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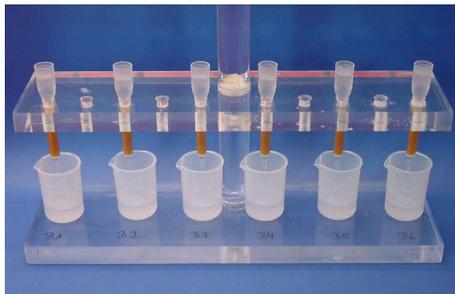
TECHNICAL NOTE

A new two-stage separation procedure for the IDMS based quantification of low Pd and Pt amounts in automotive exhaust emissions

Jochen Vogl,*[a] Christian Meyer,[a] Maren Koenig,[a] Dorit Becker,[a] Janine Noordmann,[b] Olaf Rienitz ,[b]
5 **Athanasios Mamakos,[c,d] and Francesco Riccobono [c]**

A two step separation procedure for the quantification of Pd and Pt in automotive exhaust emissions using isotope dilution mass spectrometry was established using a combination of cation
10 **and anion exchange chemistry. AG 50 W-X12 was used as cation exchange resin and DGA as weakly basic anion exchange resin. This procedure enabled the effective separation of Pd and Pt from the matrix and from interfering elements. Additionally Pd and Pt were collected in separate chromatographic fractions, which increased the precision of the isotope ratio determination by separate measurements using a single collector sector field ICPMS. The analytical procedure was**
15 **validated by analysing synthetically prepared samples and the certified reference materials BCR-723 (road dust) and IAEA-450 (algae). For the SI-traceable results complete uncertainty budgets were calculated yielding relative expanded uncertainties ($k = 2$) of $\approx$ 1 % for analyte masses in the ng range. Procedure blanks of 55 pg Pd and 3 pg Pt were obtained. Detection limits were calculated as 12 pg for Pd and 7 pg for Pt. Additionally, Pd and Pt blank levels of different filter materials are**
20 **presented as well as first results for automotive exhaust particles collected on cellulose filters.**

Introduction

Isotope dilution mass spectrometry (IDMS) is considered as one of the most powerful and most accurate method for determining amounts of substance.[1] Contrary to other calibration approaches,
25 IDMS does not directly suffer from long-time changes or drifts in instrument sensitivity. Moreover, provided isotopic exchange between 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
30 ratios are largely unaffected by instrumental drift, setup or by matrix, unless an isobaric interference is present. Due to these adavantages IDMS often is applied for quantification of platinum group elements (PGE), either for characterization of reference materials or for geochemical research.[2] Besides the spike
35 availability one crucial point is the separation of isobaric and molecular interferences, when using inductively coupled plasma mass spectrometry (ICPMS). This is more important the lower the PGE mass fractions are in the sample.

PGE analysis is in the focus since decades and therefore
40 several analyte separation and preconcentration procedures have been applied in the past. The most classical approach is the NiS fire assay, where a relatively large amount of sample (several g) is fused with a mixture of $Na_2B_4O_7 \cdot 10 H_2O$, Ni and S. After cooling down a NiS bead is formed, which contains the PGEs.
45 The complete procedure, however, is complex and laborious. As a consequence of the added reagents the blanks for Pd (60 pg -

230 pg) and Pt (60 pg - 490 pg) are relatively high and variable.[3] Additionally, a high concentration of salts is still present in the analyte solution after dissolution of the NiS bead. This additional
50 matrix disturbes the isotope ratio determination and makes the procedure unsuitable for IDMS based reference measurements unless another separation is being carried out. Furthermore, some isobaric interferences such as Cd and Hg are still present.[3]

The most commonly used separation procedures in IDMS are
55 column chromatography based techniques, as they can be easily scaled to the analytical needs. Blanks and recoveries can be optimized and most important the analyte fraction is obtained in an aqueous, often acidified solution, which in most cases can be used directly for measurements. For PGE analysis cation as well
60 as anion exchange resins have been used. When using cation exchange resins such as AG 50W-X8 in combination with hydrochloric acid Pd and Pt run through in form of chloro-complexes, while many cations are retained. Recoveries for Pd and Pt are close to 100 % and blank levels are comparativley low
65 (40 pg Pt), allowing detection limits (LOD) of 86 pg/g for Pd and 26 pg/g for Pt.[2,4] A major disadvantage is the coelution of some elements (e.g. Cd, Hg, Zr, Hf, W) generating isobaric and molecular interferences, which requires a contionuous monitoring of these elements and consequently a mathematical interference
70 correction, both increasing the measurement uncertainty and detection limits (LOD). Anion exchange resins such as AG 1-X8 offer a strong retention of Pd and Pt chloro complexes formed in hydrochloric acid. However, the retention is too strong for a quantitative elution under normal conditions and therefore the

recoveries are rather low (Pd 19 % - 35%; Pt 11 % - 22 %) while blanks are relatively high (85 pg Pd, 140 pg Pt).[5] This observation lead to a modification in the authors' lab such that the anion exchange resin was digested after sample loading and washing. This technique has been applied for the determination of the Pt mass fraction in CCQM-K75 [6] and earlier by Brzezicka et al. who ashed the anion exchange resin in a muffle furnace.[7] The advantage is a complete recovery combined with a removal of nearly all interferences to the expenses of comparatively high blanks (for Pt comparable to NiS fire assay). Hann et al. and Kanitsar et al. optimized the AG 1-X8 separation procedure such that total recoveries around 85 % and low LODs for urban aerosol samples (Pd: 25 - 36 pg/filter; Pt: 20 - 44 pg/filter) were obtained.[8,9] The main drawback here is the coelution of interfering elements such as Cu, Zn and Sr (recoveries ≈ 40%, 87 %, 35 %) with the Pd containing fraction (14 mol/L HNO_3).[8]

Alternative separation techniques for Pt such as solid phase extraction using activated carbon[10], imprinted polymers[11] or separation using immobilized microorganisms[12] were published. The solid phase extraction techniques offer LODs of ≈ 0.3 ng/mL for Pt being unsuitable for pg amounts. The separation by immobilized microorganisms yield a sufficiently low LOD (≈ 20 pg/mL) for Pt, but the eluant is an aqueous 5 mol/L NaCl solution, which is unsuitable for ICPMS analysis.[12]

None of the described separation procedures fulfill the requirements for IDMS based quantification of Pd and Pt in automotive exhaust emissions collected on filter samples with total Pd and Pt masses in the low ng to the low pg range. These requirements are low procedure blanks (< 100 pg), moderate to good recovery (> 50 %) and removal of all elements generating isobaric and molecular interferences in ICPMS. Additionally, Pd and Pt should be obtained in the same separation procedure, but in separate elution fractions to enable smaller measurement uncertainties. Therfore, we developed a two-stage separation procedure fullfilling these requirements and enabling SI-traceable results for pg amounts of Pd and Pt in automotive exhaust emissions.

Experimental

IDMS strategy

Samples and procedure blanks were spiked with 0.3 g - 0.5 g of Pd and Pt single spike solutions with ^{106}Pd and ^{194}Pt mass fractions of 10 ng/g. Spike and back-spike were measured in each IDMS sequence. Using this approach the calculation of the K-factor for correcting mass discrimination effects is not necessary as the K-factor cancels down in the IDMS equation.[1,13,14] A full uncertainty budget was calculated for each individual analysis as described earlier.[13]

The uncertainty for the mean value of independent blends was calculated by combining the uncertainties of the single results as described in eqn. 1 and adding the standard deviation of the mean as described in eqn. 2. This approach compensates for not completely known and considered uncertainty contributions deriving from sample preparation or analyte and/or matrix inhomogeneity.

$$\bar{u} = \sqrt{\frac{\sum u_i^2}{n}} \qquad \text{eqn. 1}$$

$$u_{total} = \sqrt{\bar{u}^2 + s_{mean}^2} \qquad \text{eqn. 2}$$

Chemicals, reagents, standards and reference materials

High purity water, double distilled acids and precleaned labware was used for all preparation, as described earlier.[12] H_2O_2 solution was purchased from Merck in suprapure quality. All listed reagents showed blank levels ≤ 0.4 pg/g for Pd and ≤ 0.2 pg/g for Pt. Elemental solutions used for interference checks and for simulating the matrix were prepared from ICP standard solutions (Merck, Germany). The Cl resin, the Ni resin and the DGA resin were purchased from Triskem Int., France. The AG 1-X8 resin and the AG 50W-X12 resin were both purchased from BioRad, Germany.

IAEA-450, a reference material certified for Pt in algae, was purchased directly from the International Atomic Energy Agency (IAEA, Austria). BCR-723, a reference material certified for PGEs in road dust, was purchased from the Institute for Reference Materials and Measurements (IRMM, Belgium).

The Pd and Pt single spikes used in this work (Table 1) were diluted solutions of the candidate reference materials ERM-AE140 and -AE141, which have been characterized by MC-ICPMS at PTB using two back-spikes each for Pd and Pt.

Table 1 Mass fraction and amount-of-substance fraction of the Pd and Pt single spikes used in this work

Spike solution	Mass fraction in ng/g		Amount-of-substance fraction	
	$w(^{106}\text{Pd})$	$w(^{194}\text{Pt})$	$n(^{106}\text{Pd})/n(\text{Pd})$	$n(^{194}\text{Pt})/n(\text{Pt})$
^{106}Pd	9.8624 (22)	n/a	0.985429 (31)	n/a
^{194}Pt	n/a	10.5625 (32)	n/a	0.91430 (36)

Sample preparation

Digestion of the samples and reference materials was performed in an Ethos 1600 microwave system (MLS, Germany) in 100 mL teflon vessels containing a 10 mL acid mixture of H_2O_2, H_2O, HCl and HNO_3 in a volumetric ratio of 2:2:3:3. Samples and spike were added under full gravimetric control.[13] Using a heating rate of 7.5 °C/min the vessels were heated up to 200 °C, which was kept constant for 30 min followed by a cooling step (45 min). Alternatively a high pressure asher (HPA, Anton Paar, Austria) digestion procedure was applied, which showed no differences in Pd and Pt results. Here, quartz vessels with a volume of 90 mL were filled with 6 mL of the above described acid mixture with a volumetric ratio of 1:1:2:2. The vessels were heated up in 1 h to 300 °C, which was kept constant for 1 h and followed by a cooling step.

Subsequently the digested samples were dried down in 15 mL Savillex beakers and redissolved in 0.1 mol/L HCl for chromatographic separation. The different resin materials, which were suspended in high purity water prior to use, were filled in 2 mL Eichrom columns (Triskem Int., France) and washed several times followed by a conditioning step. Then the samples were evaporated to dryness again, were finally redissolved in 2 % HCl and handed over to the isotope ratio determination.

All sample preparation was carried out under clean air conditions (< class 1000, MK Versuchsanlagen, Germany).

Mass spectrometric measurements

All, quantitative as well as isotope ratio, measurements were performed on an Element 2 sector field ICPMS (Thermo Fisher Scientific, Germany) in low resolution. Sample introduction was realized in self-aspirating mode using a MicroMist nebulizer, a

cyclonic glass spray chamber (both GlasExpansion, Australia) and an ASX-520 autosampler (Cetac, US). All measurements were performed in 2 % HCl using polyethylene sample tubes.

The optimum settings for isotope ratio determinations are listed in Table 2. For Pt isotope ratio determinations m/z 194 (spike isotope) and 195 (natural reference isotope) were measured and in the case of Pd m/z 105 (natural reference isotope), 106 (spike isotope) and 111 were measured. The latter mass was used for monitoring any possible isobaric Cd interference.

Table 2 Instrumental parameters for Pd and Pt isotope ratio determinations

Parameter	Value description
Autosampler	Cetac ASX 520
Aspiration mode	Self-aspirating
Nebulizer	GE MicroMist 100 µL/min
Spray chamber	GE Cyclonic spray chamber
Cones	Ni sampler and skimmer
Cool gas flow rate	16 L/min
Auxiliary gas flow rate	0.9 – 1.05 L/min
Sample gas flow rate	1.00 – 1.15 L/min
Guard electrode	On
Mass resolution mode	Low Resolution (m/Δm ~ 300)
RF power	1250 W
Scan type	E Scan
Magnet settling time	0.001 s
Sample time	0.002 s
Samples per peak (100%)	200
Integration window	5 %
Runs / passes	10 / 400
Total measurement time	Pt: 2.49 min, Pd: 4.13 min
Intensity in counts/s for 1 ng/g	^{194}Pt 250.000; ^{105}Pd 280.000
Intensity in counts/s for blank	^{194}Pt ≈ 300; ^{105}Pd ≈ 600 (2 % HCl)
Uptake time / rinse time	2.5 min / Pt: 5 min, Pd: 5 – 7 min
Detector Mode / deadtime	Counting Mode / 5 ns
Long term precision, isotope ratio of	0.27 % for ^{105}Pd/^{106}Pd (n = 13)
back-spike (1 s_{rel})	0.2 % for ^{194}Pt/^{195}Pt (n = 16)
Precision, single measurement,	0.3 % for ^{105}Pd/^{106}Pd
isotope ratio of back-spike (1 s_{rel})	0.2 % for ^{194}Pt/^{195}Pt

Samples were measured in blocks of 3 to 4 samples bracketed by measurements of the back-spike solution as a reference for instrumental drift control. Spike measurement was made with 6 individual spike aliquots at the end of each sequence, followed by back-spike measurement. Linear, time dependant drift correction was calculated referring to the first back-spike measurement in the sequence. Isotope ratios outside 3 s of the mean value were not used for calculation. Typical drift effects during one sequence were less than - 0.5 % for Pd and -0.2 % for Pt isotope ratios.

Results and discussion

Tested resin materials

In order to fulfill the requirements for the separation procedure, different resin materials were tested using a synthetic sample solution. The composition of this test solution was based on a screening of filters loaded with automotive exhaust emissions (Table 3) extended by elements potentially causing isobaric or molecular interferences on Pd and Pt isotopes in ICPMS.

The Cl resin was developed as an extraction chromatographic resin for Cl and I when loading the resin with silver. It also offers increased selectivity for PGE and gold. Pd and Pt (5 ng each) were loaded in 3 mol/L HCl and were eluted by HCl or HNO$_3$ with decreasing acid concentration. Even with additional elution steps using H$_2$O and NH$_4$OH as eluants, Pd recoveries were

below 15 %, whereas Pt recoveries were 60 % to 75 %. The low Pd recoveries made the resin unsuitable for the intended task.

The active sites of the "Ni resin" were diacetyl dioxime groups, which are fixed to the resin material and which form binary complexes with Ni, but also with Pd and Pt which are in the same group of the periodic system of the elements.[15] Several tests with the "Ni resin", where the sample was loaded either in ammonia (1 mol/L), citrate (pH 8 to 10) or water and eluted with HCl or HNO$_3$ (3 mol/L up to concentrated acid) resulted in recoveries of ≤ 45 % for Pd and ≤ 28 % for Pt, both coeluting in the same fraction. Due to this results the "Ni resin" was not suitable for the described task.

The anion exchange resin AG 1-X8 was tested as well and the results were similar to the observations made by Müller and Heumann.[5] The recoveries for Pd and Pt were << 50 % due to the strong retention behaviour of the resin, which also causes relatively high blank levels (0.1 ng level). Additionally, some interferences such as Mo, W, Hg partially coelute with Pd and Pt. The digestion of the resin after loading the sample is only partially successfull due to relatively high blanks (75 pg Pd, 135 pg Pt) and difficult handling (sticky resin material). Additional washing steps reduced the Pd and Pt recovery to < 90 %, while blanks of interfering elements remained high (600 pg Cd, 80 pg Ru, 8 ng Hg). These results made the AG 1-X8 resin unsuitable for IDMS analysis of Pd and Pt in the pg range.

In the case of the cation resin AG 50W-X12 the sample was loaded and eluted in 0.1 mol/L HCl. Pd, Pt and all elements, which form negatively charged chloro-complexes or which were weakly bound under these conditions such as Ge, Ru, W and Ir and partially Rb and Hg coeluted in the first fraction. The recoveries for Pd and Pt were between 95 % to 100 % and the obtained blanks were below 10 pg for Pd and Pt. Due to the incomplete matrix/interference separation the AG 50W-X12 resin did not fulfill the requirements.

Table 3 Composition of the synthetic test solution expressed as analyte mass in a test portion of 5 mL compared to the total analyte mass in the Pd and Pt fraction after separation obtained by ICPMS (Fig. 1)

Element	Analyte mass in ng [a]		Element	Analyte mass in ng	
	Test solution	Pd/Pt fraction		Test solution	Pd/Pt fraction
Pd	5	4 (1)	Sr	10	< 0.1 [b]
Pt	5	5 (1)	Ga	20	< 0.3
Ge	1	< 0.1	Mo	20	< 0.65
Rb	1	< 0.05	Pb	20	< 0.5
Y	1	< 0.03	Ni	200	< 3
Zr	1	< 0.5	Cu	200	< 10
Ru	1	< 0.2	K	600	< 50
Cd	1	0.06 (2)	Ca	600	< 100
Hf	1	< 0.06	Mg	2000	< 100
W	1	< 0.05	Zn	2000	< 100
Ir	1	< 1	Na	16800	< 1000
Hg	1	< 0.05			

[a] Relative expanded uncertainties of the gravimetrically prepared test solutions are < 1 %; expanded uncertainties for the analyte masses in Pd/Pt fraction are given in brackets.

[b] Determined after 1st separation step (cation separation)

DGA (exactly TODGA), which is a weak anion resin with N,N,N',N'-tetra-n-octyldiglycolamid functional groups, is designed for actinide and lanthanide separation. This resin also retains Pd and Pt when loaded in 3 mol/L HCl. In the first tests
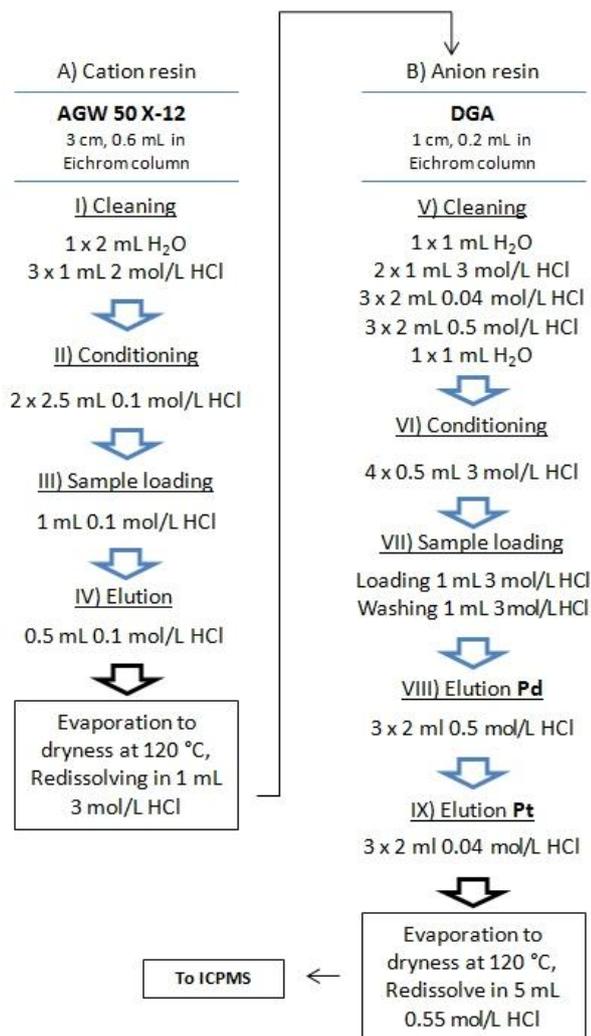
Fig. 1 Two-stage procedure for separating Pd and Pt from the matrix and interfering element

75 % of the Pd and the Pt was coeluted with 0.04 mol/L HCl. Unfortunately, also Cd, Ga, Mo, Y, Zn and Ge coeluted and blanks were relatively high for Pd ($\approx$ 300 pg) and Pt ($\approx$ 50 pg). The addition of extra washing and eluting steps reduced the blanks to < 50 pg for Pd and < 1 pg for Pt and enabled the elution of Pd (0.5 mol/L HCl fraction) prior to Pt (0.04 mol/L HCl fraction). Due to the coelution of some interfering elements the DGA resin did not completely fulfill the specified requirements.

Combination of cation and anion exchange

As the DGA resin nearly fulfilled the requirements excepting the coelution of some interferences, it was combined with the AG 50W-X12 resin, which offers a complementary retention meachanism, a complete the recovery and lowest blanks. The combination of both separations is explained in the following and a detailed flow chart is displayed in Fig. 1.

After filling the AG 50W-X12 resin in Eichrom columns the resin was cleaned with H_2O and HCl, followed by conditioning steps with 0.1 mol/L HCl. Then the sample was loaded and eluted in 0.1 mol/L HCl. The collected Pd/Pt fraction was evaporated to dryness and redissolved in 3 mol/L HCl. For the second separation 0.2 mL of the DGA resin was filled in Eichrom columns, followed by an extensive cleaning with H_2O and HCl in

order to reduce the blank. Then the resin was conditioned followed by the sample loading and cleaning, all with 3 mol/L HCl. Pd was eluted with 3 x 2 mL of 0.5 mol/L HCl and Pt was subsequently eluted with with 3 x 2 mL of 0.04 mol/L HCl. Thereafter, the sample was evaporated to dryness and redissolved in 5 mL of 2 % HCl. The so prepared samples were used for isotope ratio determinations by ICPMS. The total recovery of the whole separation procedure was tested several times during the method development and was also continuously monitored via the spike isotope. The overall recovery was > 50 % for Pd and > 70 % for Pt. A substantial loss took place, because a part of Pt coelutes with Pd from the DGA resin and vice versa. Increasing the recoveries might be possible, potentially at the expenses of a Pd/Pt coelution and an incomplete interference separation. However, recoveries above 50 % are completely sufficient for IDMS analyses, as no severe fractionation effects can be expected, especially for medium and high mass elements.

Beyond analyte recovery, the coelution of interfering elements is of major concern. This was tested by using the test solution displayed in Table 3. The analyte masses for a test portion of 5 mL are given in the first column, while in the second column the remaining analyte masses in the Pd/Pt fraction after the two stage separation are given. These are mainly "less than" values, displaying either the detection limit or the highest value of 7 individual experiments, demonstrating that most elements can be removed or even reduced by a factor of at least 20.

In order to verify that even very low amounts of interfering elements do not cause biased results, their formation rates have been checked. The main interferences for ^{105}Pd and ^{106}Pd, as listed by Meisel et al. and others,[16,17] are molecular ions (Cu-, Ga-, Zn-argides; Sr-, Rb-, Y-, Zr-oxides) excepting ^{106}Cd. Although ^{106}Cd is separated and has an isotope abundance of only 0.0125, it was continuously monitored showing values at or below the acid blank. The argide interferences were tested with 100 ng/g Cu and Dy standard solutions and showed formation rates of < 0.005 % for ^{65}Cu^{40}Ar and ^{156}Dy^{40}Ar. The oxide formation rate was < 0.07 % for ^{88}Sr^{16}O and < 0.01 % for ^{88}Sr^{16}O^{1}H, tested with a Sr standard solution (100 ng/g). The oxide formation rate tested with Y (100 ng/g) resulted in a value of 9 %, which is far too high. As the isotope ratio of ^{89}Y^{16}O/^{89}Y^{17}O did not at all agree with the ^{16}O/^{17}O ratio and as significant impurities of Zn, Ga and Sr were present in the standard, a significantly lower formation rate is probable. Nevertheless, Y was completely separated and even a high oxide formation rate would not bias the result.

In the case of ^{194}Pt and ^{195}Pt only molecular interferences such as Gd-, Sm- and Tb-argides and chlorides as well as Hf- and Yb-oxides can occur.[16,17] These formation rates were tested as well using Sr, Tb, Dy and Gd standard solutions, each containing 100 ng/g. The resulting formation rates were < 0.004 % for ^{156}Dy^{40}Ar, < 0.009 % for ^{159}Tb^{35}Cl and < 0.07 % for ^{88}Sr^{16}O. Combining the information of the molecular ion formation rates and the maximum element masses after separation it can be stated that all interferences were reduced such that the resulting bias on the isotope ratio of ^{106}Pd/^{105}Pd and ^{195}Pt/^{194}Pt is well below 3 ‰, which is the precision of the isotope ratio determination for both.

Procedure blanks

The quantification of procedure blanks is of utmost importance for accurate Pd and Pt analysis in the pg range. As preliminary test blank digestions were carried out in the digestion vessels. The resulting blank solutions were analysed by ICPMS resulting

in blanks of (9 ± 3) pg Pd and (2 ± 1) pg Pt for the HPA quartz vessels (*n* = 9) and (11 ± 6) pg Pd and (2 ± 2) pg Pt for the microwave TFM vessels (*n* = 38), given with the corresponding standard deviation.

Then procedure blanks on the complete analytical procedure were performed. As the largest part of the analyte blank derives from the column separation, the procedure blanks were spiked after column separation to avoid any overestimation of the procedure blank due to incomplete spike recovery. The first procedure blanks with ≈ 160 pg for Pd and ≈ 22 pg for Pt nearly fulfilled the requirements (< 100 pg). Further improvement lead to procedure blanks of (55 ± 13) pg Pd and (3 ± 4) pg Pt, with the corresponding standard deviation (n=18). The procedure blanks are nearly constant within each sample preparation series (n=3; *s* ≤ 4 pg Pd; *s* ≤ 2 pg Pt), while they vary slightly more between the six series. Therefore, the LODs are calculated for each sample preparation series separately and the maximum value of these individual LODs, which are LOD$_{Pd}$ = 12 pg and LOD$_{Pt}$ = 7 pg, were taken as LOD for the analytical procedure. These procedure blanks and the resulting LODs are sufficient for determining Pd and Pt masses in the ng to pg range.

Tested filter materials

Several filter materials were tested regarding net blank levels (procedure blank corrected) and ease of digestion.

Texture filters made from borosilicate microfibers reinforced with woven glass cloth and bonded with PTFE showed very high Pt blank values of 17 ng, whereas quartz fibre filters showed very high Pd blank values of 2 ng. The highest blank values of all tested filter materials made these filters unsuitable for Pd and Pt analysis in the pg range.

Polycarbonate filters have a very smooth surface, from which soot particles easily fall off. Blank measurments reveal a dramatical drop in the Pd and Pt spike recovery down to < 10 % presumably caused by the dissolved filter matrix, which made the quantification by IDMS impossible. A semiquantitative estimation showed blank values in the range of the Pd and Pt procedure blanks. The specific characteristics made polycarbonate filters unsuitable for these analyses.

Teflon filters also offer a smooth surface similar to the polycarbonate filters. Teflon filters could not be digested. Leaching at temperatures above 150 °C lead to a shrinkage of the filter material, which may enclose particles. Due to this and Pt blanks of ≈ 57 pg, teflon filters also were assessed as unsuitable.

Cellulose and cellulose-ester filters hold the collected particles stronger than teflon and polycarbonate filters due to the textile type structure. Both filter types could be completely digested and offer the lowest Pd and Pt blank values of the tested filter materials: (21 ± 3) pg Pd and (39 ± 8) pg Pt for cellulose filter, (35 ± 2) pg Pd and (10 ± 4) pg Pt for cellulose-ester filter, given with expanded uncertainties (*k* = 2). Thus, cellulose and cellulose-ester filter are suitable for the intended task.

Method validation

The method validation is based on the use of reference samples and on the calculation of complete uncertainty budgets according to the *Guide to the Expression of Uncertainty in Measurement*.[18] As for Pd and Pt in automotive exhaust emissions no suitable reference material were available, synthetic samples were prepared by doping the test solution (Table 3) on cellulose filters. Additionally, the reference materials BCR-723 and IAEA-450

were used. All samples were prepared such that a total amount of Pd and Pt from 1 ng to 10 ng was used, resulting in sample masses of 75 mg to 160 mg for BCR-723 and IAEA-450. The determined Pd and Pt mass fractions (Table 4), which were dry mass corrected, represent the mean of 3 independent analysis of the synthetic samples and 6 independent analysis of BCR-723 and IAEA-450, respectively.

The relative expanded measurement uncertainties (*k* = 2) for total Pd masses from 1 ng to 10 ng determined in one sample aliquot are typically ≤ 1 %. The significantly larger uncertainty for the mean value of BCR-723 is due to the spread between the 6 independently processed samples. It can be noted that the determined Pd mass fractions agree very well with the reference values within the associated uncertainties (Table 4). Standard deviations from 1.4 ng/g to 2.5 ng/g for 10 independent measurements of BCR-723 have been reported before by Alsenz et al.[19], while Sutherland reported a spread in published Pd mass fractions from 3.7 ng/g to 8 ng/g.[20] The GeoReM database showed a spread of Pd mass fractions from 4 ng/g to 9 ng/g and a twofold standard deviation of 2.4 ng/g for the listed IDMS results (Table 4).[21] These data clearly point to a significant inhomogeneity of BCR-723 for sample masses ≤ 0.1 g.

Similar to Pd the relative expanded measurement uncertainties (*k* = 2) for total Pt masses from 1 ng to 10 ng determined in one sample aliquot are typically ≤ 1 %. The significantly larger uncertainty for the mean value of the synthetic sample is due to a relatively large variation in the filter blanks. In the case of BCR-723 it is due to the spread between independenly processed samples. For IAEA-450, which homogeneity was demonstrated in CCQM-K75,[6] the relative expanded measurement uncertainty (*k* = 2) for the mean value is 1.5 % and thus only slightly larger than those of the single values. The determined Pt mass fractions of the synthetic sample and of the certified reference material IAEA-450 agree very well with the reference values within the associated uncertainties (Table 4).

Table 4 Determined Pd mass fractions compared with reference values for selected samples and reference materials used for method validation, given with expanded uncertainties (*k* = 2) or 2 *s* (GeoReM) in brackets.

Analyte	Sample	Matrix	Mass fraction in ng/g		
			Determined	Reference [a]	GeoReM [b]
Pd	Synthetic	Filter + Interf.	9.57 (10)	9.486 (6)	n/a
Pd	BCR-723	Road dust	6.5 (2.2)	6.1 (1.9)	5.3 (2.4)
Pt	Synthetic	Filter + Interf.	10.45 (34)	10.504 (6)	n/a
Pt	BCR-723	Road dust	88.5 (4.3)	81.3 (2.5)	89 (14)
Pt	IAEA-450	Algae	74.2 (1.1)	74 (2)	n/a

[a] Reference: gravimetric value for synthetic sample; certified value for BCR-723 and IAEA-450.
[b] Mean of the 3 IDMS results listed in GeoReM for BCR-723.[21]

In the case of BCR-723 a value slightly higher than the certified value has been obtained, which, however, agrees very well with the IDMS mean value obtained from the GeoReM database (Table 4).[21] Regarding the inhomogeneity of BCR-723 the situation is similiar to those for Pd: the spread of the analytical results in Sutherland's review on BCR-723 (74 ng/g to 97 ng/g) and in the GeoReM database (64 ng/g to 101 ng/g) clearly point to an inhomogeneity of the material with respect to Pt.[20,21] Based on the results for the reference materials and the establishment of complete uncertainty budgets, the newly developed IDMS procedure for Pd and Pt is fully validated.

Table 5 Pd and Pt masses and Pd and Pt emission in automotive exhaust particles collected on cellulose filters with the associated expanded uncertainty ($k = 2$) in brackets

Filter No.	Engine	Test cycle [a]	Analyte mass per filter in pg		Emission rate	Emission rate	
			Pd	Pt	unit	Pd	Pt
1	Gasoline	CADC 7°C	6126 (61)	338 (5)	ng/km	47.7 (1.8)	2.63 (10)
2	Gasoline	NEDC	911 (10)	4295 (25)	ng/km	33.3 (1.3)	156.9 (5.9)
3	Gasoline	CADC	5732 (57)	372 (9)	ng/km	51.6 (2.0)	3.35 (15)
4	Diesel	WHTC cold	28 (5)	336 (18)	ng/kWh	3.34 (64)	40.1 (3.0)
5	Diesel	WHTC hot	17 (5)	13 (15)	ng/kWh	2.10 (66)	1.6 (1.8)
6	Diesel	WHTC hot	100 (4)	54 (13)	ng/kWh	12.55 (82)	6.8 (1.7)

[a] CADC: Common Artemis Driving Cycle; NEDC: New European Driving Cycle; WHTC: World Harmonized Transient Cycle for heavy duty engines. NEDC and WHTC cold tests were conducted with the engine cold, while the first CADC test (Filter No. 1) was conducted at a test cell temperature of 7°C, instead of the reference 22°C.

Application to automotive exhaust samples

After validation the analytical procedure was applied to a first subset of automotive exhaust particles collected on cellulose filter to demonstrate the applicability of the developed procedure. The filter samples were collected at the European Commission - Joint Research Centre in Ispra(Italy) from the diluted exhaust of a heavy-duty diesel engine equipped with a wall-flow particulate filter and a gasoline direct injection passenger car, in accordance to the applicable European legislation (UNECE Regulations 49 and 83). The samples were taken as a whole and were analysed following the above described procedure. The results for the Pd and Pt amount were expressed in pg per filter and are listed in Table 5 together with the corresponding exhaust emission rates per distance driven (ng/km) or per consumed energy (ng/kWh). An exemplary, complete uncertainty budget for the quantification of the Pt emission rate as determined in filter No. 4 can be obtained from the electronic supplement.

The achieved relative expanded uncertainty of the determined Pd and Pt amounts was ≤ 1% for the gasoline samples with analyte masses in the ng range. The Pd and Pt emission rates for gasoline driven cars agree well with those reviewed by Ravindra et al. ranging from 7 ng Pt/km to 124 ng Pt/km and from 6 ng Pd/km to 250 ng Pd/km.[22]

The diesel engine emission rates were approximately one order of magnitude lower, suggesting an efficient collection of Pd and Pt in the particulate filter. Still, the methodology was sensitive enough to detect Pd emissions for those cases with a 4 % to 30 % relative expanded uncertainty. The collected Pt mass was close to the blank level in one test, and 4 to 19 times higher in the other 2 tests. Emission rates for diesel heavy duty vehicles retrofitted with a diesel particulate filter were reported ranging between 1.1 ng Pt /km and 4.2 ng Pt/km.[23] Emission rates for a diesel passenger car (150 hp) fitted with a diesel particulate filter were reported from 0.47 ng Pd /km to 1.01 ng Pd/km and from 2.25 ng Pt /km to 5 ng Pt/km.[24] Assuming a consumption of 6.5 L diesel per 100 km, an average density of 0.83 kg/L and an average heat value of 11.8 kWh/kg for diesel fuel the emission rates convert to emission rates from 0.74 ng Pd/kWh to 1.59 ng Pd/kWh and from 3.53 ng Pt/kWh to 7.85 ng Pt/kWh. These emission rates correspond good with the low emission rates we found. The here presented results are the first SI-traceable results with associated measurement uncertainty allowing comparability with future SI-traceable results.

Additionally, the good analytical sensitivity of the reported procedure will enable detailed investigations on the effect of operating conditions and aftertreatment technologies on vehicular PEG emissions, as well as the suitability of the established sampling procedures.

Conclusions

A two-stage separation procedure has been developed for the IDMS based quantification of Pd and Pt in automotive exhaust particles collected on cellulose filters. All interfering elements were separated by the developed procedure and Pd and Pt are obtained in different fractions with total recoveries > 50 % for Pd and > 70 % for Pt. This enables the separate measurement of Pd and Pt leading to more precise Pd and Pt isotope ratios in the spiked samples. The achieved relative expanded uncertainties ($k = 2$) are ≤ 1 % for analyte masses in the ng range. Procedure blanks are 55 pg Pd and 3 pg Pt. Calculated detection limits are $LOD_{Pd} = 12$ pg and $LOD_{Pt} = 7$ pg, respectively. The procedure has been validated by using the certified reference materials BCR-723 and IAEA-450 combined with the setup of a complete uncertainty budget. The validated procedure was succesfully applied to automotive exhaust particles collected on cellulose filter. As demonstrated by the analysed reference materials the newly developed procedure can easily be applied to accurately determine Pd and Pt mass fractions in biological and environmental materials.

Notes and references

[a] *BAM Federal Institute for Materials Testing and Research, Unter den Eichen 87, 12205 Berlin, Germany. Fax: +49 30 8104 3527; Tel: +49 30 8104 1144; E-mail: jochen.vogl@bam.de*
[b] *Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany*
[c] *European Commission Joint Research Centre Ispra, Institute for Energy and Transport, 21027 Ispra, Italy*
[d] *current address: AVL List GMBH, Hans-List-Platz 1, 8020 Graz, Austria*

1   J. Vogl, *Journal of Analytical and Atomic Spectrometry*, 2007, **22**, 475.

2   D. Savard, S. J. Barnes and T. Meisel, Geostandards and Geoanalytical Research, 2010, **34**, 281.

3   G. Ravizza and D. Pyle, *Chemical Geology*, 1997, **141**, 251.

4   T. Meisel, N. Fellner and J. Moser, *J. Anal. At. Spectrom.*, 2003, **18**, 720.

5   M. Muller and K. G. Heumann, *Fresenius J. Anal. Chem.*, 2000, **368**, 109.

6   A Shakhashiro, A Toervenyi, S Gaudino, S Rosamilia, M Belli and G C Turk, *Metrologia*, 2011, **48**, 08002 doi:10.1088/0026-1394/48/1A/08002

7   M. Brzezicka and I. Baranowska, Spectrochimica Acta Part B: Atomic Spectroscopy, 2001, **56**, 2513.

8   S. Hann, G. Koellensperger, K. Kanitsar and G. Stingeder, J. Anal. At. Spectrom., 2001, **16**, 1057.

9   K. Kanitsar, G. Koellensperger, S. Hann, A. Limbeck, H. Puxbaum and G. Stingeder, J. Anal. At. Spectrom., 2003, **18**, 239.

10   D. Li, X. Chang, Z. Hu, Q. Wang, Z. Tu and R. Li, *Microchimica Acta*, 2011, **174**, 131.

11   B. Lesniewska, M. Kosinska, B. Godlewska-Zylkiewicz, E. Zambrzycka and A. Wilczewska, *Microchimica Acta*, 2011, **175**, 273.

12   J. Malejko, M. Szygałowicz, B. Godlewska-Żyłkiewicz and A. Kojło, *Microchimica Acta*, 2012, **176**, 429.

13   J. Vogl and W. Pritzkow, *Mapan*, 2010, **25**, 135.

14   J. Vogl, M. Koenig, W. Pritzkow and G. Riebe, *J. Anal. At. Spectrom.*, 2010, **25**, 1633.

15   G. Basu, G. M. Cook and R. L. Belford, *Inorg. Chem.*, 1964, **3**, 1361.

16   T. Meisel, N. Fellner and J. Moser, *J. Anal. At. Spectrom.*, 2003, **18**, 720.

17   F. Vanhaecke, M. Resano, M. Pruneda-Lopez and L. Moens, *Anal. Chem.*, 2002, **74**, 6040.

18   JCGM 100:2008, *Evaluation of measurement data — Guide to the expression of uncertainty in measurement*, BIPM, 2008

19   H. Alsenz, F. Zereini, C. L. S. Wiseman and W. Puttmann, *Anal. Bioanal. Chem.*, 2009, **395**, 1919.

20   R. A. Sutherland, *Anal. Chim. Acta*, 2007, **582**, 201.

21   K. P. Jochum, U. Nohl, K. Herwig, E. Lammel, B. Stoll and A. W. Hofmann, Geostand. Geoanal. Res., 2005, 29, 333.

22   K. Ravindra, L. Bencs, R. Van Grieken, *Sci. Total Environ.*, 2004, **318**, 1-43.

23   S. Hu, J. D. Herner, M. Shafer, W. Robertson, J. J. Schauer, H. Dwyer, J. Collins, T. Huai and A. Ayala, *Atmospheric Environment*, 2009, **43**, 2950.

24   W. R. L. Cairns, A. De Boni, G. Cozzi, M. Asti, E. M. Borla, F. Parussa, E. Moretto, P. Cescon, C. Boutron, J. Gabrieli and C. Barbante, *Anal. Bioanal. Chem.*, 2011, **399**, 2731.

25   Emerging requirements for measuring pollutants from automotive exhaust emissions: http://www.ptb.de/emrp/partemission.html. Last accessed 03 November 2014