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Gravimetric preparation of synthetic mixtures of platinum isotopes

C.S.J. Wolff Briche*, A. Held, B. Dyckmans, M. Berglund, P. De Bièvre, P.D.P. Taylor

Institute for Reference Materials and Measurements, Joint Research Centre, B-2440 Geel, Belgium

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Abstract

Five synthetic isotope mixtures were prepared from isotopically enriched and purified platinum solutions to obtain accurately known isotope amount ratios $n(^{196}\text{Pt})/n(^{195}\text{Pt})$. Two metallic platinum powders enriched in isotopes ^{195}Pt and ^{196}Pt , respectively, were dissolved in aqua regia. The resulting hexachloroplatinic acid was reduced under hydrogen to transform it into a metallic platinum sponge. The level of impurities contained in the sponges, as well as their stoichiometry were estimated and taken into account in all calculations carried out with the isotopically enriched materials. The prepared isotope amount ratios, $n(^{196}\text{Pt})/n(^{195}\text{Pt})$, of the five mixtures were 0.099 57, 0.397 34, 0.738 00, 3.9976, and 10.005 with expanded relative uncertainty (coverage factor $k = 2$) varying from 1×10^{-3} to 2.8×10^{-3} . These mixtures were used to calibrate isotope amount ratio measurements of a platinum sample of natural isotopic composition by inductively coupled plasma mass spectrometry. (Int J Mass Spectrom 202 (2000) 9–18) © 2000 Elsevier Science B.V.

Keywords: Atomic weight; Platinum; Inductively coupled plasma mass spectrometry; Isotopic reference material; Synthetic isotope mixtures

1. Introduction

The demand for the analysis of platinum in various matrices (water, soil, blood, and urine, . . .) has significantly increased since the last decade. There is a need for certified reference materials (RMs) and isotopic reference materials (IRMs) [1]. Isotope dilution of platinum is carried out for environmental [2,3] as well as for biological and drug sample [4,5] analyses, but there are no certified IRMs available. Spikes need to be prepared and analysed “in-house”

by reverse ID-MS or by double ID-MS. In the case of reverse ID-MS, the analysis is done versus a platinum sample with natural isotopic composition and the uncertainty induced by the IUPAC (International Union for Pure and Applied Chemistry) data for the natural isotopic composition of Pt can have a very large contribution to the combined standard uncertainty of the measurement's result.

Synthetic isotope mixtures are required for calibrated isotope amount ratio measurements. Their applications include certification of IRMs for isotope dilution analysis, highly accurate mass spectrometric measurements as well as the determination of the atomic weight of elements. The isotope amount ratio of a gravimetrically prepared mixture has a smaller

* Corresponding author. Present address: Laboratory of the Government Chemist, Queens Road, Teddington, Middlesex TW1 0LY, UK.

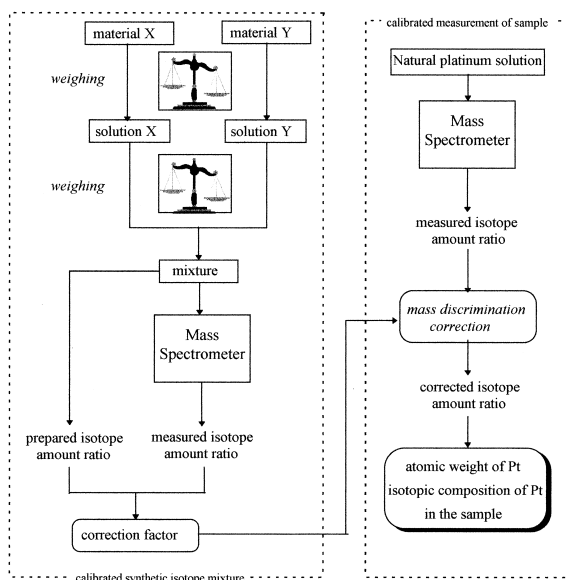


Fig. 1. Use of synthetic isotope mixtures to obtain calibrated isotope amount ratios for the atomic weight determination of platinum.

uncertainty than an isotope amount ratio measured by mass spectrometry. Consequently, mass discrimination effects occurring during mass spectrometric measurements can be corrected using the gravimetrically obtained values of the isotope amount ratios of the mixtures. The calibration of the mass spectrometer is carried out by measuring synthetic isotope mixtures prepared from isotopically enriched materials. This article describes the preparation of five synthetic isotope mixtures from two solutions enriched in isotopes ^{195}Pt and ^{196}Pt , respectively.

2. Theory

During sample preparation as well as mass spectrometric measurement, the isotopic composition of the element analysed can be affected and modified due to mass discrimination phenomena. Such effects can occur at any stage in the analytical procedure. In inductively coupled plasma mass spectrometry (ICP-MS) mass discrimination effects are mainly caused by space charge effects within the plasma and the vacuum interface region [6–8].

In order to be able to correct mass spectrometric measurements for mass discrimination effects, synthetic isotope mixtures were prepared from the two Pt solutions, named B and C, enriched in isotopes ^{195}Pt and ^{196}Pt , respectively. Aliquots from both solutions were carefully weighed and mixed to get well-defined isotope amount ratios. The prepared and measured isotope amount ratios were compared, leading to the calculation of the mass discrimination correction factor, K , defined as the ratio of the “true” value, R_i , and the measured value, R'_i , according to

$$K_i = \frac{R_i}{R'_i} = \frac{R_{\text{true}}}{R_{\text{meas}}} \quad (1)$$

The true value of an isotope amount ratio cannot be determined. In most cases, a certified IRM is measured and its certified isotope amount ratio is used to calculate the correction factor K_i . During this work, it was estimated as the value of the isotope amount ratio of the mixture prepared by gravimetry, $R_{\text{prep}} = n(^{196}\text{Pt})/n(^{195}\text{Pt})$, which is the most accurately estimated value. This K factor can then be used to correct other samples' measurements [9,10].

Each measured isotope amount ratio R'_i should be corrected by its specific K -factor K_i , as it depends on the difference in mass, β_i , of both isotopes involved in the isotope amount ratio R_i . Each K_i can be expressed as a function of β_i and a term called bias per mass unit, ε , here considered to be independent of the isotope amount ratios and the mass differences of the isotopes. Different empirical models have been developed to calculate the bias per mass unit: the linear law, the power law and the exponential law functions [11–13]. In this study, only the linear law function was employed

$$K_i = 1 + \beta_i \cdot \varepsilon \quad (2)$$

Once the bias per mass unit is calculated from the prepared and measured isotope amount ratios of the mixture, the mass discrimination factors, K_i , for all the other platinum isotope amount ratios can be calculated [Eq. (2)] and applied to the measured isotope amount ratios, R'_i . The principle of using a synthetic isotope mixture to correct mass spectrometric measurement is summarised in Fig. 1.

The prepared isotope amount ratio, $R_{\text{prep}} = n(^{196}\text{Pt})/n(^{195}\text{Pt}) = R_5(\text{mix})$, corresponds to the ratio of the amount of isotope ^{196}Pt to the amount of isotope ^{195}Pt in the mixture. As both isotopes were present in each material used for the mixture, the prepared isotope amount ratio was calculated as given in

$$\begin{aligned} R_{\text{prep}} &= \frac{n(^{196}\text{Pt, mixture})}{n(^{195}\text{Pt, mixture})} \\ &= \frac{n_5(\text{mixture})}{n_4(\text{mixture})} \\ &= \frac{n_5(\text{B}) + n_5(\text{C})}{n_4(\text{B}) + n_4(\text{C})} \quad (3) \end{aligned}$$

Note that ^{195}Pt is selected as a reference isotope, and all amount ratios are expressed relative to it. This means, for instance, that $R'_5(\text{B})$ is the measured isotope amount ratio of $n(^{196}\text{Pt})/n(^{195}\text{Pt})$ in sample B and $K_5(\text{B})$ the mass discrimination correction factor, for this ratio, in sample B. The different notations used are defined in Table 1. As no material is 100% pure, or stoichiometrically under full control, correction factors, taking these parameters into account, are introduced as given in Eq. (4).

$$\begin{aligned} R_{\text{prep}} &= \frac{m(\text{B})(1 - \delta_{\text{imp B}})(1 - \delta_{\text{sto B}})R_5(\text{B}) \sum_{i=1}^6 [M_i R_i(\text{C})] + m(\text{C})(1 - \delta_{\text{imp C}})(1 - \delta_{\text{sto C}})R_5(\text{C}) \sum_{i=1}^6 [M_i R_i(\text{B})]}{m(\text{B})(1 - \delta_{\text{imp B}})(1 - \delta_{\text{sto B}})R_4(\text{B}) \sum_{i=1}^6 [M_i R_i(\text{C})] + m(\text{C})(1 - \delta_{\text{imp C}})(1 - \delta_{\text{sto C}})R_4(\text{C}) \sum_{i=1}^6 [M_i R_i(\text{B})]} \quad (5) \end{aligned}$$

The values required for the isotope amount ratios involved in Eq. (5) are the corrected isotope amount ratios, $R_i(X)$, and not the measured values R'_i . As the materials B and C are not certified IRMs, their isotope amount ratios $R_i(\text{B})$ and $R_i(\text{C})$ were not known and needed to be measured and corrected for mass discrimination before using them in Eq. (5). The calculation of the K factors and the bias per mass unit, ε , uses an iterative calculation procedure (Fig. 2).

The iterative procedure is explained stepwise. (1) Mass spectrometric measurement of the isotope amount ratios of B, C and the mixture: $R'_i(\text{B})$, $R'_i(\text{C})$,

Table 1

Definitions of the symbols used for the treatment of the data^a

Isotope	i, j, k
Atomic mass	M_i
Amount of isotope i in material X	$n_i(X)$
Mass of material X	$m(X)$
Abundance of isotope i in material X	$f_i(X)$
“True” isotope amount ratio in material X	$R_i(X)$
Measured isotope amount ratio in material X	$R'_i(X)$
Atomic weight of element E	$A_r(E)$
Impurity correction term in material X	$\delta_{\text{imp } X}$
Nonstoichiometry correction term in material X	$\delta_{\text{sto } X}$
Mass discrimination correction factor for isotope amount ratio R_i	K_i
Bias per mass unit	ε
Gravimetrically prepared isotope amount ratio	R_{prep}
Standard uncertainty of variable z	$u(z)$
Combined uncertainty of variable z	$u_c(z)$

^a The 6 platinum isotopes were indexed with numbers from 1 to 6 according to their increasing mass, the reference isotope was ^{195}Pt , consequently, its index number was 4: $n_4 = n(^{195}\text{Pt})$.

$$n_i(X) = \frac{R_i(X) m(X)}{\sum_{j=1}^p R_j} (1 - \delta_{\text{imp } X})(1 - \delta_{\text{sto } X}) \quad (4)$$

By inserting $n_i(X)$ in Eq. (3) and expressing $M(X)$ as a function of M_i and $R_i(X)$, the prepared isotope amount ratio is expressed as Eq. (5).

and $R'_5(\text{mix})$ [corresponding to the gravimetrically prepared isotope amount ratio of the mixture: $R'_5(\text{mix})$]. (2) First calculation of the prepared isotope amount ratio of the mixture: $^1R'_5(\text{mix})$, using the measured isotope amount ratios $R'_i(\text{B})$ and $R'_i(\text{C})$ in Eq. (5). (3) First iteration: $j = 1$. (4) Calculation of the K -factor $^jK_5 = ^jR_5(\text{mix})/R'_5(\text{mix})$. (5) Calculation of the bias per mass unit $^j\varepsilon$ using the linear law function corresponding to the iteration step j . (6) Re-calculation of all the K -factors jK_i , corresponding to the different isotope amount ratios using the linear law for the iteration step j . (7) Correction of all the

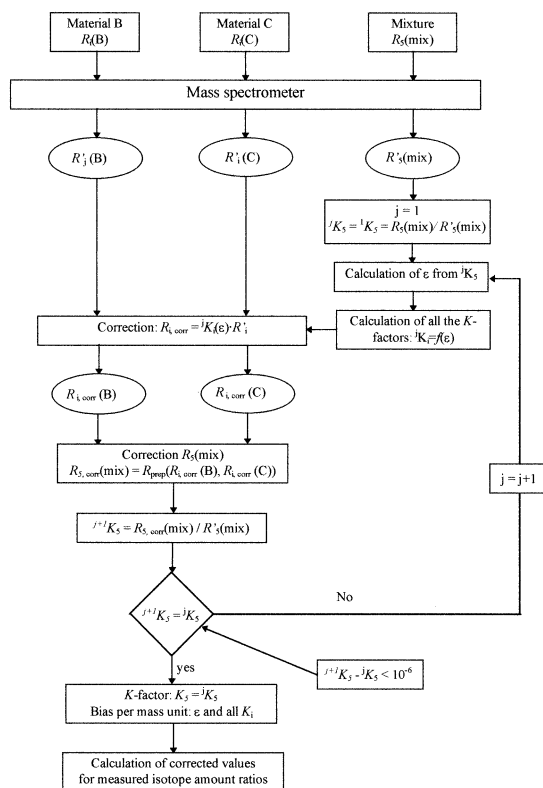


Fig. 2. Iterative procedure used to calculate the mass discrimination correction factor (K factor). The notation used is explained in Table 1. The superscript index j put in front of the variables jR , jK , and ${}^j\epsilon$ indicates the number of the iteration step.

measured isotope amount ratios of B and C: ${}^jR_{i,\text{corr}}(\text{B})$, ${}^jR_{i,\text{corr}}(\text{C})$. (8) Re-calculation of the prepared isotope amount ratio ${}^{j+1}R_5(\text{mix})$ using the corrected isotope amount ratios ${}^jR_{i,\text{corr}}(\text{B})$ and ${}^jR_{i,\text{corr}}(\text{C})$ in Eq. (5). (9) Next iteration: $j = j + 1$.

Steps (4)–(9) were repeated until the difference between two consecutive K factors, jK_5 and ${}^{j+1}K_5$, was smaller than 10^{-6} . This calculation was done for the five prepared synthetic isotope mixtures.

3. Experimental

3.1. Reagents

Materials B and C (Chemotrade GmbH, Düsseldorf, Germany), isotopically enriched in isotopes

Table 2
Operating conditions of the inductively coupled plasma mass spectrometer

Nebulisers	V-groove and micro-concentric nebuliser MCN 100 (CETAC Technologies Inc., Omaha, USA)
Nebuliser gas flow	$\sim 0.8 \text{ L min}^{-1}$ for the V-groove $\sim 1 \text{ L min}^{-1}$ for the MCN
Sample aspiration rate	$\sim 1 \text{ mL min}^{-1}$ for the V-groove $\sim 100\text{--}120 \mu\text{L min}^{-1}$ for the MCN
Plasma gas flow	$\sim 14 \text{ L min}^{-1}$
Intermediate flow	$\sim 1.5 \text{ L min}^{-1}$
Electron multiplier	Galileo 1870V
Dead time	19.3 ns
Forward power	1400 W
Data acquisition mode	peak jump, 3 points per peak for ratio measurements scanning for impurity analysis
Dwell time	20 ms
Quadrupole settle time	30 ms
Acquisition time	60 s per run (6–10 runs) for ratio measurements 30 s per run (3 runs) for impurity analysis

${}^{195}\text{Pt}$ and ${}^{196}\text{Pt}$, respectively, were powders with very fine particles, and had a metallic grey colour. The platinum solutions were prepared using sub-boiling distilled water and acids (HCl and HNO_3) produced at the Institute for Reference Materials and Measurements (IRMM) [14,15]. The concentrations of the acids were about $7\text{--}7.5 \text{ mol L}^{-1}$ for HCl and about 14 mol L^{-1} for HNO_3 . Aqua regia was volumetrically prepared from HCl and HNO_3 in the proportions 3 to 1.

3.2. Instrumentation

A VG Plasmaquad 2+ (VG Elemental, Winsford, UK) was used for the measurements of the isotope amount ratios as well as the purity analysis (Table 2). The system used for the reduction under hydrogen consisted of a quartz tube, inserted in an oven, both ends of which were connected to valves to be able to switch between different gases and to regulate flow rates [16]. The temperature was monitored using a thermocouple placed on the outside of the quartz tube.

3.3. Weighing

All the weighings were performed in a room with controlled temperature and humidity. The samples were left equilibrating in that room for several hours before weighing. Each sample was weighed several times and compared to calibrated weights on a Sartorius RC210S balance (Sartorius AG, Göttingen, Germany). The IRMM working weights are calibrated against the IRMM primary 1 kg standard, which is regularly compared to an International Kilogram Prototype. It was thus possible to get a determination of the absolute sample mass, ensuring the comparability and traceability to SI.

3.4. Purification of the isotopically enriched materials

As the enriched materials contained black particles, probably platinum black or graphite, insoluble in aqua regia, they had to be removed prior to the gravimetric preparation of the mixtures. The materials B and C were treated as described in Fig. 3. In step (3), the solution was filtered through the frit of a BioRad polypropylene column (BioRad Laboratories, Richmond, VA, USA) to remove any insoluble particles. After step (4), the beaker containing H_2PtCl_6 was kept in a dessicator until the reduction was carried out. The purification procedure was performed in the ultraclean chemical laboratory (UCCL) at IRMM [14]. The metrological weighings and step (1), involving metallic powder, were done outside the UCCL in order to avoid the spread of metallic powder inside the laboratory.

The quartz beaker containing the dry H_2PtCl_6 residue was placed into the reduction oven. After the system was flushed with argon to remove the air, a low flow of H_2 was introduced. The oven was heated slowly to $220\text{ }^\circ\text{C}$ and kept at this temperature for about 1 h 20 min. The temperature was then raised to $700\text{ }^\circ\text{C}$ (within 50 min) and maintained during 30 min. The hydrogen flow was replaced by an argon flow and a calcination was performed at $900\text{ }^\circ\text{C}$ for 30 min. The heating was then stopped and the oven was left to cool down under argon for 20 h.

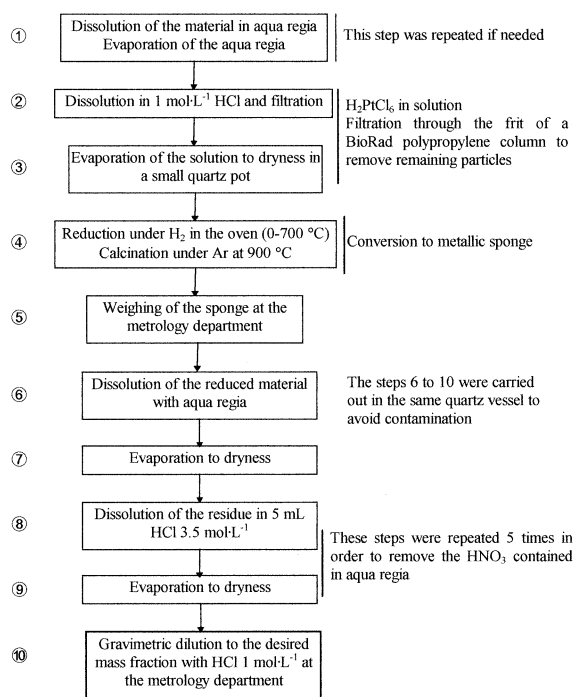


Fig. 3. Description of the procedure for the preparation of the platinum solutions.

3.5. Preparation of the platinum solutions B, C and mixtures

The isotopically enriched platinum sponges B and C were weighed into quartz weighing boats and placed into quartz flasks, in which the dissolution was carried out [Fig. 3, steps (6) to (10)]. A $1\text{ mol}\cdot\text{L}^{-1}$ HCl solution was used to dilute the solutions to a platinum mass fraction of approximately $1\text{ mg}\cdot\text{g}^{-1}$ of solution. Solutions B and C were stored in quartz flasks in sealed plastic bags. Aliquots of solutions B and C were weighed and mixed to obtain prepared isotope amount ratios between 0.1 and 10 (Table 3). The solutions were left equilibrating at least one week before any aliquot was taken out.

3.6. Purity and stoichiometry of the materials

As no chemical purity was stated for the enriched materials, solutions B and C were analysed for impurity by ICP-MS. The latter was equipped with a

Table 3
Weighing data for the mixtures prepared from solutions B and C

Mixtures	Mass of solution B (g)	Mass of solution C (g)	$n(^{196}\text{Pt})/n(^{195}\text{Pt})$	$u_c(R_s)$
Mix 1	9.249 1 ± 0.000 5	0.814 25 ± 0.000 08	0.099 57	0.000 14
Mix 2	5.681 4 ± 0.000 2	4.316 3 ± 0.000 2	0.738 00	0.000 41
Mix 3	0.712 12 ± 0.000 07	9.767 2 ± 0.000 5	10.005	0.010
Mix 4	7.150 0 ± 0.000 5	2.850 6 ± 0.000 2	0.397 34	0.000 26
Mix 5	1.806 8 ± 0.000 2	8.238 5 ± 0.000 5	3.997 6	0.002 6

microconcentric nebuliser (MCN) to limit sample's usage (about 300 μL per measurement). The measurement procedure consisted of 3 runs of 30 s each for a (semi)quantitative analysis of the impurities. Indium at a mass fraction of 10 $\text{ng} \cdot \text{g}^{-1}$ was added to each sample (including the blank) and used as internal standard to correct for matrix suppression, drifts in sample uptake due to the use of the MCN and instrumental drifts.

For Li, B, Na, Mg, Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Ag, Cd, Ba, Pb, Bi, an external calibration solution (10 $\text{ng} \cdot \text{g}^{-1}$) was made up from the ICP-multi-element standard solution IV (Merck, Darmstadt, Germany) which was measured under the same conditions as the sample.

For the other elements, the response curve of the

instrument, recorded at startup by measuring a solution containing 10 $\text{ng} \cdot \text{g}^{-1}$ Be, Mg, Co, In, La, Pb, Bi, and U, was used. The different abundances and ionisation efficiencies of the elements, and the sensitivity of the instrument at the moment of the measurement were taken into account. The response curve is approximated by a parabola with a maximum at mass-to-charge ratio between 100 and 150. For all samples analysed, a blank subtraction was realised using a solution of 1 $\text{mol} \cdot \text{L}^{-1}$ HCl. Some elements, e.g. K, Na, and Ca could not be quantified with the ICP-MS due to interferences inherent to the instrument. The results of the impurity analysis are given in Table 4. The detection limit for each element was defined as ten times the standard uncertainty of blank measurements divided by the sensitivity.

Table 4
Impurities in materials B and C, mass fraction in $\mu\text{g} \cdot \text{g}^{-1}$ in the solid material (sponge obtained after reduction)

Element	Material B ^a	Material C ^a	Element	Material B ^a	Material C ^a	Element	Material B ^a	Material C ^a
Li	11	6.3	Rh	0.16	0.54	Dy	<0.01	0.016
Be	<0.04	<0.04	Pd	18	0.076	Ho	<0.002	<0.002
B	<15	<15	Ag	4.7	<3	Er	<0.01	0.033
Al	13	12	Cd	0.45	8.5	Tm	<0.004	<0.004
Sc	<0.09	0.11	Sn	<1.8	<1.8	Yb	<0.03	<0.03
Ti	0.94	3.3	Sb	<0.02	0.02	Lu	<0.003	0.007
Mn	0.26	0.15	Te	<2.4	1.6	Hf	<0.02	<0.02
Fe	48	<30	Cs	<0.006	<0.006	Ta	<0.005	<0.005
Cu	38	25	Ba	0.47	1.8	W	0.062	0.3
Co	0.077	0.049	La	6.7	0.093	Re	<0.015	<0.15
Zn	111	42	Ce	0.2	0.28	Os	<0.08	<0.08
Rb	<0.03	<0.03	Pr	0.013	0.01	Ir	4.7	0.6
Sr	0.19	<0.06	Nd	0.03	0.065	Hg	<16	<16
Y	<0.02	<0.02	Sm	<0.03	<0.03	Tl	<0.1	0.43
Zr	<0.07	<0.07	Eu	<0.02	<0.02	Pb	5.2	7.1
Nb	0.022	<0.012	Gd	<0.02	0.031	Bi	<0.2	1.1
Ru	0.12	<0.07	Tb	<0.01	<0.01			

^a For the elements not detected the detection limit is indicated by < detection limit.

3.7. Isotope amount ratio measurements

For isotope amount ratio measurements, the ICP-MS was equipped with a V-groove nebuliser (Table 2). All solutions were diluted to a mass fraction of 20 ng Pt/g of an aqueous matrix containing 2% HNO₃ and 2% H₂O₂. This matrix was chosen in order to reduce the memory effect encountered during platinum analysis using ICP-MS [17]. In between each Pt sample, the instrument was rinsed with a blank solution containing 2% HNO₃ and 2% H₂O₂ during at least 15–20 min. A blank solution was analysed before each Pt sample and blank correction was done automatically.

For the solutions B and C, the ion currents for the six platinum stable isotopes, ¹⁹⁰Pt, ¹⁹²Pt, ¹⁹⁴Pt, ¹⁹⁵Pt, ¹⁹⁶Pt, and ¹⁹⁸Pt were recorded as well as *m/z* 202 in order to correct for possible interferences from mercury (no osmium was detected). The baseline recorded at *m/z* = 202 showed that mercury was present, but it did not differ between the blank solution and the samples. Thus no further correction than the blank subtraction was done for the isotope ¹⁹⁸Pt. For the synthetic isotope mixtures, only the ion currents for the isotopes ¹⁹⁵Pt and ¹⁹⁶Pt were measured. Ten runs of 60 s were done for each of the solutions, B, C and the synthetic mixtures.

4. Results and discussion

The impurity content of the isotopically enriched materials was calculated by summing the mass fractions of all the elements measured in the material and the detection limits for those which were not detected (Table 4). The elements for which no detection limit is given were not measured. No individual uncertainty on the measurement of each impurity was calculated. The relative uncertainty on the total impurity content was set conservatively at 100% in order to account for elements that could not be determined, i.e. K, Na, and Ca, and for those elements where the detection limit was used as amount content. Using the detection limits could lead to an overestimation of the total amount of impurities, on the other hand, only metallic impurities have been measured, whereas for instance

the gaseous impurities could not be determined. Following these considerations the total amount of impurity in the enriched materials was estimated to be $300 \pm 300 \mu\text{g} \cdot \text{g}^{-1}$ for material B and $180 \pm 180 \mu\text{g} \cdot \text{g}^{-1}$ for material C. Even though the standard uncertainties stated on the impurity content are large, the contribution of the impurity uncertainty to the prepared isotope amount ratio of the different mixtures is not the major component in the uncertainty budget (Fig. 4). As a consequence, the semiquantitative analysis of the impurities performed on the enriched materials was considered sufficient for the purpose of this study.

The sponge obtained after the reduction was considered metallic as no significant mass difference was observed when a larger amount of pure metallic platinum was treated under the same conditions, indicating that no significant amount of gas was adsorbed on the metal's surface. The materials B and C used for the preparation of the synthetic isotope mixtures were consequently considered as stoichiometrically pure but an uncertainty was stated. The correction term applied for possible nonstoichiometry was $\delta_{\text{sto}} = 0 \pm 1 \times 10^{-4}$ (as mass fraction) for both materials B and C.

4.1. Calculation of the mass discrimination factor

For each synthetic isotope mixture, the prepared isotope amount ratio $R_{\text{prep}} = n(^{196}\text{Pt})/n(^{195}\text{Pt})$ was calculated according to Eq. (5). The iterative calculation procedure described previously was used. The results of these calculations are given in Table 3, with an uncertainty budget for each mixture represented in Fig. 4. All the combined uncertainties were calculated according to the guidelines in the ISO/BIPM guide [18] and the EURACHEM guide [19]. The main contribution, to the uncertainty of the prepared isotope amount ratio, is from the measured isotope amount ratios of B and C. For isotope amount ratios close to 1 (mix 2), the contribution of uncertainties from impurities and weighings reached the same level as contribution from the measured isotope amount ratios (Fig. 4).

The corresponding mass discrimination factor, K_5 ,

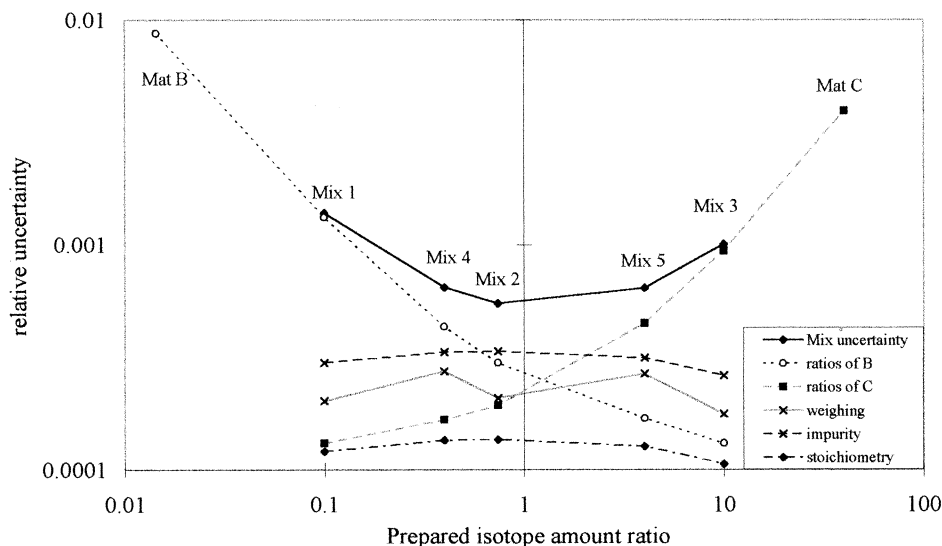


Fig. 4. Uncertainty budget for the prepared isotope amount ratios of the different synthetic isotope mixtures.

was calculated as R_{prep}/R'_5 . The combined standard uncertainty stated for K_5 for each individual mixture was calculated according to

$$u_c^2[K_5(\text{mix})] = \left(\frac{-R_{\text{prep}}}{R'^2_5(\text{mix})} \right)^2 u^2[R'_5(\text{mix})] + \frac{1}{R'^2_5(\text{mix})} u_c^2(R_{\text{prep}}) \quad (6)$$

It takes into account the contribution of the uncertainty of the measured and prepared isotope amount ratios for the respective mixture.

The correction factor K_5 was calculated by iteration for each mixture (Table 5). The average mass discrimination factor is $K_5 = 1.009\,94$ with an associated combined standard uncertainty of $u_c(K_5) = 0.000\,89$ (0.09%) calculated according to

Table 5

K factors corresponding to the prepared isotope amount ratio of the mixtures obtained after iteration

Mixture	K -factor K_5	$u_c(K_5)$
Mix 1	1.010 139	0.0022
Mix 2	1.010 100	0.0023
Mix 3	1.006 385	0.0020
Mix 4	1.009 711	0.0018
Mix 5	1.013 363	0.0013

$$u_c(K_5) = \frac{1}{\sqrt{5}} \sqrt{\frac{\sum_{i=1}^5 u_c^2(K_{5,\text{mix } i})}{5}} \quad (7)$$

which takes into account the five values of K_5 obtained for each mixture. The bias per mass unit, calculated from K_5 , is $\varepsilon = 0.009\,94$ using Eq. (2). As there is only one mass unit difference between ^{196}Pt and ^{195}Pt , the expression of the bias per mass unit is

$$\varepsilon = 1 - K_5 \quad (8)$$

The combined standard uncertainty of the bias per mass unit is equal to $u_c(\varepsilon) = 0.000\,89$ (9%). From this value of the bias per mass unit, the mass discrimination factors, K_i , corresponding to the different isotope amount ratios, R_i , were recalculated [Eq. (2)] and used to correct all the isotope amount ratios measured.

4.2. Determination of the isotopic composition of the enriched materials

The corrected isotope amount ratios of materials B and C (Table 6) led to the isotopic composition as well as the atomic weight of the materials. A complete

Table 6

Isotopic composition and atomic weight of the two isotopically enriched platinum materials B and C

	Mat B	u_c	Mat C	u_c
Amount of reduced Pt (mg)	57.570	0.005	59.441	0.005
Amount of solution (g)	57.624	0.005	60.522	0.005
Pt amount content (mg Pt per g solution)	0.999 06	0.000 12	0.982 14	0.000 16
	Amount fraction (%)	U^* ($k = 2$)	Amount fraction (%)	U^* ($k = 2$)
^{190}Pt	0.001 6 ^b	0.003 2	0.0017 ^b	0.0034
^{192}Pt	0.006 61	0.000 76	0.0069	0.0016
^{194}Pt	1.150	0.022	0.784	0.014
^{195}Pt	97.381	0.022	2.4054	0.0042
^{196}Pt	1.397 5	0.002 4	96.515	0.018
^{198}Pt	0.063 4	0.008 0	0.287	0.010
atomic weight $A_r(\text{Pt})$	194.968 85	0.000 44	195.930 53	0.000 46

^a U : expanded uncertainty with a coverage factor $k = 2$.

^b For isotope ^{190}Pt , it was not possible to detect an ion current so the detection limit was used with a 100% uncertainty stated as combined standard uncertainty on it.

description of these calculations has been reported earlier (Table 6) [20]. For the isotope ^{190}Pt , it was not possible to detect an ion current for both materials B and C. Consequently, the detection limit for $n(^{190}\text{Pt})$ was used and calculated as 3 times the standard deviation of the background count signal divided by the sensitivity. A conservative relative standard uncertainty of 100% was applied to the estimated amount ratio $n(^{190}\text{Pt})/n(^{195}\text{Pt})$.

5. Conclusions

This article describes the purification and isotopic characterisation of two metallic platinum materials enriched in isotopes ^{195}Pt and ^{196}Pt . From these materials, five synthetic isotope mixtures have been gravimetrically prepared with accurately known isotope amount ratios. The values of the respective prepared isotope amount ratios $n(^{196}\text{Pt})/n(^{195}\text{Pt})$ were 0.099 57, 0.397 34, 0.738 00, 3.9976, and 10.005 with relative expanded standard uncertainty (coverage factor $k = 2$) varying from 1×10^{-3} to 2.8×10^{-3} .

These mixtures were used to determine a factor to correct the mass discrimination effects occurring in the inductively coupled plasma mass spectrometer. Measurements of these samples showed that mass dependent effects occurring during ICP-MS measure-

ments were independent from the value of the measured isotope amount ratio $n(^{196}\text{Pt})/n(^{195}\text{Pt})$ in the range 0.1–10 usually used for ICP-MS measurements. These mixtures were used to calibrate the isotope amount ratios of a Pt isotope reference material (IRMM-010) with a natural isotopic composition [20]. They were also used to certify an IRM enriched in isotope ^{194}Pt [17].

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