



Certification Report
for the
Reference Materials
ERM-AE140 and ERM-AE141

**Pd and Pt single spikes certified for their Pd and Pt mass fraction
and isotopic composition**

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1. Abstract

Isotope dilution mass spectrometry often is applied for the quantification of platinum group elements in environmental and geological samples. In most cases, however, certified spike solutions offering complete uncertainty statements and SI-traceability are missing.

This report describes the production and certification of two isotope reference materials, ERM-AE140 and ERM-AE141, serving as calibrated spike solutions for IDMS based quantification of Pd and Pt, respectively. Both materials were produced by dissolving highly enriched isotopes ^{106}Pd and ^{194}Pt and determining the mass fraction of ^{106}Pd and ^{194}Pt in the final solution by reverse IDMS. Two independent back-spikes were produced for each material from high purity Pd and Pt. Characterization measurements were carried out by MC-ICPMS.

For ERM-AE140 the certified mass fractions are $w(^{106}\text{Pd}) = 20.24(5)$ mg/kg and $w(\text{Pd}) = 20.54(5)$ mg/kg. For ERM-AE141 the certified mass fractions are $w(^{194}\text{Pt}) = 18.18(11)$ mg/kg and $w(\text{Pt}) = 19.90(12)$ mg/kg. These values are traceable to the International System of Units (SI) in the shortest possible way.

2. Introduction

The quantification of platinum group elements (PGE) often is carried out by using isotope dilution mass spectrometry (IDMS) either for reference material characterization or for environmental and/or geochemical research. The main reasons for the application of IDMS are the required accuracy and the low PGE mass fractions in the sample. A crucial point in IDMS is, however, the availability of certified spikes. Unfortunately, no such certified spike solutions are available yet for PGE.

So-called spikes are solutions of isotopically enriched elements, which are 'spiked' to samples thus enabling an accurate quantification of element concentrations. Based on its proven records, especially in reference material certification, IDMS is considered as one of the most powerful and most accurate methods for determining amounts of substance (Vogl 2007). Contrary to other calibration approaches, IDMS does not directly suffer from long-time changes or drifts in instrument sensitivity. Moreover, provided isotopic exchange between the sample and spike is ensured, losses of analyte do not affect the analytical result. Both advantages are based on the fact that IDMS only requires isotope ratio measurements and isotope ratios are largely unaffected by instrumental drift, setup or by matrix, unless an isobaric interference is present (Vogl and Pritzkow 2010).

To fill this gap two single PGE spikes, one ^{106}Pd and one ^{194}Pt spike, have been produced and characterized. The selection of the isotopes, the production of the solutions and the ampoulation will be described in this report. Details on the characterization of these spike solutions by reverse IDMS using a primary assay for Pd and Pt will be given. The whole certification procedure for becoming certified reference materials under the ERM® label is described in detail.

3. Experimental Section

3.1. Principal Procedure

Enriched stable isotopes of various elements can be purchased in solid form from different providers such as Oak Ridge National Laboratories (ORNL, Tennessee, USA) or Isoflex (Moscow, Russia). When dissolving such enriched isotopes, however, no traceable mass fraction or isotopic composition of the respective element can be obtained, because the purity, the enrichment and sometimes the stoichiometry of the provided compound is not accurately known (Vogl *et al.* 2012). In most cases uncertainty and traceability statements are missing.

Therefore, the mass fraction and the isotopic composition of the respective element have to be determined by a so-called reverse IDMS (eqn. 2). Here, the spike is mixed with a primary assay with known mass fraction of the element, a so-called back-spike. The isotope ratio in the spike/back-spike blend is determined by mass spectrometry and the mass fraction of the spike, w_y , can be calculated by solving the IDMS equation for w_y . In double IDMS the IDMS (eqn. 1) and the reverse IDMS (eqn. 2) equation is combined to one equation (eqn. 3). More details on this can be obtained from Vogl and Pritzkow 2010.

IDMS equation:
$$w_x = w_{y,b} \cdot \frac{M_x \cdot m_y}{M_b \cdot m_x \cdot a_{x,b}} \cdot \frac{(R_y - R_{xy})}{(R_{xy} - R_x)}$$
 eqn. 1

Reverse IDMS equation:
$$w_{y,b} = \frac{a_{z,b} \cdot M_b \cdot m_z}{M_z \cdot m_{y'}} \cdot w_z \cdot \frac{(R_{zy} - R_z)}{(R_y - R_{zy})}$$
 eqn. 2

Double IDMS equation¹:
$$w_x = w_z \cdot \frac{m_y \cdot m_z}{m_x \cdot m_{y'}} \cdot \frac{(R_y - R_{xy})}{(R_{xy} - R_x)} \cdot \frac{(R_{zy} - R_z)}{(R_y - R_{zy})}$$
 eqn. 3

For explanation of the variables see the Appendix with the exemplary uncertainty budgets.

3.2. Selection of isotopes

Quantification by IDMS requires two isotopes preferably free from any interference, where one of them represents the major abundant natural isotope and the other represents the enriched spike isotope. For elements with only two isotopes no selections can be made, but for elements with three and more isotopes their suitability for IDMS usually varies significantly and the selection of the two isotopes being used is of major importance. For the selection of isotopes the following points need to be considered:

- Isotopes should be as far as possible free from interferences
- Natural reference isotope should be the major abundant isotope, simply to obtain highest signal intensities
- Spike isotope should be preferably one of the least abundant isotopes in nature
- Spike isotope should be preferably close in mass to the natural reference isotope
- Costs for the enriched isotopes have to be considered

		Cd 106 1.25 %	Cd 107	Cd 108 0.89 %	Cd 109	Cd 110 12.49 %	Cd 111 12.80 %	Cd 112 24.13 %
	Ag 104	Ag 105	Ag 106	Ag 107 51.84	Ag 108	Ag 109 48.16 %	Ag 110	Ag 111
Pd 102 1.02 %	Pd 103	Pd 104 11.14 %	Pd 105 22.33 %	Pd 106 27.33 %	Pd 107	Pd 108 26.46 %	Pd 109	Pd 110 11.72 %
Rh 101	Rh 102	Rh 103 100 %	Rh 104	Rh 105	Rh 106	Rh 107	Rh 108	
Ru 100 12.60 %	Ru 101 17.06 %	Ru 102 31.55 %	Ru 103	Ru 104 18.62 %	Ru 105	Ru 106		

Fig. 1: Zoom of the nuclide chart to show the Pd isotopes together with isobaric interferences

¹ Double IDMS equation, when no isotopic variation between sample and back-spike occurs.

Palladium:

All Pd isotopes show isobaric interferences, excepting ^{105}Pd (Fig. 1). The isotope abundance is comparable to those of ^{106}Pd and ^{108}Pd . Therefore, ^{105}Pd is selected as the natural reference isotope. The low abundant isotopes ^{102}Pd and ^{104}Pd are interfered by Ru, which often appears in the samples together with other PGEs. Additionally, ^{102}Pd costs 25 times as much as ^{106}Pd and ^{104}Pd still costs twice as much as ^{106}Pd . So ^{102}Pd and ^{104}Pd are not suitable as spike isotopes. ^{106}Pd , ^{108}Pd and ^{110}Pd are all interfered by Cd isotopes, whereby ^{106}Pd and ^{108}Pd are interfered by the least abundant Cd isotopes which can be easily separated during sample preparation. ^{106}Pd is closest in mass to the natural reference isotope ^{105}Pd and so ^{106}Pd is selected as the spike isotope.

Platinum:

^{190}Pt and ^{192}Pt are interfered by Os isotopes, while ^{196}Pt and ^{198}Pt are interfered by Hg isotopes (Fig. 2). The remaining isotopes ^{194}Pt and ^{195}Pt are equally high abundant. ^{195}Pt is selected as the natural reference isotope and ^{194}Pt is selected as the spike isotope.

The figure shows a zoomed-in portion of a nuclide chart. The central focus is on the Platinum (Pt) isotopes, which are arranged in a diagonal line from top-left to bottom-right. The isotopes shown are Pt 190, Pt 191, Pt 192, Pt 193, Pt 194, Pt 195, Pt 196, Pt 197, and Pt 198. Each Pt isotope cell contains its mass number, relative abundance (as a percentage), and half-life (where applicable). Pt 190 is highlighted in yellow. Surrounding the Pt isotopes are other elements: Hg (194-200), Au (192-199), Ir (189-196), and Os (188-194). These elements are shown in various colors (blue, red, black) to represent different categories or states. The background is black, and the text is white or yellow for emphasis.

			Hg 194	Hg 195	Hg 196 0.15 %	Hg 197	Hg 198 9.97 %	Hg 199 16.87 %	Hg 200 23.10 %
		Au 192	Au 193	Au 194	Au 195	Au 196	Au 197 100 %	Au 198	Au 199
Pt 190 0.014 % 6.5·10 ¹¹ a α : 100%	Pt 191 2.83 d	Pt 192 0.78 %	Pt 193 50 a	Pt 194 32.97 %	Pt 195 33.83 %	Pt 196 25.24 %	Pt 197 19.89 h	Pt 198 7.16 %	
	Ir 189	Ir 190	Ir 191 37.3 %	Ir 192	Ir 193 62.7 %	Ir 194	Ir 195	Ir 196	
	Os 188 13.29 %	Os 189 16.21 %	Os 190 26.36 %	Os 191	Os 192 40.93 %	Os 193	Os 194		

Fig. 2: Zoom of the nuclide chart to show the Pt isotopes together with isobaric interferences

3.3. Chemicals, Reagents and Labware

All dilutions and manipulations have been carried out by using ultrapure water obtained from a Milli-Q Advantage A10 water purification system. Nitric acid and hydrochloric have been purchased p.a. grade and have been purified by twofold subboiling distillation (1st stage quartz still, 2nd stage Teflon still). Hydrogen peroxide was purchased suprapure grade. Only quartz, PTFE, PFA or PP labware have been used in this project.

For the preparation of the CRMs isotopically enriched Pd and isotopically enriched Pt have been used. The primary assays used as back-spikes have been prepared from high-purity Pd and Pt. According to the BAM quality standard for IDMS two high-purity materials from different sources have been used to prepare two completely independent back-spike solutions for each element. The details of the starting materials for spikes and back-spikes are displayed in Table 1.

Table 1: Details of the starting materials used for the preparation of the Pd and Pt spike and back-spike solutions

Element	Starting material	Purity in g/g	Supplier	Type of material	Selected isotope ²	Isotope amount fraction
Pd	metal	> 0.9999	ORNL Batch 191391	enriched	¹⁰⁶ Pd	0.9848
Pt	metal	> 0.9999	ORNL Batch 235401	enriched	¹⁹⁴ Pt	0.9146
Pd	metal	> 0.999	Heraeus	natural	¹⁰⁵ Pd	0.2733 (3)
Pd	metal	> 0.9999	Alfa Aesar Lot: NM71723	natural	¹⁰⁵ Pd	0.2733 (3)
Pt	metal	> 0.999	Heraeus	natural	¹⁹⁵ Pt	0.3378 (24)
Pt	metal	> 0.9999	Alfa Aesar Lot: NM60298	natural	¹⁹⁵ Pt	0.3378 (24)

3.4. Gravimetric Determinations

The preparation of solutions has been carried out under full gravimetric control. To enable this, a few practical aspects have to be considered, as the weighing process is influenced by different effects such as buoyancy, electrostatic effects and evaporation. Moisture content of compounds has to be considered separately so it occurs. Other stability issues do not apply here.

Buoyancy or more exactly air buoyancy expresses the difference in air buoyancy between the object to be weighed and the built-in reference of the balance, which causes a bias. The effect is well-known and corrections are applied according to eqn. 4 whenever reference weighing is performed, e.g. for RM characterisation (Kehl *et al.* 2000, Reichmuth *et al.* 2004). In Eqn. 2 m_{x_obs} is the reading of the balance, ρ_{air} , ρ_{bal} and ρ_x are the densities of the air, the built-in weights of the balance and of the sample. For objects with a density of around $10^3 \text{ kg}\cdot\text{m}^{-3}$ (e.g. water) the resulting bias is in the order of 10^{-3} relative and should be corrected for (Pozivil *et al.* 2006).

$$m_x = m_{x_obs} \cdot \frac{\left(1 - \frac{\rho_{air}}{\rho_{bal}}\right)}{\left(1 - \frac{\rho_{air}}{\rho_x}\right)} \quad \text{eqn. 4}$$

Electrostatic charging of plastic containers cannot be corrected for, but it may be reduced or even avoided by specific tools compensating the electrostatic charge. This can be accomplished best by blowing ionized nitrogen onto the container's surface with a ring ionizer combined with a blow-out gun (Type RI 65 P 7187 500, Haug GmbH, Leinfelden-Echterdingen, Germany). This device cannot be used when powders have to be weighed on open plastic trays. Logically, for any handling only cotton gloves should be used, because plastic gloves would produce new electrostatic charges. Gloves in

² For spikes the enriched isotope is listed, for back-spikes the selected natural isotope is listed. Data from accompanying documents or IUPAC tables with expanded uncertainties in brackets (Berglund & Wieser 2011)

general are required to avoid fingerprints on the container, which could easily make up a mass bias of a tenth of a mg.

The weighing of solutions into a container seems to be an easy task. However, performing it on a reference level some specific aspects have to be considered. It is advisable to fill a polypropylene syringe with the solution and place a pipette tip on the tip of the syringe to reduce the orifice and a sealed pipette tip to close the reduced orifice. Then the filled syringe is being weighed, the desired mass is being dosed into the container and the syringe is being weighed back. This gives the exact mass of the solution which has been released. When pouring the solution into the container and weighing the mass difference in the container, first the relation of container mass to solution mass is less advantageous (weighing a mouse on an elephant's back) and second during the pouring step solvent will evaporate, which will not be considered. The syringe approach considers this, because the released mass is being determined. Consequently, all prepared solutions have to be monitored for their mass during storage, because from each bottle the solvent (water or dilute acid) will evaporate in small amounts and will change the mass fraction of the solution. Monitoring the mass of the solution can be used to correct for this.

All solutions within this project have been prepared considering these facts. Complete uncertainty budgets were set up for each weighing/solution. Exemplary uncertainty budgets for Pd and Pt back-spike solutions are listed in Tables 14 and 15 of the Appendix.

3.5. Preparation of the candidate reference materials and the back-spike solutions

The enriched materials ^{106}Pd and ^{194}Pt and the high-purity materials with natural isotopic composition listed in Table 1 were used to prepare spike and back-spike stock solutions as follows:

^{106}Pd and ^{194}Pt were dissolved in 2 mL aqua regia at a temperature of 60 °C. High-purity Pt was etched with $\text{HCl}:\text{H}_2\text{O}_2$ (vol. ratio 4:1) for 1 min, rinsed 5 times with ultrapure water and dried at a temperature of 105°C before dissolution in 2 ml aqua regia at a temperature of 60 °C. High-purity Pd was etched with HCl 6 mol/L for 1 min, rinsed 5 times with ultrapure water and dried at a temperature of 105 °C before dissolution in 2 mL aqua regia at a temperature of 60 °C.

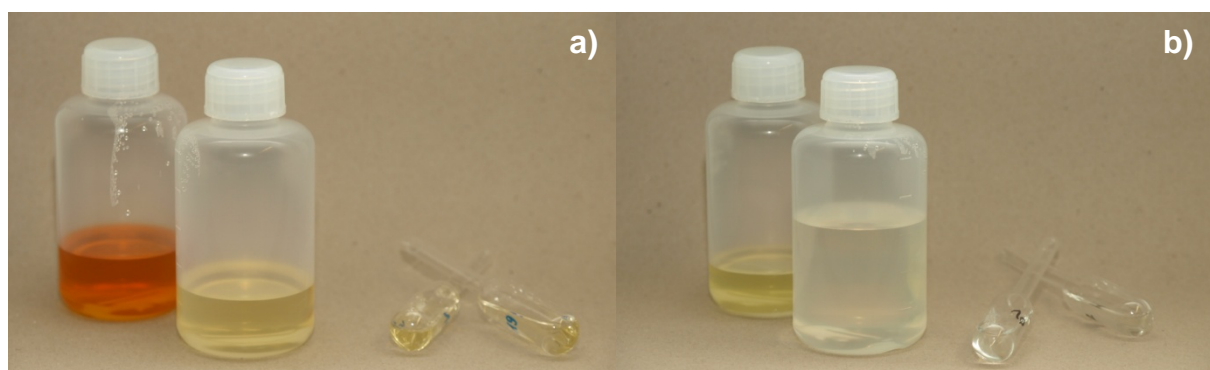


Fig. 3: Parent solutions, final solutions and flame-sealed ampoules of the candidate materials ERM-AE140 (a) and -AE141 (b)

The exact masses of Pd, Pt and the acid solutions used for the preparation together with their corresponding standard uncertainties are displayed in Table 2. The mixing process has been carried out under full gravimetric control as described above in the section “Gravimetric Determination”. Subsequently ultrapure water and hydrochloric acid has been added to reach Pd and Pt mass fractions of approximately 200 mg/kg in HCl 20%. The exact mass fractions of the stock solutions and of the dilutions are also displayed in Table 2. These stock solutions have been filled in pre-cleaned PFA-bottles. The bottles have been closed tightly, labelled, sealed in plastic bags and stored in a refrigerator at (5 ± 3) °C.

The diluted solutions of the spikes with mass fractions of approximately 20 mg/kg, were pumped into quartz ampoules (see Fig. 3) by using a peristaltic pump. The pump tubes were conditioned by pumping a separate portion of the spike solutions for 30 min. The filling process has been tested beforehand gravimetrically to guarantee a minimum filling quantity of 7 mL. The quartz ampoules were cooled down in an ice bath before flame-sealing to avoid any loss by evaporation of solvent. Then the ampoules were cooled down to room temperature, labelled and sealed in polyethylene bags. This way 116 ampoules of Pd spike ERM-AE140 and 115 ampoules of Pt spike ERM-AE141 were produced.

Table 2: Masses of Pd, Pt and total solution obtained during the preparation of the solutions together with the Pd and Pt mass fractions resulting from the gravimetric data; combined standard uncertainties are given in brackets

Material	Starting material	Mass in g		Mass fraction	
		Starting material	Solution	HCl in g/g	Pd in mg/kg
¹⁰⁶ Pd stock	¹⁰⁶ Pd	0.0383636(28)	196.83254(15)	0.20	194.8759(97)
ERM-AE140	¹⁰⁶ Pd stock	105.52340(63)	1002.06480(75)	0.20	20.5216(10)
Pd RS1	Pd, Heraeus	0.0603996(27)	271.8333(11)	0.20	221.855(64)
Pd RS2	Pd, Alfa Aesar	0.0616930(25)	247.8365(11)	0.20	248.6643(67)

Material	Starting material	Mass in g		Mass fraction	
		Starting material	Solution	HCl in g/g	Pt in mg/kg
¹⁹⁴ Pt stock	¹⁹⁴ Pt	0.0322401(28)	162.98730(15)	0.20	197.692(11)
ERM-AE141	¹⁹⁴ Pt stock	101.93560(89)	1013.6332(13)	0.20	19.8808(11)
Pt RS3	Pt, Heraeus	0.0830582(46)	254.1993(11)	0.20	326.373(21)
Pt RS4	Pt, Alfa Aesar	0.0530913(41)	248.6751(11)	0.20	213.2689(84)

Using the isotope enrichment given by ORNL the nominal, gravimetrically based mass fraction of the spike isotope in the candidate materials ERM-AE140 and -AE141 calculates $w(^{106}\text{Pd}) = 20.2047(84)$ µg/g solution and $w(^{194}\text{Pt}) = 18.173(19)$ µg/g solution, respectively, with their combined standard uncertainties given in brackets.

3.6. Homogeneity

The here described reference materials have been produced solely by dissolution of pure elements and subsequent dilution. Such dilute solutions of one species of the target element in principle are homogenous for their mass fractions and also for the isotopic composition. Therefore, the materials are assumed as homogeneous. Contamination issues can be neglected, because laboratory blank levels for Pd and Pt are in the low pg range as reported recently (Vogl *et al.* 2014).

The characterization which has been carried out on three units spread over the whole filling sequence proves this, without any hint for inhomogeneity (see chapter characterization). An uncertainty contribution for inhomogeneity therefore has not been added to the overall uncertainty.

3.7. Stability

Long-term experience over two decades with the BAM spike and back-spike solutions as well as work carried out at the *Institute for Reference Materials and Measurements* (IRMM, Geel, Belgium) and the *National Institute of Standards and Technology* (NIST, Gaithersburg, USA) demonstrate that acidified aqueous solutions containing one element with mass fractions in the mg/kg range can be stored under conditions, whereby the mass fraction and the isotopic composition is not altered.

The only factors which affect the stability of such solutions are contamination, adsorption on container walls, evaporation of solvent and redox-reactions. Contamination until first use at the customer's lab is excluded by using pre-cleaned and flame-sealed quartz ampoules. The pure quartz material of the ampoules also prevents adsorption on container walls, especially in 20 % HCl. Evaporation is prevented by flame-sealing of the ampoules. Redox reactions cannot take place as no oxidation and/or reducing agents are present. Therefore, such solutions are assumed to be stable.

For NIST SRM 3138, an ampouled Pd solution with ≈ 10 mg/g Pd in ≈ 10 % HCl, a shelf-life of 10 years is given. For NIST SRM 3140, an ampouled Pt solution with ≈ 10 mg/g Pt in ≈ 10 % HCl, the current shelf-life is 17 years. BAM spike and back-spike solutions, which are stored in PFA bottles and which are evaporation corrected by continuous gravimetric control, are stable since 1995. The ^{198}Pt spike and the Pt back-spike solution are stable since their production in 2005.

For ERM-AE140 and -AE141 no uncertainty for instability is added due to the above described reasons. The minimum shelf-life is 10 years counted from the date of certification.

3.8. Characterization

3.8.1. Mass spectrometric measurements

The characterization of the Pd and Pt spike is carried out by applying reverse IDMS as described in chapter 3.1 "Principal Procedure". Three ampoules were used for Pd and Pt each to prepare 4 blends per ampoule, two of each with a different back-spike solution. All Pd and Pt isotope ratios have been determined by MC-ICPMS using the Neptune instrument (Thermo Fisher Scientific, Bremen, DE) at PTB, Braunschweig in standard configuration (see Table 3). The measurements were carried out in

blocks of six sample measurements (back-spike, isotope CRM (Pt), blends, spike). Each block was separated by two measurements of the second back-spike (Pd RS2, Pt RS4), which was used for drift monitoring. Additionally, the sequences were set up such, that all blends were measured a second time after the first series was finished. The back-spike measurements showed relative standard deviations of around 0.016 % for $^{105}\text{Pd}/^{106}\text{Pd}$ and 0.021 % for $^{194}\text{Pt}/^{195}\text{Pt}$ over 27 h and 25 h, respectively. This was regarded insignificant and therefore no drift correction was carried out. The repeated blend measurements agreed within < 0.01 % for Pd and < 0.02 % for Pt, given as half of the difference between two measurements and expressed in percent.

Table 3: Configuration and measurement parameters of the Neptune MC-ICPMS, PTB, Braunschweig

Parameter	Value description
Autosampler	Cetac ASX 100
Aspiration mode	Self-aspirating
Nebulizer	PFA 100 $\mu\text{L}/\text{min}$
Spray chamber	Cyclonic spray chamber
Cones	Ni sampler and skimmer (H)
Cool gas flow rate	16 L/min
Auxiliary gas flow rate	0.75 L/min
Sample gas flow rate	1.00 – 1.15 L/min
Guard electrode	On
Mass resolution mode	Low Resolution ($M/\Delta M \approx 300$)
RF power	1200 W
Integration time	16 s
Blocks / cycles	1 / 28
Total measurement time	Pt: 7.6 min, Pd: 8.7 min
Total intensity for 200 ng/g	Pt: ~ 8.5 V; Pd: ~ 8.8 V
Intensity for blank (2 % HCl)	$^{195}\text{Pt} \sim 0.2 \text{ mV}$; $^{105}\text{Pd} \sim 0.2 \text{ mV}$
Repeatability, long term, isotope ratio of back-spike (1 RSD)	0.016 % for $^{105}\text{Pd}/^{106}\text{Pd}$ (n = 14, 27 h) 0.021 % for $^{194}\text{Pt}/^{195}\text{Pt}$ (n = 16, 25 h)
Repeatability, single measurement, isotope ratio of back-spike (1 RSD)	< 0.005 % for $^{105}\text{Pd}/^{106}\text{Pd}$ < 0.005 % for $^{195}\text{Pt}/^{194}\text{Pt}$

Interferences in general lead to biased results. Therefore, it has to be verified that they only occur below an insignificant level, otherwise corrections have to be made. The main interferences in ICPMS for Pd and Pt have been published before (Meisel *et al.* 2003, Vanhaecke *et al.* 2002). For Pd isobaric interferences (^{102}Ru , ^{104}Ru , ^{106}Cd) as well as molecular interferences (Cu-, Ga-, Zn-argides; Sr-, Rb-, Y-, Zr-oxides) can occur, which may affect the main isotope ratio $^{105}\text{Pd}/^{106}\text{Pd}$. For Pt the situation is slightly different: Although isobaric (^{190}Os , ^{192}Os , ^{196}Hg) and molecular interferences (Gd-, Sm-, Tb-argides and -chlorides; Hf-, Yb-oxides) can occur, the main isotope ratio $^{195}\text{Pt}/^{194}\text{Pt}$ is not affected.

The level of interfering elements was checked by high resolution ICPMS in spike and back-spike solutions at a mass fraction of ≈ 200 ng/g Pd or Pt, respectively. The elements causing molecular interferences such as Cu, Zn, Sm and Gd were found at mass fractions below 0.05 ng/g in these solutions. With typical oxide, chloride and argide formation rates below 0.1 %, 0.01 % and 0.005 %, respectively (Vogl *et al.* 2014), the resulting contribution of molecular interferences to the Pd and Pt signal is $< 5 \cdot 10^{-7}$ relative. Elements causing isobaric interferences such as Ru, Cd, Os and Hg were found at mass fractions below 0.01 ng/g in the spike and back-spike solutions (≈ 200 ng/g Pd or Pt). Nevertheless, these elements were continuously monitored throughout all measurements (see cup configuration in Table 4) and were found at or below the instrumental background.

A specific case of interferences are hydride molecular ions, which are caused by the analyte isotopes itself and lead to an interference on the neighbour mass. For highly precise measurements hydride interferences may affect the isotope ratio determination and therefore have to be checked for. This was carried out directly at the Neptune ICPMS with a 200 ng/g Pt solution. The resulting intensity on ^{198}Pt was ≈ 0.64 V and on m/z 199 an intensity of $1.8 \cdot 10^{-5}$ V was obtained. Considering that beside $^{198}\text{Pt}^1\text{H}$ also ^{199}Hg is present, the hydride formation rate was calculated as $< 2.85 \cdot 10^{-5}$. In the case of Pd the hydride formation rate could not be calculated, because on m/z 107 and 109 a sufficiently high Ag intensity of 11500 cps could be detected, which disturbs the hydride interference. Therefore, the same hydride formation rate as for Pt is assumed. This hydride formation rate is smaller than the long-term repeatability and even smaller than the repeatability within one measurement and therefore can be neglected.

Table 4: Faraday cup alignment of the Neptune MC-ICPMS, PTB, Braunschweig, for Pd and Pt measurements with nominal isotopes

Cup	L4	L3	L2	L1	C	H1	H2	H3	H4
Pd	^{101}Ru	^{102}Pd	^{104}Pd	^{105}Pd	^{106}Pd	n/a	^{108}Pd	^{110}Pd	^{111}Cd
Pt	Not used	^{190}Pt	^{192}Pt	n/a	^{194}Pt	^{195}Pt	^{196}Pt	^{198}Pt	^{199}Hg

3.8.2. Isotopic composition of the spikes

Palladium

For Palladium no isotope reference material is available and therefore the correction factor for mass discrimination has to be determined with a natural Palladium sample and by using the IUPAC tabulated data (Berglund and Wieser 2011).

Three ampoules have been measured three times each giving a standard deviation for each ampoule of < 0.2 % for $n(^{105}\text{Pd})/n(^{106}\text{Pd})$, the mean values of the three ampoules is 0.087 % (Table 5). The mean values for the observed Pd isotope ratios and the corrected Pd isotope ratios in ERM-AE140 are displayed in Table 5. No difference between single ampoules could be observed. The standard deviations of the isotope ratios below 0.005 are dominated by the very low signal intensities of the low abundant isotopes. The combined uncertainties (for exemplary budget see Appendix) of the isotope ratios are dominated by the uncertainties of IUPAC data and the repeatability of the observed isotope ratios.

Table 5: Observed Pd isotope ratios with their relative standard deviations and mass discrimination corrected Pd isotope ratios with their combined uncertainties for ERM-AE140

Isotope ratio	Observed isotope ratios in V/V		Corrected isotope ratios in mol/mol	
	Value	s_{rel} in %	Value	u_c
$n(^{102}\text{Pd})/n(^{106}\text{Pd})$	0.00007328	0.52	0.000079140	0.000000528
$n(^{104}\text{Pd})/n(^{106}\text{Pd})$	0.00120002	0.26	0.00124694	0.00000530
$n(^{105}\text{Pd})/n(^{106}\text{Pd})$	0.00739410	0.087	0.0075177	0.0000152
$n(^{108}\text{Pd})/n(^{106}\text{Pd})$	0.00497644	0.17	0.0047854	0.0000112
$n(^{110}\text{Pd})/n(^{106}\text{Pd})$	0.00124372	0.31	0.00115585	0.00000546

From the corrected isotope ratios the isotope amount fractions of Pd were calculated and therefrom the molar mass. The resulting values with their associated combined uncertainties are displayed in Table 6 and show the high isotopic enrichment of this spike. The determined isotope abundance of ^{106}Pd agrees well with the data provided by ORNL (Table 1) within their expanded uncertainties.

Table 6: Isotope amount fractions and molar mass for Pd in ERM-AE140 with their associated combined uncertainties

Quantity	Value	u_c	$u_{c,rel}$ in %
$n(^{102}\text{Pd})/n(\text{Pd})$	0.000077987	0.000000521	0.67
$n(^{104}\text{Pd})/n(\text{Pd})$	0.00122877	0.00000521	0.42
$n(^{105}\text{Pd})/n(\text{Pd})$	0.0074082	0.0000149	0.20
$n(^{106}\text{Pd})/n(\text{Pd})$	0.9854304	0.0000207	0.0021
$n(^{108}\text{Pd})/n(\text{Pd})$	0.0047157	0.0000110	0.23
$n(^{110}\text{Pd})/n(\text{Pd})$	0.00113901	0.00000538	0.47
$M(\text{Pd})$ in g/mol	105.9073123	0.0000373	0.000035

Platinum

The isotopic composition of ERM-AE141, the enriched ^{194}Pt spike, was determined by using the isotope reference material IRMM-010 for correcting mass discrimination. It was observed that the K -factors for all isotope ratios were not consistent. When calculating mass discrimination coefficients, ϵ_{lin} , only those for $^{195}\text{Pt}/^{194}\text{Pt}$ and $^{196}\text{Pt}/^{194}\text{Pt}$ agreed with values of ≈ 0.01 . For $^{198}\text{Pt}/^{194}\text{Pt}$ an ϵ_{lin} value ≈ 0.006 was obtained and for $^{190}\text{Pt}/^{194}\text{Pt}$ and $^{192}\text{Pt}/^{194}\text{Pt}$ ϵ_{lin} values of ≈ -0.01 and ≈ -0.0007 were obtained. This bias is presumably due to the inaccuracy of the quadrupole ICPMS technique which has been used for the certification measurements especially for the low abundant isotopes. Therefore, the ratios $^{195}\text{Pt}/^{194}\text{Pt}$ and $^{196}\text{Pt}/^{194}\text{Pt}$ are assumed to be true within the given uncertainty and they are

used to calculate the *K*-factors also for the other isotope ratios via the exponential law. More details on the fractionation laws can be obtained from Pritzkow *et al.* 2007.

Table 7: Observed Pt isotope ratios with their relative standard deviations and mass discrimination corrected Pt isotope ratios with their combined uncertainties for ERM-AE141

Isotope ratio	Observed isotope ratios in V/V		Corrected isotope ratios in mol/mol	
	Value	s_{rel} in %	Value	u_c
$n(^{190}\text{Pt})/n(^{194}\text{Pt})$	0.000001143	27.27	0.000001184	0.000000280
$n(^{192}\text{Pt})/n(^{194}\text{Pt})$	0.000335753	0.117	0.00034172	0.00000193
$n(^{195}\text{Pt})/n(^{194}\text{Pt})$	0.074608490	0.0033	0.073884	0.000359
$n(^{196}\text{Pt})/n(^{194}\text{Pt})$	0.017848200	0.0090	0.017493	0.000107
$n(^{198}\text{Pt})/n(^{194}\text{Pt})$	0.002074075	0.0234	0.0020221	0.0000146

Three ampoules have been measured three times each giving a standard deviation for each ampoule of 0.009 % for $n(^{195}\text{Pt})/n(^{194}\text{Pt})$, the mean values of the three ampoules is 0.003 % (Table 7). All observed Pt isotope ratios and the corrected Pt isotope ratios in ERM-AE141 are displayed in Table 7. No difference between single ampoules could be observed. The standard deviations of the isotope ratios below 0.01 are dominated by the very low signal intensities of the low abundant isotopes. The combined uncertainties (for exemplary budget see Appendix) of the isotope ratios are dominated by the uncertainties of the isotope reference material IRMM-010, which was used for correcting the mass discrimination, excepting the ratio $n(^{190}\text{Pt})/n(^{194}\text{Pt})$, where the repeatability of the isotope ratio determination contributes most.

Table 8: Isotope amount fractions and molar mass for Pt in ERM-AE141 with their associated combined uncertainties

Quantity	Value	u_c	$u_{c,rel}$ in %
$n(^{190}\text{Pt})/n(\text{Pt})$	0.000001083	0.000000256	24
$n(^{192}\text{Pt})/n(\text{Pt})$	0.00031243	0.00000188	0.60
$n(^{194}\text{Pt})/n(\text{Pt})$	0.914292	0.000367	0.040
$n(^{195}\text{Pt})/n(\text{Pt})$	0.067552	0.000302	0.45
$n(^{196}\text{Pt})/n(\text{Pt})$	0.0159939	0.0000928	0.58
$n(^{198}\text{Pt})/n(\text{Pt})$	0.0018488	0.0000130	0.70
$M(\text{Pt})$ in g/mol	194.069174	0.000467	0.00024

From the corrected isotope ratios the isotope amount fractions of Pt were calculated and therefrom the molar mass. The resulting values with their associated combined uncertainties are displayed in

Table 8. The determined isotope abundance of ^{194}Pt agrees well with the data provided by ORNL (Table 1) within their expanded uncertainties.

3.8.3. ^{106}Pd and ^{194}Pt mass fractions in ERM-AE140 and -AE141

The mass fractions of ^{106}Pd and ^{194}Pt in ERM-AE140 and -AE141 were determined by reverse IDMS as outlined in chapter 3.1. For this purpose three ampoules of each material were used to prepare the spike back-spike blends. For each ampoule 4 blends were prepared, 2 blends with each back-spike (see Table 2). In total 12 blends were prepared for each material. Each blend was measured twice with the Neptune MC-ICPMS. The mean of both measurements was used and half of the difference between both single measurements was used as standard uncertainty. The gravimetric data, the observed isotope ratios and the resulting mass fractions, $w_{y,b}$, of ^{106}Pd and ^{194}Pt are displayed in Table 9 and 10. Exemplary uncertainty budgets for $w_{y,b}$ of ^{106}Pd and ^{194}Pt are given in the Appendix.

Table 9: Mass of spike and back-spike, observed isotope ratios and resulting ^{106}Pd mass fractions in ERM-AE140 listed for each blend with the corresponding standard uncertainty

Blend	Amp. No.	Back-spike	Mass in g ³		Isotope ratio ³ $^{105}\text{Pd}/^{106}\text{Pd}$	^{106}Pd mass fraction in mg/kg
			Spike	Back-spike		
Pd-18-1-1	18	RS1	1.06639(10)	1.05018(10)	0.1771278(34)	20.2330(232)
Pd-18-1-2	18	RS1	0.97734(10)	1.06832(10)	0.1914963(19)	20.2302(232)
Pd-18-2-1	18	RS2	1.01239(10)	1.00858(10)	0.1759524(44)	20.2304(224)
Pd-18-2-1	18	RS2	1.00715(10)	1.002156(10)	0.1783033(32)	20.2379(225)
Pd-51-1-1	51	RS1	1.00493(10)	1.001243(10)	0.1800932(2)	20.2469(233)
Pd-51-1-2	51	RS1	1.01239(10)	1.00799(10)	0.1785671(44)	20.2374(233)
Pd-51-2-1	51	RS2	0.98893(10)	1.01216(10)	0.1795008(135)	20.2402(226)
Pd-51-2-1	51	RS2	1.02677(10)	1.00337(10)	0.1733373(74)	20.2407(225)
Pd-112-1-1	112	RS1	0.96620(10)	0.99345(10)	0.1829472(107)	20.2348(233)
Pd-112-1-2	112	RS1	1.04606(10)	1.01944(10)	0.1757803(66)	20.2261(233)
Pd-112-2-1	112	RS2	1.00674(10)	0.99266(10)	0.1745647(116)	20.2336(225)
Pd-112-2-1	112	RS2	1.00254(10)	1.02528(10)	0.1794501(208)	20.2318(227)
Mean						20.2353
s						0.0057
s_{rel} in %						0.028
u_{c}						0.0229
$u_{\text{c,rel}}$ in %						0.11
Gravimetric value⁴						20.2047 (84)

³ Observed data: mass is not corrected for buoyancy; isotope ratios are not corrected for mass discrimination.

⁴ Mass fraction of spike isotope, $w_{y,b}$, calculated from gravimetric data and from purity and isotopic enrichment provided by ORNL (see Table 1)

The ^{106}Pd mass fractions for each blend agree excellent with each other within 0.028 % (s_{rel}). This is nearly a factor of 4 lower than the combined uncertainty for each blend, where the main contribution derives from the large uncertainties of the IUPAC tabulated data for natural Pd. The data in Table 9 give no evidence for any inhomogeneity or for a bias with the bottling sequence.

The determined ^{106}Pd mass fraction agrees excellent with the value obtained from the gravimetric preparation within the standard uncertainties. The gravimetric value is based on the gravimetric data from the preparation and the isotopic composition and the purity obtained from the ORNL analysis report. The data from the ORNL analysis report provide neither measurement uncertainties nor traceability statements. Therefore, only the determined value is used for the certification, as it provides a complete uncertainty statement and full SI-traceability.

Table 10: Mass of spike and back-spike, observed isotope ratios and resulting ^{194}Pt mass fractions in ERM-AE141 listed for each blend with the corresponding standard uncertainty

Blend	Amp. No.	Back- spike	Mass in g ⁵		Isotope ratio ⁵ $^{195}\text{Pt}/^{194}\text{Pt}$	^{194}Pt mass fraction in mg/kg
			Spike	Back-spike		
Pt-24-3-1	24	RS3	1.06875(10)	0.99967(10)	0.323240(61)	18.1844(558)
Pt-24-3-2	24	RS3	0.99352(10)	1.00795(10)	0.338601(54)	18.1766(557)
Pt-24-4-1	24	RS4	1.00916(10)	1.06072(10)	0.336929(60)	18.1889(557)
Pt-24-4-2	24	RS4	1.06311(10)	1.07336(10)	0.329319(55)	18.1889(557)
Pt-75-3-1	75	RS3	1.02902(10)	1.00375(10)	0.331077(58)	18.1826(557)
Pt-75-3-2	75	RS3	1.04877(10)	1.01475(10)	0.329593(63)	18.1787(557)
Pt-75-4-1	75	RS4	1.04430(10)	1.00754(10)	0.320940(58)	18.1848(554)
Pt-75-4-2	75	RS4	1.04520(10)	1.05163(10)	0.328728(61)	18.1834(558)
Pt-115-3-1	115	RS3	1.01098(10)	1.12605(10)	0.356782(59)	18.1845(557)
Pt-115-3-2	115	RS3	1.03390(10)	1.01267(10)	0.331823(47)	18.1854(556)
Pt-115-4-1	115	RS4	1.04027(10)	1.01473(10)	0.322901(42)	18.1904(556)
Pt-115-4-2	115	RS4	1.06412(10)	1.03030(10)	0.321584(48)	18.1853(556)
Mean						18.1845
s						0.0040
s_{rel} in %						0.022
u_{c}						0.0557
$u_{\text{c,rel}}$ in %						0.31
Gravimetric value ⁶						18.173 (19)

The ^{194}Pt mass fractions for each blend agree excellent with each other within 0.022 % (s_{rel}). This is nearly a factor of 18 lower than the combined uncertainty for each blend, where the main contribution derives from the large uncertainties of the applied isotope reference material IRMM-010. The data in Table 10 give no evidence for any inhomogeneity or for a bias with the bottling sequence.

⁵ Observed data: mass is not corrected for buoyancy; isotope ratios are not corrected for mass discrimination.

⁶ Mass fraction of spike isotope, $w_{\text{y,b}}$, calculated from gravimetric data and from purity and isotopic enrichment provided by ORNL (see Table 1)

The determined ^{194}Pt mass fraction agrees excellent with the value obtained from the gravimetric preparation within the standard uncertainties. The gravimetric value is based on the gravimetric data from the preparation and the isotopic composition and the purity obtained from the ORNL analysis report. The data from the ORNL analysis report provide neither measurement uncertainties nor traceability statements. Therefore, the determined value is used only for the certification, as it provides a complete uncertainty statement and full SI-traceability.

4. Certification

For the certification of a reference material all data altering or affecting the quantity value to be certified or its combined uncertainty have to be collected and used for establishing the certified quantity value. Commonly, the results from homogeneity, stability and characterization are combined.

As explained above homogeneity and stability issues do not affect the Pd and Pt solutions, which are bottled in flame-sealed quartz ampoules. The certified quantity values of the discussed reference materials (Table 11 and 12) derive only from the characterization study.

Table 11: Certified quantity values of ERM-AE140 with their expanded uncertainties $U = k \cdot u_c$ with $k = 2$

Quantity	Unit	Value	u_c	U	U_{rel} in %
$w(^{106}\text{Pd})$	mg/kg	20.235	0.023	0.046	0.23
$w(\text{Pd})$	mg/kg	20.535	0.023	0.046	0.23
$n(^{102}\text{Pd})/n(^{106}\text{Pd})$	mol/mol	0.00007914	0.00000053	0.0000011	1.3
$n(^{104}\text{Pd})/n(^{106}\text{Pd})$	mol/mol	0.0012469	0.0000053	0.000011	0.85
$n(^{105}\text{Pd})/n(^{106}\text{Pd})$	mol/mol	0.007518	0.000015	0.000030	0.40
$n(^{108}\text{Pd})/n(^{106}\text{Pd})$	mol/mol	0.004785	0.000011	0.000022	0.47
$n(^{110}\text{Pd})/n(^{106}\text{Pd})$	mol/mol	0.0011559	0.0000055	0.000011	0.95
$n(^{102}\text{Pd})/n(\text{Pd})$	mol/mol	0.00007799	0.00000052	0.0000010	1.3
$n(^{104}\text{Pd})/n(\text{Pd})$	mol/mol	0.0012288	0.0000052	0.000010	0.85
$n(^{105}\text{Pd})/n(\text{Pd})$	mol/mol	0.007408	0.000015	0.000030	0.40
$n(^{106}\text{Pd})/n(\text{Pd})$	mol/mol	0.985430	0.000021	0.000041	0.0041
$n(^{108}\text{Pd})/n(\text{Pd})$	mol/mol	0.004716	0.000011	0.000022	0.46
$n(^{110}\text{Pd})/n(\text{Pd})$	mol/mol	0.0011390	0.0000054	0.000011	0.94
$M(\text{Pd})$	g/mol	105.907312	0.000037	0.000075	0.000070

Table 12: Certified quantity values of ERM-AE141 with their expanded uncertainties $U = k \cdot u_c$ with $k = 2$

Quantity	Unit	Value	u_c	U	U_{rel} in %
$w(^{194}\text{Pt})$	mg/kg	18.185	0.056	0.11	0.61
$w(\text{Pt})$	mg/kg	19.900	0.061	0.12	0.62
$n(^{190}\text{Pt})/n(^{194}\text{Pt})$	mol/mol	0.00000118	0.00000028	0.00000056	47
$n(^{192}\text{Pt})/n(^{194}\text{Pt})$	mol/mol	0.0003417	0.0000019	0.0000039	1.1
$n(^{195}\text{Pt})/n(^{194}\text{Pt})$	mol/mol	0.07388	0.00036	0.00072	0.97
$n(^{196}\text{Pt})/n(^{194}\text{Pt})$	mol/mol	0.01749	0.00011	0.00021	1.2
$n(^{198}\text{Pt})/n(^{194}\text{Pt})$	mol/mol	0.002022	0.000015	0.000029	1.4
$n(^{190}\text{Pt})/n(\text{Pt})$	mol/mol	0.00000108	0.00000026	0.00000051	47
$n(^{192}\text{Pt})/n(\text{Pt})$	mol/mol	0.0003124	0.0000019	0.0000038	1.20
$n(^{194}\text{Pt})/n(\text{Pt})$	mol/mol	0.91429	0.00037	0.00073	0.080
$n(^{195}\text{Pt})/n(\text{Pt})$	mol/mol	0.06755	0.00030	0.00060	0.89
$n(^{196}\text{Pt})/n(\text{Pt})$	mol/mol	0.015994	0.000093	0.00019	1.2
$n(^{198}\text{Pt})/n(\text{Pt})$	mol/mol	0.001849	0.000013	0.000026	1.4
$M(\text{Pt})$	g/mol	194.06917	0.00047	0.00093	0.00048

The Pd and Pt single spike isotope reference materials ERM-AE140 and -AE141 are primarily intended to be used as isotopically enriched spikes for Pd and Pt quantification by IDMS. The combined uncertainty of the Pd and Pt mass fractions is limited by the uncertainty of the IUPAC data for Pd or the certified Pt isotope ratios in IRMM-010.

In the cases where the Pd and/or the Pt in the sample show no isotope variation against the IUPAC values the measurement uncertainty can be reduced by applying a quasi double IDMS analysis. When no isotopic variation occurs, the isotopic composition of Pd/Pt in the used back-spikes and the isotopic composition of Pd/Pt in the sample is equal and cancel when the equations of IDMS and reverse IDMS are combined to the double IDMS equation (see chapter 3.1). For the analyst using ERM-AE140 and/or -AE141, however, the data of the reverse IDMS (spike characterization) are not available. To offer the analyst a quasi double IDMS approach, the Pd and Pt mass fractions in ERM-AE140 and -AE141 were calculated again, but with the IUPAC values for the molar mass in the back-spike M_z and the isotopic abundance of isotope b in the back-spike a_{zb} are treated as constants. The so calculated mass fractions of the spikes (Table 13) can be used for Pd and/or Pt quantification by IDMS in samples showing no isotopic variation against the IUPAC isotopic composition. The same IUPAC values (Table 13) have to be used again treated as constants.

Table 13: Derived quantity values of ERM-AE140 and -AE141 to be used for quasi double IDMS: expanded uncertainties were calculated with IUPAC values treated as constant.

Quantity	Unit	Value	<i>U</i>	<i>U</i> _{rel} in %
$w(^{106}\text{Pd})$	mg/kg	20.235	0.011	0.053
$w(\text{Pd})$	mg/kg	20.535	0.011	0.053
$w(^{194}\text{Pt})$	mg/kg	18.184	0.012	0.066
$w(\text{Pt})$	mg/kg	19.900	0.021	0.10
Applied IUPAC values (Berglund et al. 2011, Böhlke et al. 2005)				
$n(^{106}\text{Pd})/n(\text{Pd})$	mol/mol	0.2733		
$n(^{194}\text{Pt})/n(\text{Pt})$	mol/mol	0.3286		
$M(\text{Pd})$	g/mol	106.42		
$M(\text{Pt})$	g/mol	195.084		

These certified reference materials (CRM) are traceable to the International System of units (SI) in the shortest possible way, by calibrating all instruments (balance, mass spectrometer) against SI-traceable calibrators. For Pd isotope measurements the SI traceable calibrator was high purity Pd with natural isotopic composition tabulated by IUPAC, for Pt isotope measurements the SI traceable calibrator IRMM-010, which is a primary isotope reference material. Mass fractions in ERM-AE140 and -AE141 are determined by reverse IDMS applied as primary method of measurement. The back-spike solutions used for reverse IDMS were prepared from high purity Pd and Pt metal under full gravimetric control by using SI-traceable weights.

Measurements calibrated against these ERM will, therefore, also be traceable to the SI.

These reference materials should be stored under normal laboratory conditions (between 5 °C and 25 °C), where the risk of mechanical damage is low. Once opened, the solution should be transferred into a new closable vial or bottle, which preferably is weight monitored to enable a correction for evaporation loss during further storage.

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Appendix: Exemplary uncertainty budgets

Table 14: Uncertainty budget for the Pd mass fraction in the back-spike RS2

Quantity	Value	Standard uncertainty	Unit	Type A/B	Description	Index
$m_{z-total}$	222947.6333	0.0882	µg	A	Observed total mass of high purity Pd	0.3 %
m_{z-tare}	161254.600	0.153	µg	A	Observed tare weight at microbalance	0.8 %
Lin_z	0.0	1.15	µg	B	Non-linearity of microbalance	48.0 %
$Lin2_z$	0.0	0.0	µg	*	Non-linearity 2 of microbalance	0.0 %
Cal_z	0.0	0.346	µg	B	Tolerance of calibration weights of microbalance	4.3 %
$Drift_z$	0.0	0.346	µg	B	Drift of microbalance	4.3 %
p_{svp}	26.44	0.0	mbar	**	Saturation vapour pressure of water at the given temperature	
T_0	273.15	0.0	K	**	Temperature conversion from °C to K	
T_{air}	24.000	0.289	°C	B	Air temperature in °C	0.1 %
$humidity$	80.000	0.577	%	B	Relative air humidity	0.0 %
p_{air}	1018.000	0.577	mbar	B	Air pressure	0.0 %
ρ_{wz}	8000.0	10.0	kg/m ³	B	Density of the weights, microbalance	0.0 %
ρ_z	12020.0	10.0	kg/m ³	B	Density of the high purity Pd	0.0 %
$Purity_z$	0.9999700	0.0000173	kg/kg	B	Purity of the high purity Pd	41.1 %
$m_{sol-total}$	314.4035000	0.0000408	g	A	Observed total mass of solution	0.0 %
m_{bottle}	66.567400	0.0000510	g	A	Observed tare weight at analytical balance	0.0 %
Lin_{sol}	0.0	0.000115	g	B	Non-linearity of analytical balance	0.0 %
$Lin2_{sol}$	0.0	0.000346	g	B	Non-linearity 2 of analytical balance	0.3 %
Cal_{sol}	0.0	0.000433	g	B	Tolerance of calibration weights of analytical balance	0.4 %
$Drift_{sol}$	0.0	0.0	g	*	Drift of analytical balance	
ρ_{wsol}	7950.0	10.0	kg/m ³	B	Density of the weights of the analytical balance	0.0 %
ρ_{sol}	1098.00	1.15	kg/m ³	B	Density of RS2 solution	0.2 %
w_z	248.67512	0.00672	µg/g	B	Pd mass fraction in RS2, combined standard uncertainty	
w_z	248.675	0.013	µg/g	B	Pd mass fraction in RS2, expanded uncertainty ($k = 2$)	

* value and uncertainty is zero

** value is constant

Equation system for Tables 14 and 15:

$$m_{z-bc} = (m_{z-total} - m_{z-tare}) + Lin_z + Lin2_z + Cal_z + Drift_z;$$

$$\rho_{air} = 0.3485 * p_{air} / (T_0 + T_{air}) - 0.00132 * p_{svp} * humidity / (T_0 + T_{air});$$

$$k_{mz} = (1 - (\rho_{air} / \rho_{wz})) / (1 - (\rho_{air} / \rho_z));$$

$$m_z = m_{z-bc} * k_{mz} * Purity_z;$$

$$m_{sol-bc} = (m_{sol-total} - m_{bottle}) + Lin_{sol} + Lin2_{sol} + Cal_{sol} + Drift_{sol};$$

$$k_{sol} = (1 - (\rho_{air} / \rho_{wsol})) / (1 - (\rho_{air} / \rho_{sol}));$$

$$m_{sol} = m_{sol-bc} * k_{sol};$$

$$w_z = m_z / m_{sol};$$

Table 15: Uncertainty budget for the Pt mass fraction in the back-spike RS4

Quantity	Value	Standard uncertainty	Unit	Type A/B	Description	Index
$m_{z\text{-total}}$	72048.92	1.13	μg	A	Observed total mass of high purity Pt	29.1 %
$m_{z\text{-tare}}$	18957.650	0.822	μg	A	Observed tare weight at microbalance	15.4 %
Lin_z	0.0	1.15	μg	B	Non-linearity of microbalance	30.3 %
$Lin2_z$	0.0	0.0	μg	*	Non-linearity 2 of microbalance	0.0 %
Cal_z	0.0	0.346	μg	B	Tolerance of calibration weights of microbalance	2.7 %
$Drift_z$	0.0	0.346	μg	B	Drift of microbalance	2.7 %
p_{svpW}	26.44	0.0	mbar	**	Saturation vapour pressure of water at the given temperature	
T_0	273.15	0.0	K	**	Temperature conversion from °C to K	
T_{air}	22.000	0.289	°C	B	Air temperature in °C	0.0 %
<i>humidity</i>	82.000	0.577	%	B	Relative air humidity	0.0 %
p_{air}	1025.000	0.577	mbar	B	Air pressure	0.0 %
ρ_{wz}	8000.0	10.0	kg/m^3	B	Density of the weights, microbalance	0.0 %
ρ_z	21450.0	10.0	kg/m^3	B	Density of the high purity Pt	0.0 %
$Purity_z$	0.9999700	0.0000173	kg/kg	B	Purity of the high purity Pt	19.2 %
$m_{\text{sol-total}}$	315.3118400	0.0000400	g	A	Observed total mass of solution	0.0 %
m_{bottle}	66.6367600	0.0000600	g	A	Observed tare weight at analytical balance	0.0 %
Lin_{sol}	0.0	0.000115	g	B	Non-linearity of analytical balance	0.0 %
$Lin2_{\text{sol}}$	0.0	0.000346	g	B	Non-linearity 2 of analytical balance	0.1 %
Cal_{sol}	0.0	0.000433	g	B	Tolerance of calibration weights of analytical balance	0.2 %
$Drift_{\text{sol}}$	0.0	0.0	g	*	Drift of analytical balance	
ρ_{wsol}	7950.0	10.0	kg/m^3	B	Density of the weights of the analytical balance	0.0 %
ρ_{sol}	1098.00	1.15	kg/m^3	B	Density of RS4 solution	0.0 %
w_z	213.26886	0.00842	$\mu\text{g}/\text{g}$	B	Pt mass fraction in RS4, combined standard uncertainty	
w_z	213.269	0.017	$\mu\text{g}/\text{g}$	B	Pt mass fraction in RS4, expanded uncertainty ($k = 2$)	

* value and uncertainty is zero

** value is constant

Table 16: Uncertainty budget for the ^{106}Pd mass fraction in ERM-AE140 as determined in blend Pd-112-1-1

Quantity	Value	Standard uncertainty	Unit	Type A/B	Description	Index
M_z	106.42000	0.00500	g/mol		Molar mass of back-spike material	
M_b	105.9034841	0.0000127	g/mol		Molar mass of spike isotope Pd-106	
A_{r-106}	105.90348400	0.00000500	1		Atomic weight of Pd-106, IUPAC	0.0 %
A_{r-Pd}	106.42000	0.00500	1		Atomic weight of Pd, IUPAC	0.2 %
N_A	$602.2141990 \cdot 10^{21}$	$47.0 \cdot 10^{15}$	mol^{-1}		Avogadro number	0.0 %
u	$1.660538730 \cdot 10^{-27}$	$130 \cdot 10^{-36}$	kg		Atomic mass unit	0.0 %
a_{z106}	0.273300	0.000300	mol/mol		Isotope amount fraction of Pd-106 in the back-spike, IUPAC	91.2 %
R_{z0}	0.8036175	0.0000257	V/V		Observed ratio 105/106 in back-spike	0.1 %
R_{y0}	0.00739410	0.00000562	V/V		Observed isotope ratio 105/106 in spike	0.0 %
K_{mz}	1.00094393	0.00000913	kg/kg		Buoyancy correction factor for back-spike solution	
K_{my}	1.00094393	0.00000913	kg/kg		Buoyancy correction factor for spike sol.	
ρ_a	1.2000	0.0100	kg/m^3		Density of air	0.0 %
ρ_w	8000.0	10.0	kg/m^3		Density of balance weights	0.0 %
ρ_{zsol}	1098.00	4.62	kg/m^3		Density of back-spike solution	0.0 %
ρ_{ysol}	1098.00	4.62	kg/m^3		Density of spike solution	0.0 %
w_{z1}	20.46633	0.00595	$\mu\text{g/g}$		Pd mass fraction of back-spike RS1	6.4 %
K_{VV1}	1.0		1		Evaporation correction factor of RS1	
K_{VF1}	1.0		1		Dilution factor of RS1	
m_{z9}	993.450	0.100	mg		Observed mass back-spike, RS1-112-A	0.8 %
m_{y9}	966.200	0.100	mg		Observed mass spike in RS1-112-A	0.8 %
R_{zyo9}	0.1829472	$11.0 \cdot 10^{-6}$	V/V		Observed ratio 105/106 in RS1-112-A	0.5 %
w_{yb9}	20.2348	0.0233	$\mu\text{g } ^{106}\text{Pd/g}$		Mass fraction of Pd-106 in RS1-112-A, standard combined uncertainty	
w_{yb9}	20.235	0.047	$\mu\text{g } ^{106}\text{Pd/g}$		Mass fraction of Pd-106 in RS1-112-A, expanded uncertainty, $k = 2$	

$$K_{mz} = (1 - (\rho_a / \rho_w)) / (1 - (\rho_a / \rho_{zsol}));$$

$$K_{my} = (1 - (\rho_a / \rho_w)) / (1 - (\rho_a / \rho_{ysol}));$$

$$M_b = A_{r-106} * N_A * u * 1000;$$

$$M_z = A_{r-Pd} * N_A * u * 1000;$$

$$w_{yb9} = (M_b * a_{z106} / M_z) * w_{z1} * K_{VV1} * K_{VF1} * ((m_{z9} * K_{mz}) / (m_{y9} * K_{my})) * ((R_{z0} - R_{zyo9}) / (R_{zyo9} - R_{y0}));$$

Table 17: Uncertainty budget for the ^{194}Pt mass fraction in ERM-AE141 as determined in blend Pt-115-1-1

Quantity	Value	Standard uncertainty	Unit	Type A/B	Description	Index
M_z	195.08400	0.00450	g/mol		Molar mass of back-spike material	
M_b	193.9626632	0.0000217	g/mol		Molar mass of spike isotope Pt-194	
A_{r-194}	193.96266300	0.00000300	1		Atomic weight of Pt-194, IUPAC	0.0 %
A_{r-Pt}	195.08400	0.00450	1		Atomic weight of Pt, IUPAC	0.2 %
N_A	$602.2141990 \cdot 10^{21}$	$47.0 \cdot 10^{15}$	mol^{-1}		Avogadro number	0.0 %
u	$1.660538730 \cdot 10^{-27}$	$130 \cdot 10^{-36}$	kg		Atomic mass unit	0.0 %
a_{z194}	0.32860	0.00100	mol/mol		Isotope amount fraction of Pt-194 in the back-spike, IUPAC	91.2 %
R_{z0}	1.0380330	0.0000623	V/V		Observed ratio 105/106 in back-spike	0.1 %
R_{y0}	0.07460849	0.00000209	V/V		Observed isotope ratio 105/106 in spike	0.0 %
K_{mz}	1.00094393	0.00000913	kg/kg		Buoyancy correction factor for back-spike solution	
K_{my}	1.00094393	0.00000913	kg/kg		Buoyancy correction factor for spike sol.	
ρ_a	1.2000	0.0100	kg/m^3		Density of air	0.0 %
ρ_w	8000.0	10.0	kg/m^3		Density of balance weights	0.0 %
ρ_{zsol}	1098.00	4.62	kg/m^3		Density of back-spike solution	0.0 %
ρ_{ysol}	1098.00	4.62	kg/m^3		Density of spike solution	0.0 %
w_{z3}	20.69814	0.00145	$\mu\text{g/g}$		Pd mass fraction of back-spike RS3	6.4 %
K_{VV3}	1.0	1.0	1		Evaporation correction factor of RS3	
K_{VF3}	1.0	1.0	1		Dilution factor of RS1	
m_{z9}	1126.050	0.100	mg		Observed mass back-spike, RS3-115-A	0.8 %
m_{y9}	1010.980	0.100	mg		Observed mass spike in RS3-115-A	0.8 %
R_{zy09}	0.3567821	0.0000571	V/V		Observed ratio 105/106 in RS3-115-A	0.5 %
w_{yb9}	18.1845	0.0577	$\mu\text{g } ^{194}\text{Pt/g}$		Mass fraction of Pt-194 in RS3-115-A, standard combined uncertainty	
w_{yb9}	18.18	0.11	$\mu\text{g } ^{194}\text{Pt/g}$		Mass fraction of Pt-194 in RS3-115-A, expanded uncertainty, $k = 2$	

$$K_{mz} = (1 - (\rho_a / \rho_w)) / (1 - (\rho_a / \rho_{zsol}));$$

$$K_{my} = (1 - (\rho_a / \rho_w)) / (1 - (\rho_a / \rho_{ysol}));$$

$$M_b = A_{r-194} * N_A * u * 1000;$$

$$M_z = A_{r-Pt} * N_A * u * 1000;$$

$$w_{yb9} = (M_b * a_{z194} / M_z) * w_{z3} * K_{VV3} * K_{VF3} * ((m_{z9} * K_{mz}) / (m_{y9} * K_{my})) * ((R_{z0} - R_{zy09}) / (R_{zy09} - R_{y0}));$$