-standard solution (checked gravimetrically)
20	Pd	0.5 g	Microwave assisted dissolution with aqua regia	ICP-OES, calibration with commercial standard solution
21	Pt, Pd, Rh	1 g	Decomposition with Na_2CO_3/$Na_2B_4O_7$/S, Ni-collection, dissolution in HCl. Separation of precious metals with SnTe-precipitation	ICP-OES, calibration with commercial standard solution
22	Pt, Pd, Rh	6-8 g	Cu-collection, dissolution with aqua regia	ICP-OES, calibration with pure chemicals, Y as int. standard
23	Pt, Pd, Rh	2 g	Pb-collection, dissolution in acid	ICP-OES
24	Pt, Pd, Rh	3.5 g	Decomposition by fusion, Au-collection, dissolution with aqua regia	ICP-OES

5.2 Analytical results and statistical evaluation

The analytical results of the certification inter-laboratory comparison are listed in Tables 5 to 7. 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

Lab./Meth.	11/I	2/RFA	3/I	4/I	15/I	7/I	3/I	22/I	16/I	19/I	12/I	19/FOES
M_i [mg/kg]	1385	1403	1404	1403	1419	1409	1410	1386	1414	1408	1415	1410
	1387	1401	1402	1408	1398	1411	1408	1404	1407	1414	1413	1420
	1384	1399	1407	1405	1414	1410	1415	1412	1407	1412	1415	1417
	1393	1398	1402	1408	1419	1405	1415	1431	1406	1414	1409	1414
	1398	1399	1418	1411	1402	1409	1401	1406	1414		1417	
	1393	1395	1399	1403	1401	1410	1408	1420	1411		1422	
M [mg/kg]	**1390.0**	**1399.2**	**1405.3**	**1406.3**	**1408.8**	**1409.0**	**1409.5**	**1409.8**	**1409.8**	**1412.0**	**1415.2**	**1415.3**
s [mg/kg]	5.514	2.714	6.743	3.204	9.579	2.098	5.244	15.316	3.656	2.828	4.309	4.272
s_{rel}	0.004	0.002	0.005	0.002	0.007	0.001	0.004	0.011	0.003	0.002	0.003	0.003

Lab./Meth.	8/I-S	14/I	17/I	6/I-2	6/I-1(R)	10/I	8/I-NiS	18/I	24/I	23/I		
M_i [mg/kg]	1420	1415	1417	1418	1401	1422	1414	1436	1439	1437		n
	1419	1414	1416	1408	1441	1413	1416	1422	1423	1437		22
	1418	1418	1421	1416	1437	1419	1432	1413	1414	1439		
	1413	1412	1411	1420	1407	1419		1417	1419	1437		
	1414	1424	1420	1416	1405	1420		1437	1441	1439		
	1411	1418	1416	1423	1418	1421		1416	1439	1442		
M [mg/kg]	**1415.8**	**1416.8**	**1416.8**	**1416.8**	**1418.2**	**1419.0**	**1420.7**	**1423.5**	**1429.2**	**1438.5**		**1413.9**
s [mg/kg]	3.656	4.215	3.545	5.076	17.140	3.162	9.866	10.483	11.873	1.975	s_M [mg/kg]	9.95
											$\bar{s}_i$ [mg/kg]	6.70
s_{rel}	0.003	0.003	0.003	0.004	0.012	0.002	0.007	0.007	0.008	0.001		0.0070

Cu-collection
Pb-collection
Ni-collection
NiS-collection
fusion
Te-precipitation
aqua regia

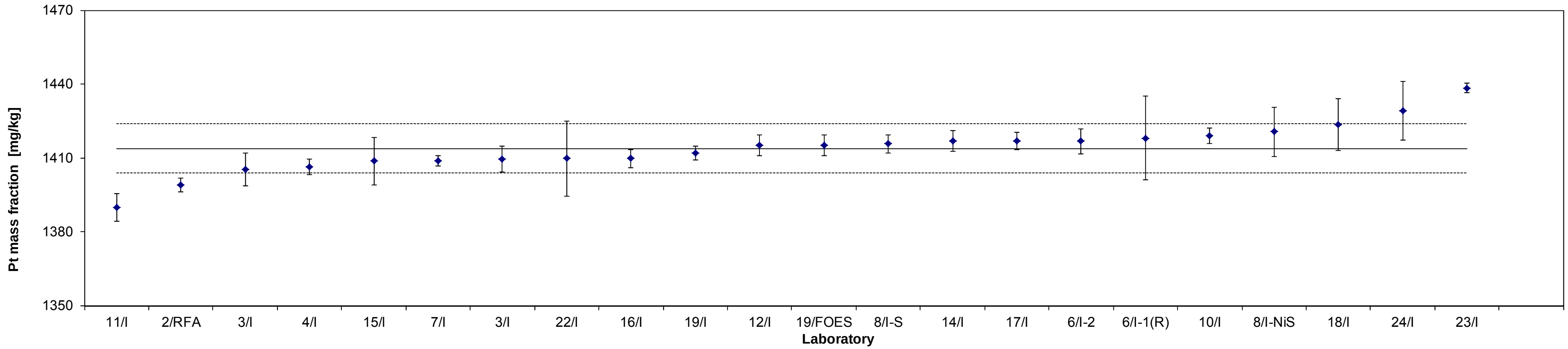

Table 5: Results for platinum

Lab./Meth.	17/I	21/I	10/I	12/I(R)	11/I	2/RFA	15/I	14/I	22/I	7/I	8/I-NiS	8/I-S	6/I-2	3/I	6/I-1(R)	16/I	3/I	20/I	4/I	19/FOES	23/I	24/I	18/I		
M_i [mg/kg]	1570.0	1587	1571	1583	1588.0	1588	1588	1591	1575	1599.0	1600.0	1602.0	1598.0	1598	1585.0	1605	1607.0	1605	1611	1617.0	1610.0	1636.0	1635		n
	1570.0	1559	1577	1574	1589.0	1588	1589	1583	1583	1594.0	1594.0	1600.0	1602.0	1599	1638.0	1601	1603.0	1612	1611	1613.0	1617.0	1603.0	1630		23
	1575.0	1593	1573	1582	1575.0	1585	1591	1592	1594	1594.0	1590.0	1593.0	1593.0	1608	1588.0	1608	1603.0	1618	1610	1613.0	1607.0	1607.0	1615		
	1568.0	1575	1578	1580	1582.0	1587	1592	1579	1596	1594.0		1593.0	1601.0	1607	1594.0	1599	1600.0	1592	1610	1614.0	1614.0	1610.0	1608		
	1572.0	1540	1572	1582	1572.0	1589	1594	1587	1614	1594.0		1599.0	1599.0	1591	1606.0	1605	1597.0	1610	1605		1623.0	1623.0	1625		
	1574.0	1581	1572	1573	1594.0	1582	1568	1590	1604	1592.0		1596.0	1594.0	1592	1601.0	1600	1619.0		1611		1622.0	1626.0	1629		
M [mg/kg]	**1571.5**	**1572.5**	**1573.8**	**1579.0**	**1583.3**	**1586.5**	**1587.0**	**1587.0**	**1594.3**	**1594.5**	**1594.7**	**1597.2**	**1597.8**	**1599.2**	**1602.0**	**1603.0**	**1604.8**	**1607.4**	**1609.7**	**1614.3**	**1615.5**	**1617.5**	**1623.7**		**1596.35**
s [mg/kg]	2.665	19.736	2.927	4.382	8.571	2.588	9.550	5.099	14.038	2.345	5.033	3.764	3.656	7.195	19.298	3.521	7.705	9.819	2.338	1.893	6.411	12.818	10.191	s_M [mg/kg]	14.748
																								$\bar{s}_i$ [mg/kg]	8.189
s_{rel}	0.002	0.013	0.002	0.003	0.005	0.002	0.006	0.003	0.009	0.001	0.003	0.002	0.002	0.004	0.012	0.002	0.005	0.006	0.001	0.001	0.004	0.008	0.006		0.009

Cu-collection Pb-collection Ni-collection

NiS-collection fusion Te-precipitation aqua regia

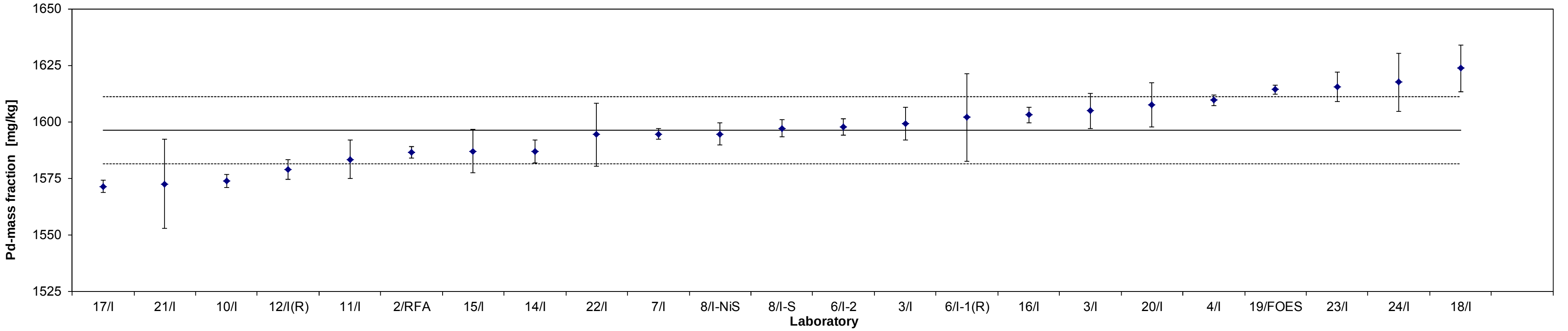

Table 6: Results for palladium

Lab./Meth.	16/I	6/I-2	17/I	6/I-1	5/I	18/I	11/I	10/I	22/I	14/I	3/I	24/I	12/I	19/FOES	15/I	7/I	2/RFA	19/I	21/I	4/I	3/I	8/I-S	8/I-NiS	23/I	6/I-1(R)		
M_i [mg/kg]	204.7	204.1	205.0	210.1	207.8	209.1	209.0	208.9	204.4	209.7	204.9	215.1	210.0	210.0	211	212.0	211.0	212.0	210	212.0	216.9	213.7	213.0	213.3	212.7		*n*
	202.9	206.4	206.0	207.1	207.6	208.1	205.0	207.9	208.0	209.7	208.3	208.3	209.7	211.0	212	211.0	211.0	211.0	213	212.0	209.1	211.2	213.3	215.9	211.1		25
	202.3	203.7	205.0	204.5	207.7	209.4	209.0	207.7	209.4	210.3	215.8	207.5	211.3	209.0	212	212.0	211.0	212.0	208,5	212.0	218.1	213.2	214.7	216.0	216.2		
	202.4	204.9	205.0	207.8	209.1	207.8	208.0	211.1	212.4	210.2	211.9	206.7	209.6	211.0	210	209.0	212.0	210.0	216,7	210.0	215.1	211.8		215.5	216.7		
	204.7	204.0	206.0	208.4	209.3	208.9	212.0	208.8	209.3	209.5	206.9	210.5	210.3		211	212.0	211.0		209,9	213.0	204.2	213.2		214.0	212.6		
	204.3	206.0	206.0	205.8	206.9	207.2	209.0	208.8	211.8	208.8	211.1	211.5	209.9		209	210.0	211.0		213,6	211.0	208.0	212.0		212.9	220.8		
***M* [mg/kg]**	**203.6**	**204.9**	**205.5**	**207.3**	**208.1**	**208.4**	**208.7**	**208.9**	**209.2**	**209.7**	**209.8**	**209.9**	**210.1**	**210.3**	**210.8**	**211.0**	**211.2**	**211.3**	**211.5**	**211.7**	**211.9**	**212.5**	**213.7**	**214.6**	**215.0**		**209.97**
s [mg/kg]	1.141	1.126	0.548	1.971	0.935	0.852	2.251	1.208	2.882	0.540	3.918	3.115	0.622	0.957	1.169	1.265	0.408	0.957	2.121	1.033	5.586	0.985	0.907	1.371	3.584	s_M [mg/kg]	2.778
																										$\bar{s}_i$ [mg/kg]	1.983
s_{rel}	0.006	0.005	0.003	0.010	0.004	0.004	0.011	0.006	0.014	0.003	0.019	0.015	0.003	0.005	0.006	0.006	0.002	0.005	0.010	0.005	0.026	0.005	0.004	0.006	0.017		0.013

Cu-collection Pb-collection Ni-collection

NiS-collection fusion Te-precipitation aqua regia

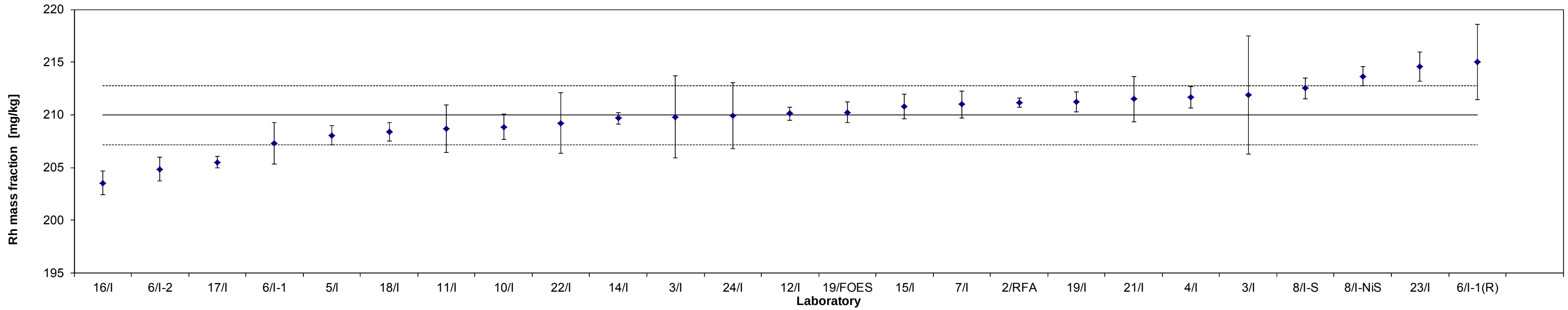

Table 7: Results for rhodium

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.
The statistical evaluation of the data was performed using the software program SoftCRM 1.2.2. [7].
The following results were obtained:

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

Number of data sets	22
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)	Laboratories 11, 23
Nalimov (α = 0.01)	Laboratory 23
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
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal

The outlying results (Labs. 11 and 23) were not removed.

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

Number of data sets	23
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
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal

Tab. 10: Outcome of statistical tests on the results obtained for Rh

Number of data sets	25
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)	---
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
Kolmogorov-Smirnov-Lilliefors Test (α = 0.01)	Distribution: normal
Skewness & Kurtosis Test (α = 0.05)	Distribution: normal
Skewness & Kurtosis Test (α = 0.01)	Distribution: normal

The straggler (Lab. 16) was not removed.

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):

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

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):

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

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
s_M : standard deviation of the laboratories' means

Table 11: Uncertainty calculation

	uncertainty contribution from							
	M	n	s_M	u_{ilc}	u_{prec}	u_{bb}	$u_{combined}$	U
	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Pt	1413.9	22	9.9500	2.1213	2.8700	2.6765	4.4610	8.9220
Pd	1596.3	23	14.7200	3.0693	3.4530	2.4376	5.2236	10.4471
Rh	210.0	25	2.7800	0.5560	0.8500	0.3866	1.0868	2.1736

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

$$U = k \cdot u_{\mathrm{combined}} \qquad (5)$$

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

6 Instructions for use

6.1 Area of application

The main area of application is to check the accuracy 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 effective 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 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] ISO Guide 31, Reference materials -- Contents of certificates, labels and accompanying documentation, 2015

[3] ISO Guide 34, General requirements for the competence of reference material producers, 2009

[4] ISO Guide 35, Reference materials - General and statistical principles for certification. Third edition, 2006

[5] Guidelines for the development and production of BAM Reference Materials, 2016

[6] Technical Guidelines for the Production and Acceptance of a European Reference Material (www.erm-crm.org)

[7] Bonas G, Zervou M, Papaeoannou T, Lees M: Accred Qual Assur (2003) 8:101-107

[8] ISO/IEC Guide 98-3, Uncertainty in measurement – Part 3: Guide to the expression of uncertainty in measurement (GUM:1995), 2008

8 Information on and purchase of the CRM

Information and purchase is done by

Bundesanstalt für Materialforschung und -prüfung (BAM)
Division 1.6: Inorganic Reference Materials
Richard-Willstätter-Str. 11, D-12489 Berlin
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 - 8104 1117
E-mail: sales.crm@bam.de
http://www.bam.de/en/fachthemen/referenzmaterialien/index.htm

Each unit of ERM®-EB504a 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.

9 Appendix

Appendix: Homogeneity testing

Platinum

Summary						
Bottle	*Number*	*Sum*	*Mean*	*Variance*		
25	4	0.51431	0.1285775	4.6889E-07		
28	4	0.51634	0.129085	3.2357E-07		
56	4	0.51584	0.12896	8.1533E-08		
57	4	0.52084	0.13021	6.3087E-07		
130	4	0.51759	0.1293975	1.0643E-07		
198	4	0.52137	0.1303425	7.7369E-07		
281	4	0.51813	0.1295325	3.6358E-08		
315	4	0.51701	0.1292525	1.3064E-06		
321	4	0.51694	0.129235	1.289E-07		
370	4	0.51713	0.1292825	5.9736E-07		
487	4	0.51495	0.1287375	3.2692E-08		
491	4	0.51906	0.129765	1.5996E-06		
521	4	0.51709	0.1292725	5.4023E-07		
583	4	0.51905	0.1297625	2.292E-06		
628	4	0.51928	0.12982	1.7378E-06		
642	4	0.51715	0.1292875	3.1869E-07		
667	4	0.52071	0.1301775	2.0108E-06		
678	4	0.51693	0.1292325	1.2825E-08		
734	4	0.51634	0.129085	2.823E-07		
			0.12942184			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	1.6903E-05	18	9.3904E-07	1.34341553	0.19719847	1.78780884
Within groups	3.9843E-05	57	6.9899E-07			
Total	5.6745E-05	75				
within-sd	0.000836			status:	homogeneous	
effective n	4.00					
s_bb	0.000245					
s_bb_min	0.000181					
u_bb	0.000245	0.244972				
u_bb(rel.)	0.18928154					

Palladium

Summary						
Bottle	*Number*	*Sum*	*Mean*	*Variance*		
25	4	0.65371	0.1634275	1.7204E-06		
28	4	0.65564	0.16391	7.6113E-07		
56	4	0.65379	0.1634475	3.5809E-07		
57	4	0.65747	0.1643675	1.9716E-06		
130	4	0.65716	0.16429	3.2267E-07		
198	4	0.65772	0.16443	1.6877E-06		
281	4	0.65435	0.1635875	2.3829E-07		
315	4	0.65641	0.1641025	4.7136E-07		
321	4	0.65604	0.16401	9.4867E-08		
370	4	0.65297	0.1632425	4.9209E-07		
487	4	0.65461	0.1636525	5.0916E-07		
491	4	0.65604	0.16401	1.2227E-06		
521	4	0.6522	0.16305	9.0721E-06		
583	4	0.65582	0.163955	6.6817E-07		
628	4	0.65705	0.1642625	2.4391E-06		
642	4	0.65649	0.1641225	4.8358E-08		
667	4	0.65905	0.1647625	2.7464E-06		
678	4	0.65523	0.1638075	3.0123E-07		
734	4	0.65423	0.1635575	2.6429E-07		
			0.16389447			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	1.4047E-05	18	7.8038E-07	0.58398495	0.89657972	1.78780884
Within groups	7.6169E-05	57	1.3363E-06			
Total	9.0216E-05	75				
within-sd	0.001156			status:	homogeneous	
effective n	4.00					
s_bb	0					
s_bb_min	0.00025					
u_bb	0.00025	0.250156				
u_bb(rel.)	0.15263261					

Rhodium

Summary						
Bottle	*Number*	*Sum*	*Mean*	*Variance*		
25	4	0.05556	0.01389	2.1133E-08		
28	4	0.05577	0.0139425	1.0425E-08		
56	4	0.05553	0.0138825	6.7583E-09		
57	4	0.05599	0.0139975	5.8917E-09		
130	4	0.05594	0.013985	1.3667E-09		
198	4	0.05638	0.014095	2.91E-08		
281	4	0.05597	0.0139925	2.5583E-09		
315	4	0.05575	0.0139375	5.2917E-09		
321	4	0.05606	0.014015	1.9E-09		
370	4	0.05573	0.0139325	1.2292E-08		
487	4	0.05566	0.013915	2.9667E-09		
491	4	0.056	0.014	2.9933E-08		
521	4	0.05563	0.0139075	5.6158E-08		
583	4	0.05607	0.0140175	4.825E-09		
628	4	0.0562	0.01405	1.38E-08		
642	4	0.0557	0.013925	8.1E-09		
667	4	0.05626	0.014065	4.6433E-08		
678	4	0.05584	0.01396	4.4E-09		
734	4	0.05592	0.01398	5E-09		
			0.01397316			
ANOVA						
Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	2.5584E-07	18	1.4213E-08	1.00641822	0.46684639	1.78780884
Within groups	8.05E-07	57	1.4123E-08			
Total	1.0608E-06	75				
within-sd	0.000119			status:	homogeneous	
effective n	4.00					
s_bb	4.76E-06					
s_bb_min	2.57E-05					
u_bb	2.57E-05	0.025717				
u_bb(rel.)	0.1840453					