Speciation of Pt(II) and Pt(IV) in spiked extracts from road dust using on-line liquid chromatography-inductively coupled plasma mass spectrometry

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Abstract

The emission of platinum from automobile catalytic exhaust converters is well known and the accumulation of Pt in road dust has been studied by the analysis of total Pt contents. However, there are few studies on the speciation of the emitted Pt-compounds in the environment. A separation method with HPLC-UV has been developed by Nachtigall et al. [Chromatogr. A 775 (1997) 197] with aqueous standards of Pt(II)- and Pt(IV)-chloro complexes. Due to the limited selectivity and sensitivity of the UV-detection this method is not suitable for Pt-speciation in road dust extracts. Therefore, in this study the method of Nachtigall et al. was modified to realize an on-line coupling to ICP-MS with the advantage of Pt-specific detection. Calibration was performed with aqueous standards and spiked road dust extracts. Calibration curves were linear with low residual standard deviation (1.3–3.1% for the aqueous standards) and approximately 10-times lower detection limits compared to the HPLC-UV-method. Moreover, the stability of the model species was investigated using isocratic as well as gradient separation. Isotopic ratios of ^{194}Pt, ^{195}Pt, ^{196}Pt and ^{198}Pt were determined for quality control. A new mathematical correction method for the HfO-interference on the ^{195}Pt-signal was developed. Additionally, the elution pattern of further elements in the road dust extracts was monitored and total element contents were determined in unspiked road dust extracts.
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1. Introduction

Background concentrations of platinum in soils and sediments are in the low microgram per kilogram range as reported by Artelt et al. [1] (5 µg/kg in the earth's crust) and Hodge and Stallard [2] (3.8 µg/kg in oceanic sediments). High natural concentrations are found in deposits, e.g. in South Africa (4–10 mg/kg) [2]. About 125 t of platinum were produced from these deposits in 1988 worldwide [3]. The traditional application range of platinum was limited to chemically resistant instruments and jewellery. However, the high activity of platinum based homogeneous and heterogeneous catalysts opened

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new fields of application. In particular, automobile catalytic exhaust converters are applied in large numbers since 1975 in the USA [2] and since 1984 in Germany [4]. Already in 1984 the automobile industry in the USA consumed one-half of the total used amount of platinum metals [2]. With the use of cisplatin and further Pt-compounds as chemotherapeutic agents for the treatment of human cancer another new application of Pt-species started in the 1980s [5].

With respect to emissions of Pt into the environment the catalytic exhaust converters are the most relevant sources of the mentioned applications. Due to high temperatures, fast changing oxidative/reductive conditions and mechanical abrasion platinum group elements are released from the catalyst. Consequently, increased Pt contents were measured in the soil directly besides roads, which decrease rapidly with growing distance from the road [4]. For example, a Pt content of 81.3 μg/kg was certified in a dust sample collected in an Austrian road tunnel. This material was produced as certified reference material (CRM 723) for the determination of total contents of Pt, Rh and Pd in road dusts [6].

The high catalytic activity of platinum [7], the high cytotoxic effect of several Pt-compounds [5] and the high allergenic potential in particular of Pt-chloro complexes [8] call for a detailed investigation of the chemical speciation of Pt in contaminated road dusts. Earlier investigations showed that less than 10% of the Pt in road dusts is water soluble and therefore bioavailable [9]. The main part is finely dispersed metallic platinum attached to aluminium oxide particles [1,9].

Previous studies used $PtCl_4^{2-}$ and $PtCl_6^{2-}$ as model compounds for soluble Pt in road dust [9–12] which is supported by the high chloride content of approximately 0.5% in the road dust [9] and the high allergenic potential of the Pt-chloro complexes. The speciation analysis of these compounds has to cope with the rapid transformation by exchange of chloro ligands in aqueous solution as major problem [13]. Spieker et al. proposed a transformation pathway for $PtCl_6^{2-}$ based on EXAFS-measurements [12]. This scheme shows that the hexachloro complex is in aqueous solution only stable at low pH and excess chloride; otherwise, a huge variety of mixed chloro-aquo-hydroxo complexes occurs.

Different techniques have been used so far for the characterization of Pt-chloro complexes in aqueous solutions. Lederer et al. used thin-layer chromatography with densitometric detection (after reaction with iodine or $SnCl_2/HCl$) [11]. Spieker et al. applied EXAFS without need of a separation device [12]. Michalke et al. developed an on-line CE-ICP-MS method [13]. Most promising is the HPLC-UV-method from Nachtigall et al. using an ion exchange column which was able to separate Pt(II)- and Pt(IV)-chloro complexes and additionally to detect transformation products [10]. A major disadvantage of this method is the rather unselective UV-detection which works with aqueous standard solutions, but not with real samples, e.g. an extract from road dust. Moreover, the detection limits of 9 μg Pt/l for $PtCl_4^{2-}$ and 7 μg Pt/l for $PtCl_6^{2-}$ are not sufficient for the low concentrations of these compounds expected in real samples.

An on-line HPLC-ICP-MS coupling would enable Pt-detection with significantly lower detection limits and less interferences. Besides this, it is possible to detect the elution behaviour of species of other trace elements in parallel. However, the chromatographic conditions applied by Nachtigall et al. include up to 300 mM sodium perchlorate (at pH 1.3 with HCl) and a flow rate of 2 ml/min which is certainly not suitable for on-line ICP-MS detection.

Therefore, based on the method of Nachtigall et al. the chromatographic conditions were modified in the present study to realise an on-line HPLC-ICP-MS hyphenation for the speciation of Pt(II) and Pt(IV). The method was validated with aqueous standards as well as spiked road dust extracts with respect to an application for the characterization of Pt-species in road dust.

2. Experimental

2.1. Chemicals

K_2PtCl_4 (purum) and Na_2PtCl_6 (puriss.) were purchased from Fluka, Buchs, Switzerland. Sodium perchlorate (p.a.) and hydrochloric acid (30%, suprapur) were obtained from Merck, Darmstadt, Germany. Nitric acid (65%, p.a, from Merck) was further purified by subboiling distillation. Deionised

water (18 MΩ/cm) was prepared with a Millipore system.

2.2. Road dust sample

The reference material BCR-723 from the Institute for Reference Materials and Measurements (IRMM), Geel, Belgium with a certified Pt content of $81.3 \pm 3.3 \, \mu g/kg$ was used for all extractions. This material was collected from the ceiling of an Austrian road tunnel in 1998 and the fraction $<90 \, \mu m$ was used for certification [6].

2.3. Instruments and methods

A HP 1050 Ti system with quaternary gradient pump, variable wavelength UV detector and autosampler was used for HPLC. Separation was performed on an IonPac AG11 column (50 mm × 4 mm, from Dionex, Idstein, Germany). Detection wavelength was 215 nm and the injection volume was 40 μl. The HPLC was coupled on-line to an ELAN 5000 quadrupol ICP-MS (Perkin-Elmer, Sciex, Canada) equipped with a Meinhard-nebulizer and a cyclon spray chamber using PEEK-capillaries. Post-column dilution with 10% HNO_3 (1.25 ml/min flow rate supplied by a peristaltic pump) was realised through a PEEK-T-piece; Rh (1 μg/l) was added to the HNO_3 as internal standard. Plasma power was 1250 W; the nebulizer gas flow rate was adjusted towards maximum Rh-intensity and was typically between 750 and 900 ml/min. The isotopes ^{194}Pt, ^{195}Pt, ^{196}Pt, ^{198}Pt, ^{178}Hf, ^{57}Fe, ^{65}Cu, ^{66}Zn, ^{208}Pb and ^{103}Rh were monitored. The HPLC flow rate was set to 0.5 ml/min. In analogy to Nachtigall et al. an isocratic as well as a gradient method were applied. Isocratic separation was performed with 75 mM sodium perchlorate (pH 1.4 with HCl) (eluent A). Gradient elution started with 96% B (40 mM HCl, pH 1.4) and 4% A, rising to 52% A in 7 min and then to 100% A in 1 min.

Stock solutions (500 mg Pt/l) of K_2PtCl_4 and Na_2PtCl_6 were freshly prepared in 1 M HCl every day. Dilution to the required concentration was done directly before injection in three steps with 1 M HCl and 20 mM HCl resulting in a final HCl concentration of 20 mM.

The chromatographic recovery was determined by HPLC-UV with fraction collection at the Pt(II)-

and Pt(IV)-retention times under omission of the post-column dilution. For comparison, injections were repeated without column and the eluate was collected for 4 min. This procedure was performed in duplicate separately for 25 μg Pt/l as K_2PtCl_4, for 25 μg Pt/l as Na_2PtCl_6 and for a mixture of 25 μg Pt/l each of K_2PtCl_4 and Na_2PtCl_6. Fractions were diluted with water and Rh containing HNO_3 to 5 ml and the total Pt content was measured with ICP-MS. Pt-standard solutions were prepared with matching perchlorate concentration to compensate matrix effects.

2.4. Preparation of road dust extracts

One gram road dust was extracted with 5 ml of 20 mM HCl by shaking on a horizontal shaker for 2 h at room temperature. The raw extract was centrifuged at 1500 g for 10 min (Sigma 2D, Christ, Osterode, Germany). After collecting with a plastic syringe, the supernatant was membrane filtered (0.45 μm, Membrex, polyester-membrane, membraPure, Bodenheim, Germany). Spiked extracts were prepared by adding 10 μl of an adequately diluted Pt-species standard solution in 20 mM HCl to 490 μl road dust extract.

For comparison, extractions with 20 mM HCl, 100 mM HCl and 1 M HCl (two replicates each) were performed with half an hour shaking. Total concentrations of Pt and Hf in the extracts were determined by ICP-MS. Total contents of Cu, Zn, Fe, Mn, Pb and Ca were measured with a JY-70 ICP-AES (Jobin Yvon Instruments, S.A., France).

2.5. Data evaluation

The quantification of the Pt-species and the total Pt contents was performed by calculating the concentration with its confidence interval ($P = 95\%$) from the calibration curve for each sample. The individual replicates were combined by calculating the mean values which were then used for the calculation of the recoveries. The uncertainties for the mean values and the recoveries were derived by propagation of error. If the confidence intervals of the replicates did not overlap, the standard deviation was used alternatively because in these cases the standard deviation is larger than the result from the propagation of error.

3. Results

3.1. Modification of the HPLC-UV-method from Nachtigall et al.

An IonPac AG11 column was chosen instead of the IonPac AS5, because the AG11 material is similar, but according to the manufacturer shows often a better separation performance. Preliminary experiments with various columns showed that the Pt-chloro complexes are strongly retained on anion exchange columns. This is confirmed by the drastic chromatographic conditions used by Nachtigall et al. Therefore, a guard column with only 50 mm length was used to avoid unnecessarily long interaction between the analytes and the stationary phase and to shorten the retention times.

For the ICP-MS coupling a volatile buffer like ammonium chloride is advantageous, especially when high salt concentrations have to be applied. Therefore, elution of the Pt-species was tried with up to 100 mM ammonium chloride at pH 2, but only a very low percentage of the total injected platinum was recovered from the AG11 column. This is probably partly explained by the fact that the ammonium hexachloroplatinate is hardly soluble in water [14].

Consequently, the perchlorate eluent was adopted. The flow rate was reduced to 0.5 ml/min. With UV-detection alone the change of the retention times of Pt(II) and Pt(IV) was studied isocratically under increased dilution of the 300 mM perchlorate eluent (pH 1.3) with deionized water. An exponential increase of the retention times with decreasing perchlorate concentration was found. As a compromise, 75 mM were chosen as maximum perchlorate concentration to keep the analysis time per run below 35 min while on the other hand the final perchlorate concentration after post-column dilution was limited to less than 25 mM (dilution factor is approximately 3.5).

3.2. Elution pattern and recovery of aqueous chloro-platinum standards with HPLC-ICP-MS

Aqueous standards (in 20 mM HCl) of the single species K_2PtCl_4 and Na_2PtCl_6 as well as their mixture at a concentration level of 25 μg Pt/l each were characterized with the isocratic ion exchange method. ^{195}Pt chromatograms are presented in Fig. 1. The Pt(II)-chloro complex elutes as single well shaped peak at 11.4 min with only one small additional peak in the void (Fig. 1a). The Pt(IV)-standard shows a main peak at 21.0 min and a small peak at 11.1 min, which is the retention time of Pt(II) (Fig. 1b). The chromatogram of the mixed standard equals the sum of the single standard chromatograms (Fig. 1c).

Pt-recoveries for the three standard solutions were determined by HPLC-UV with fraction collection and off-line Pt determination by ICP-MS. Results are given in Table 1. The Pt content of the Pt(II) single species standard was well recovered with $(94 \pm 7)\%$ in the fraction of the peak at 11.4 min. Therefore, this peak is assigned as Pt(II)-peak. The Pt content of the fraction around 21 min was near or below the limit of detection (LOD). For the Pt(IV) single species standard $(103 \pm 13)\%$ of the injected Pt were found in the peak at 21.0 min, which is assigned as Pt(IV)-peak. The small Pt(II)-peak accounts for about 10% of total platinum. The values from the mixed standard indicate for the Pt(II)- and the Pt(IV)-peak a recovery of $(38 \pm 3)\%$ and $(45 \pm 6)\%$ of total platinum, respectively, which is a bit lower than expected from the results of the single standards for a 1:1 mixture (the optimum result would be 50% in each peak). One explanation might be a higher amount of Pt in the void peak compared to the single species standards, which is due to time dependent hydrolysis products. Generally, the total recovery (sum of Pt(II) and Pt(IV)) is within a good range of $(100 \pm 20)\%$.

Table 1
Pt-recoveries for the isocratic separation of single and mixed standards of K_2PtCl_4 and Na_2PtCl_6 in 20 mM HCl (25 μg Pt/l of each species)

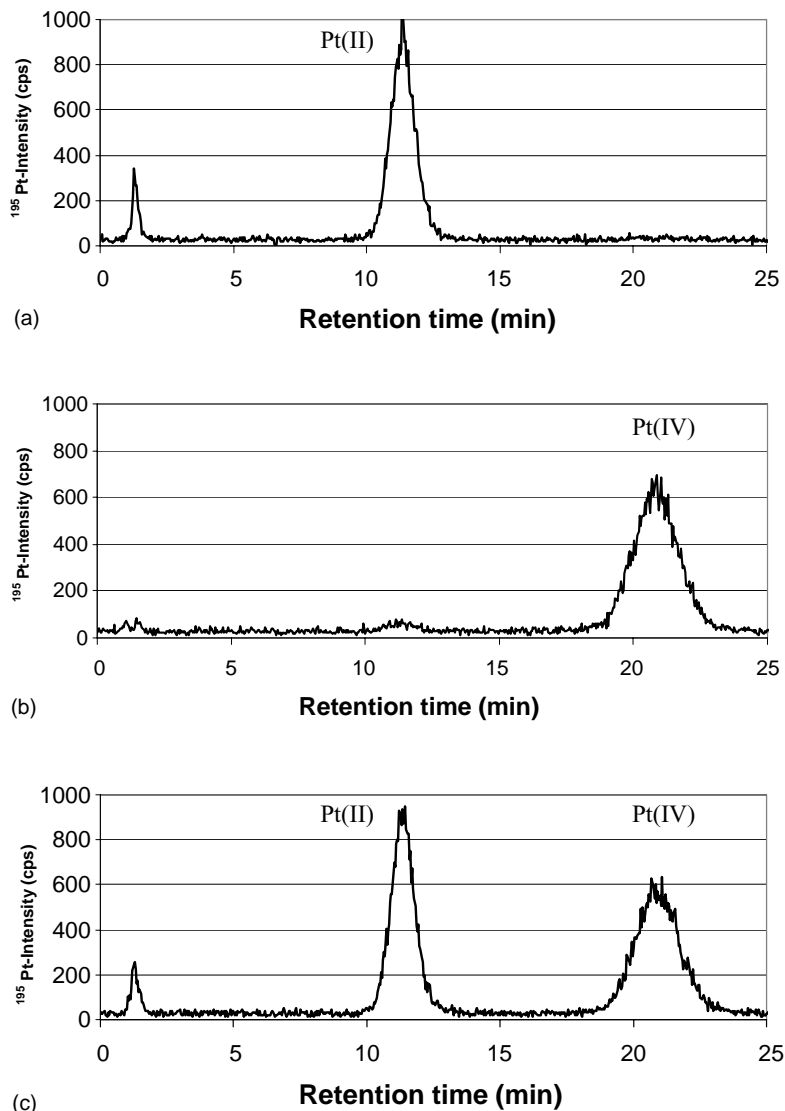|	Pt-recovery in Pt(II)-peak (%)	Pt-recovery in Pt(IV)-peak (%)	Sum of Pt-recoveries in Pt(II)- and Pt(IV)-peak (%)
K_2PtCl_4	94 ± 7	6 ± 6	100 ± 10
Na_2PtCl_6	9 ± 5	103 ± 13	112 ± 14
$K_2PtCl_4 + Na_2PtCl_6$	38 ± 3	45 ± 6	83 ± 7

Fig. 1. Isocratic separation of single and mixed chloro-platinum standards in 20 mM HCl with on-line IEC-ICP-MS: (a) 25 μg Pt/l as K_2PtCl_4; (b) 25 μg Pt/l as Na_2PtCl_6; (c) 25 μg Pt/l each of K_2PtCl_4 and Na_2PtCl_6.

The small Pt(II)-peak in the chromatogram of Na_2PtCl_6 might be due to a contamination of the solid substance. However, a reduction of Pt(IV) to Pt(II) during injection is more likely. Reductive conditions, e.g. caused by SO_2 [15] are necessary for this transformation which were neither present in the sample solution nor in the eluent. This is confirmed by a comparison of redox potentials for the reduction

of $PtCl_6^{2-}$ to $PtCl_4^{2-}$ ($E_0 = 0.73$ V) and for the oxidation of water to oxygen ($E_0 = 1.23$ V). [16,17] Calculations according to the Nernst equation showed that the potentials change not significantly (less than 0.2 V) when adapted to the experimental conditions (e.g. 20 mM HCl, Pt-concentrations in the mM or μM range). According to this data Pt(IV) is stable in 1 M HCl and 20 mM HCl against a reduction to Pt(II).

Therefore, a transformation of Pt(IV) to Pt(II) in the standard solution before injection is rather unlikely. During separation the chromatographic conditions are also oxidative ($E_0(ClO_4^-/ClO_3^-) = 1.23$ V). However, during injection the sample is in contact with metallic parts of the autosampler which are mainly made out of titanium, but probably include some stainless steel parts. These might account for the reduction of a small amount of Pt(IV). At first, manual injection with a plastic syringe with steel needle was applied. In this case, about 25% of the injected Pt(IV) were detected in the Pt(II)-peak. Probably, reduction occurred on the surface of the injection needle.

A Pt(IV)-standard (2500 µg Pt/l) was injected by autosampler and fractions of the Pt(II)- and Pt(IV)-peak were collected. Both fractions were injected twice into the HPLC-ICP-MS system by autosampler. As expected, only a Pt(II)-peak was detected in the Pt(II)-fraction besides the usual small peak in the void. However, the chromatograms of the Pt(IV)-fraction were nearly identical to those of the Pt(IV)-standard solutions. A major Pt(IV)-peak and a minor Pt(II)-peak were detected with a ratio of approximately 19:1. As discussed above, an oxidation of Pt(II) to Pt(IV) is much more likely in the eluent than a reduction; therefore, the reduction occurs obviously during injection. But the extent of this species-transformation is less than 10% of the Pt(IV) amount and therefore causes no significant interference. This effect has only to be considered if the Pt(II)-concentration in the sample is much lower than the Pt(IV)-concentration.

Another interesting question is the molecular structure of the analytes in the eluent solution. The initial chloro complexes may be transformed to perchlorato complexes by ligand exchange. Pascal and Favier [18] report in a review on inorganic perchlorato complexes that the basicity of ClO_4^- is only slightly lower than that of Cl^- and that the perchlorato ligand is able to compete with water if the coordination sphere of the metal is large enough to accept several bonds. This prerequisite is certainly given for Pt as a transition metal. Unfortunately, there is no information on perchlorato-Pt complexes available in the literature so far. UV-Vis absorption spectroscopy might turn out to be a suitable analytical technique to study the real solution structure of the Pt-chloro complexes in the perchlorate eluent.

3.3. Calibration with aqueous chloro-platinum standards

In analogy to the determination of the recoveries, calibration experiments were performed separately for the Pt(II)-species, the Pt(IV)-species and their mixture using the isocratic method. [195]Pt-intensities were normalized to the internal standard [103]Rh before integration; peak areas were used for data evaluation. Calibration levels were in all cases the same between 5 and 25 µg Pt/l of each species. Three replicates of the 25 µg/l standards were performed to determine the precision; the remaining standards were measured only once. The standard deviation of the baseline of a blank run (20 mM HCl) at the respective retention times of the peaks was used for the calculation of the limit of detection. The characteristic data are summarized in Table 2. Calibration curves are linear within the working range with low residual standard deviations. Detection limits are approximately 10-times lower than those of the HPLC-UV-method of Nachtigall et al. Good precision of the peak areas was obtained with less than 10% R.S.D.

These data prove the stability of the Pt(II)- and Pt(IV)-model compounds and in particular the constancy of the Pt(II)/Pt(IV)-ratio in the calibration solutions as well as a constant recovery which is independent of the analyte concentration.

Table 2
Characteristic data of the calibration with K_2PtCl_4, Na_2PtCl_6 and their mixture in 20 mM HCl

	K_2PtCl_4	Na_2PtCl_6	Mixed standard	
			Pt(II)	Pt(IV)
Calibration range (µg Pt/l)	5–25	5–25	5–25	5–25
Linearity[a]	Yes	Yes	Yes	Yes
Residual standard deviation (%)	1.3	3.0	3.1	2.0
LOD (µg Pt/l)[b]	0.7	0.9	0.6	0.6
R.S.D. of peak area (%) ($n = 3$)[c]	9.5	3.3	5.3	5.0

[a] Residual standard deviation of the linear regression model is significantly lower than that of a regression with a polynomial of second degree (F-test).

[b] LOD = $3 \times$ S.D. $\times c/h$ with S.D.: standard deviation of the baseline (blank sample) and c, h: concentration and peak height of an appropriate calibration standard.
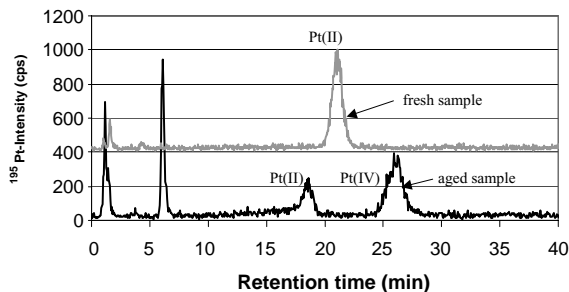
[c] 25 µg/l standard.

Fig. 2. Gradient elution of K_2PtCl_4 in 20 mM HCl (25 µg Pt/l) directly after dilution (upper trace with an offset of 400 cps) and after 1 week storage at room temperature (lower trace). The [195]Pt-intensity was related to [103]Rh as internal standard.

3.4. Gradient elution of aqueous chloro-platinum standards

As demonstrated by Nachtigall et al. a gradient method is necessary to separate the so called "hydrolysis products" of the chloro-platinum species which elute in the isocratic method as one peak near the void. In Fig. 2 (upper trace) the [195]Pt chromatogram of a freshly diluted Pt(II)-standard (25 µg Pt/l) from a freshly prepared stock solution is presented. Besides the increased retention time the result is very similar to that of the isocratic separation (Fig. 1a). In contrast, at the gradient elution of a freshly prepared Pt(IV)-standard 20–25% of total platinum were detected at the Pt(II) retention time and only the remaining part at the Pt(IV) retention time. Obviously, the low perchlorate concentration at the beginning of the gradient method supports the reduction of Pt(IV) to Pt(II). Therefore, the main focus was laid on the isocratic method which allows the reliable quantification of the original Pt(II)- and Pt(IV)-peaks. However, the gradient method is useful for a closer investigation of the "hydrolysis products". As an example, the chromatogram of the sample from Fig. 2 (upper trace) after 1 week storage at room temperature is shown in Fig. 2 (lower trace). The Pt(II)-peak is now detected in much lower intensity at an earlier retention time. The drift in retention times is caused by a series of measurements of road dust extracts between the runs of the upper and the lower trace in Fig. 2 and is a general effect and not specific for the aged sample. A considerable amount of Pt(II) was oxidised to Pt(IV) which is consistent with the above mentioned redox poten-

tials. Additionally, a sharp peak is detected clearly separated from the void peak. This is probably a hydrolysis product formed by exchange of a chloride ion by water as suggested by Nachtigall et al. [10]. This exchange reduces the charge of the complex from −2 to −1 so the hydrolysis product is much less retained on the anion exchange column and eluted much earlier than the original complexes. In analogy, the void peak might contain a dichloro-diaquo-platinum complex with charge zero.

3.5. Stability of diluted aqueous standards

The stability of the chloro-platinum species in diluted solutions is an important aspect for the storage of samples, e.g. road dust extracts before analysis. Therefore, standard solutions of K_2PtCl_4, Na_2PtCl_6 and their mixture with 25 µg Pt/l of each species were prepared in 20 mM HCl in analogy to the calibration solutions. The samples were analysed directly after dilution and aliquots were filled up in glass autosampler vials and stored frozen at −20 °C. These samples were analysed after 5, 6 and 12 days of storage. The long-term stability of the Pt(II) complex is very bad; after 5 days of storage more than 90% of the initial content was transformed. About one-half of the transformation products were detected near the void, the other half at the Pt(IV)-retention time. After 12 days of storage Pt(II) was nearly quantitatively oxidised to Pt(IV) and recovered in the Pt(IV)-peak. Consequently, the Pt(IV) complex is stable and not reduced under the applied conditions. The difference in peak areas was less than 10% of the initial value. According to this, Pt(II)-peak areas of the mixed standard are rapidly decreasing and Pt(IV)-peak areas are increasing. This implies that samples should be analysed directly after extraction to avoid artefacts from sample storage. In water the oxidation of Pt(II) to Pt(IV) would be lower than in 20 mM HCl, but the hydrolysis of the chloro-Pt-species would be enhanced, especially at low concentrations of the analytes.

3.6. Elution pattern and recovery of spiked road dust extracts

The chromatograms of 20 mM HCl road dust extracts spiked with K_2PtCl_4, Na_2PtCl_6 and their

mixture are very similar to those of the aqueous standards (Fig. 1). Only the retention times are shorter. This effect is due to the high matrix load of the road dust extracts and has to be compensated by column purging with 0.5% HNO_3, 0.5% TMAH and methanol. However, the resolution of the Pt(II)- and Pt(IV)-peaks is not negatively affected.

In analogy to the aqueous standards the recovery of the Pt-species in the spiked extracts was determined by HPLC-off-line-ICP-MS. For a K_2PtCl_4 spiked extract (25 μg Pt/l) the Pt(II)-species was well recovered in the Pt(II)-peak (93 ± 7% of total Pt), while the Pt content in the Pt(IV)-fraction was below the limit of detection. For a Na_2PtCl_6 spiked extract (25 μg Pt/l) the recovery of Pt(IV) in the Pt(IV)-peak was a bit lower with (74 ± 13)%; in the Pt(II)-fraction the Pt content was below the limit of detection. For the mixed spike (1:1) also good recoveries of (47 ± 3)% of total Pt in the Pt(II)-peak and (40 ± 6)% of total Pt in the Pt(IV)-peak were obtained.

3.7. Calibration with spiked road dust extracts

Calibration experiments were performed in the same way as for the aqueous standards with spiked road dust extracts. An unspiked extract was used as blank for the determination of the detection limit. Additionally, solutions of the single and mixed standards in 20 mM HCl were measured directly before and after the matrix calibration solutions to establish a recalibration curve for the aqueous standards. Quantification of the Pt(II)- and Pt(IV)-model species in the spiked extracts was performed on the basis of this recalibration. Linear regressions of the resulting concentrations versus the spiked concentrations were calculated to check for constant and proportional systematic errors caused by the road dust matrix. All relevant results are given in Table 3. Moreover, the mean recoveries of the five calibration standards and the two replicates of the highest standard are supplied as additional information.

Linearity, precision and detection limits are not significantly different from the respective values of the calibration without matrix. Mean recoveries are within a good range of 80–105%. The recovery linear regressions show no proportional systematic errors (except for Pt(II)-spiked extracts due to the low uncertainty of the slope) and only small but not significant constant systematic errors. This proves that the matrix of the road dust extracts has no significant effect on the separation and quantification of the Pt-chloro complexes.

3.8. Isotopic ratios and hafnium-oxide-interference

Due to its multi-isotopic character platinum offers the possibility of detecting several isotopes in parallel. The isotopic ratios are in many cases a

Table 3
Characteristic data of the calibration with road dust extracts (20 mM HCl) spiked with K_2PtCl_4, Na_2PtCl_6 or their mixture

	Calibration range (μg Pt/l)	Linearity[a]	Residual standard deviation (%)	LOD (μg Pt/l)[b]	R.S.D. of peak area (%) (n = 3)[c]	Mean recovery (%)[d]	Slope of recovery linear regression	Intersection of recovery linear regression with y-axis
K_2PtCl_4	5–25	Yes	0.8	0.3	3.3	105 ± 2	1.05 ± 0.03	0.04 ± 0.42
Na_2PtCl_6	10–50	Yes	3.9	0.9	4.5	95 ± 5	1.01 ± 0.12	−2.82 ± 3.94
Mixed spike								
Pt(II)	5–25	Yes	5.6	0.5	3.9	104 ± 5	1.04 ± 0.18	0.17 ± 2.93
Pt(IV)	5–25	Yes	11.5	1.1	5.4	80 ± 10	0.99 ± 0.35	−3.21 ± 5.72

Recalibration was performed with aqueous standards to check for constant and proportional systematic errors caused by the extract matrix.

[a] Residual standard deviation of the linear regression model is significantly lower than that of a regression with a polynomial of second degree (*F*-test).

[b] LOD = 3 × S.D. × c/h with S.D.: standard deviation of the baseline (blank sample) and *c*, *h*: concentration and peak height of an appropriate calibration standard.

[c] Calibration standard with the highest concentration.

[d] Mean recovery of the analytes in the spiked extracts determined on the basis of a calibration with aqueous standards.

suitable indicator for interferences, e.g. by cluster-ions on the measured isotopes. In the case of Pt the HfO-interference is well known and cannot be resolved by a quadrupole mass analyzer [19].

The signals of all Pt-isotopes with relevant abundance (^{194}Pt, ^{195}Pt, ^{196}Pt and ^{198}Pt) were evaluated in chromatograms of spiked road dust extracts (25 µg Pt/l of each species as single or mixed spike, three replicates each). Isotopic ratios were calculated from the peak areas. The results were compared to the respective ratios obtained from the natural isotopic abundances given in the literature [3] and are summarized in Table 4. The experimental values are in good agreement with the theoretical values except for ^{198}Pt which has a comparatively low abundance of only 7.2%. These results indicate that there is no relevant interference on the Pt-detection at the retention times of the Pt(II)- and Pt(IV)-peaks. This is confirmed by the Hf-signal which shows only one peak in the void.

However, a correction of the Hf-oxide-interference is necessary for the determination of total Pt in road dust extracts by quadrupole ICP-MS. Lustig et al. proposed a mathematical correction method based on the measurement of ^{195}Pt and ^{179}Hf [19]. A correction factor was calculated from the signal intensities of standard solutions containing a defined Hf-concentration and either 100 ng/l Pt or no Pt. One disadvantage of this method is the necessity to measure additional calibration solutions and the time delay between the determination of the correction factor and the measurement of the sample. Meanwhile, the oxide rate might change and moreover it might be affected by the matrix of the sample solution.

Therefore, an alternative mathematical correction was developed which needs only the intensities of ^{194}Pt, ^{195}Pt and ^{196}Pt measured in the sample. The prerequisite is that there is no relevant other interference besides HfO on the three Pt-isotopes and the ^{179}Hf^{16}O-intensity should not exceed about 50% of the total intensity measured at m/z 195. Eq. (1) describes the total intensity ^{195}I measured at $m/z = 195$ as sum of the real Pt-intensity and the intensities of the different HfO-clusters. The respective equations for $m/z = 194$ and $m/z = 196$ were established in analogy.

$$^{195}I = {}^{195}_{Pt}I + {}^{179}Hf^{16}O I + {}^{178}Hf^{17}O I + {}^{177}Hf^{18}O I \quad (1)$$

The HfO-intensities are expressed as function of the Hf-concentration c_{Hf} and the abundances f of the isotopes using k as proportionality factor (Eq. (2)).

$$^{n}Hf^{m}O I = k \times f_{n_{Hf}} \times f_{m_{O}} \times c_{Hf} \quad (2)$$

Eqs. (3) and (4) show as example for ^{195}Pt the combination of the Eqs. (1) and (2). In analogy, the same relation was established for ^{194}Pt and ^{196}Pt.

$$^{195}I = {}^{195}_{Pt}I + k \times c_{Hf} \times {}^{195}h \quad (3)$$

$$^{195}h = f_{179_{Hf}} \times f_{16_O} + f_{178_{Hf}} \times f_{17_O} + f_{177_{Hf}} \times f_{18_O} \quad (4)$$

Two of the resulting three equations of type (3) allow the elimination of the remaining two unknown variables (the factor k and the Hf-concentration). Therefore, the corrected ^{195}Pt-intensity was calculated from the 194/195-pair as well as the 195/196-pair

Table 4
Mean isotopic ratios of the relevant Pt-isotopes ^{194}Pt (32.9% natural abundance), ^{195}Pt (33.8%), ^{196}Pt (25.3%) and ^{198}Pt (7.2%) [3] calculated from the peak areas of the Pt(II)- and Pt(IV)-peaks of spiked road dust extracts ($n = 3$)

	K$_2$PtCl$_4$	Na$_2$PtCl$_6$	K$_2$PtCl$_4$ + Na$_2$PtCl$_6$	
	Pt(II)-peak	Pt(IV)-peak	Pt(II)-peak	Pt(IV)-peak
^{195}Pt/^{194}Pt-ratio	1.03 ± 0.02	1.02 ± 0.04	1.01 ± 0.02	1.00 ± 0.01
^{195}Pt/^{194}Pt compared to literature (%)	100 ± 2	99 ± 4	99 ± 2	97.8 ± 0.3
^{195}Pt/^{196}Pt-ratio	1.34 ± 0.01	1.32 ± 0.03	1.32 ± 0.05	1.36 ± 0.03
^{195}Pt/^{196}Pt compared to literature (%)	100 ± 1	98 ± 2	99 ± 4	102 ± 2
^{195}Pt/^{198}Pt-ratio	4.70 ± 0.07	4.53 ± 0.01	4.39 ± 0.07	4.24 ± 0.10
^{195}Pt/^{198}Pt compared to literature (%)	100 ± 1	96.6 ± 0.2	93 ± 1	90 ± 2

(Eq. (5)).

$$\underset{\mathrm{Pt}}{^{195}}I = \frac{^{195}I - (^{195}h/^{i}h) \times {}^{i}I}{1 - {}^{195}h \times f_{i_{\mathrm{Pt}}}/({}^{i}h \times f_{195_{\mathrm{Pt}}})}$$

$$(\text{with } i = 194 \text{ or } i = 196) \qquad (5)$$

With the values of the isotope abundances taken from the literature the relatively simple Eqs. (6) and (7) for the corrected ^{195}Pt-intensity are obtained.

$$I_{\mathrm{corr}}(194)$$
$$= \underset{\mathrm{Pt}}{^{195}}I = 1.974198 \times {}^{195}I - 1.000848 \times {}^{194}I \quad (6)$$

$$I_{\mathrm{corr}}(196)$$
$$= \underset{\mathrm{Pt}}{^{195}}I = 1.412123 \times {}^{195}I - 0.550583 \times {}^{196}I \quad (7)$$

The mean of both results for the ^{195}Pt-intensity provides a suitable correction of the HfO-interference; usually, the results from both isotope-pairs are in good agreement.

The method was tested with 100 ng/l Pt-standards in the presence of defined Hf-concentrations as well as with Pt-blank solutions containing the same Hf-concentrations. Table 5 summarizes the percentage ratios of the ^{195}Pt-intensities in the Hf containing samples and the ^{195}Pt-intensities in the corresponding samples with the same Pt-concentrations and Hf-blank levels. These ratios were calculated with the original ^{195}Pt-intensities, the ^{195}Pt-intensities corrected with the method from Lustig et al. and with the

^{195}Pt-intensities corrected with the newly developed method. Both correction methods provide good results for the Pt containing samples with a Hf–Pt-ratio of up to 100 (bold typeface in Table 5). The 1000-fold excess of Hf is beyond the application range of the new correction method. The Lustig-method is able to provide even in this case the correct intensity. This is probably due to the fact that the relatively high Hf-concentration of 10 µg/l was used for the calculation of the correction factor. The error of the mathematical correction increases with rising Hf–Pt-ratio which is in particular demonstrated by the test solutions with Pt-blank values. The 100 µg/l Hf sample without Pt shows that the new method provides for high interferences too high values while the values from the Lustig-method are too low.

3.9. Detection of further elements and characterisation of unspiked extracts

There are high amounts of easily extractable species of, e.g. Fe, Cu, Zn and Pb in the road dust. These elements were measured in parallel to the Pt-isotopes and Hf which was monitored because of the discussed HfO-interference. Chromatograms of ^{57}Fe, ^{65}Cu, ^{66}Zn, ^{195}Pt, ^{178}Hf and ^{208}Pb are displayed in Fig. 3 for a road dust extract spiked with 25 µg/l each of Pt(II) and Pt(IV). Fe, Cu and Zn elute as single intensive peaks near the void volume. In contrast, Pb

Table 5
Validation of the developed mathematical correction for the HfO-interference on ^{195}Pt using standard solutions with different Pt- and Hf-concentrations in 10% HNO$_3$ ($n = 2$)

Pt (µg/l)	Hf (µg/l)	Percentage ratio of ^{195}Pt-intensities of the respective sample and the corresponding sample with the same Pt content but without Hf[a]			$I_{\mathrm{corr}}(194)/I_{\mathrm{corr}}(196)$ (%)[c]
		Without correction	With Lustig correction[b]	With new correction method	
0	0	100 ± 14	97 ± 14	88 ± 21	121 ± 7
0	1	189 ± 21	91 ± 12	92 ± 19	98 ± 9
0	10	1021 ± 99	93 ± 12	212 ± 21	104 ± 3
0	100	9779 ± 940	−256 ± 78	752 ± 76	119 ± 5
0.1	0	100 ± 2	**100 ± 2**	**100 ± 3**	**101 ± 1**
0.1	1	106 ± 4	**96 ± 4**	**97 ± 4**	**100 ± 1**
0.1	10	132 ± 2	**100 ± 3**	**103 ± 4**	**101 ± 2**
0.1	100	445 ± 7	99 ± 2	139 ± 9	100 ± 4

For comparison, the method of Lustig et al. [19] was also applied.

[a] Intensities were normalised to ^{103}Rh.

[b] 10 µg/l Hf samples were used for calculation of the correction factor.

[c] Percentage ratio of corrected ^{195}Pt-intensities using Eq. (6) (^{194}Pt-isotope) on the one hand and Eq. (7) (^{196}Pt-isotope) on the other hand.
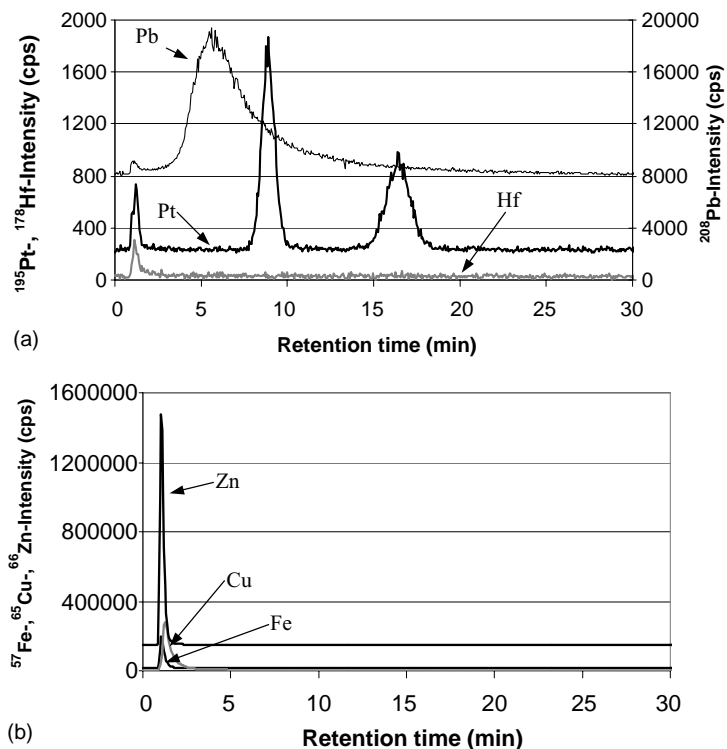
Fig. 3. HPLC-ICP-MS chromatograms of [57]Fe, [65]Cu, [66]Zn, [178]Hf, [195]Pt and [208]Pb for a road dust extract spiked with 25 μg Pt/l each of K_2PtCl_4 and Na_2PtCl_6. An offset was used for better visibility for Pt (200 cps), Pb (7500 cps) and Zn (150 000 cps).

shows only a small peak in the void and a huge broad peak between a retention time of 3 and 12 min. These are probably anionic lead complexes like $[PbCl_3]^-$ or $[PbCl_4]^{2-}$ which are either already present in the road dust or formed from soluble lead species in presence of the eluent. The broadness of the peak is explained by the high concentration of these species in the extract and maybe by interconversion of the complexes. Hf elutes as small peak in the void so there is no HfO-interference at the retention time of the Pt(II)- and Pt(IV)-chloro complexes.

Additionally, road dust samples were extracted with 20 mM HCl, 100 mM HCl and 1 M HCl to obtain an overview of the pH dependent mobilisation of Pt, Hf and further elements. Moreover, a characterisation of some matrix elements was intended to show the complex composition of the extracts. Therefore, the results in Table 6 are given as concentrations in the undiluted extracts (1 g road dust with 5 ml extractant). Total concentrations of Pt and Hf in the extracts were

determined with ICP-MS under consideration of the described HfO-correction method. Pb, Cu, Zn, Fe, Mn and Ca were analysed with ICP-AES. The pH in the 20 mM extract and the 100 mM extract is neutral and far higher than the pH of the extractants which was 1.7 and 1.0, respectively. This shows the high buffer

Table 6
Total element concentrations and pH-values in road dust extracts ($n = 2$)

	20 mM HCl	100 mM HCl	1 M HCl
pH	7.2 ± 0.2	7.2 ± 0.2	0.7 ± 0.1
Pt (μg/l)	0.33 ± 0.02	0.32 ± 0.02	0.18 ± 0.02
Hf (μg/l)	4.2 ± 0.2	4.4 ± 0.2	20.8 ± 0.3
Pb (mg/l)	1.88 ± 0.05	1.94 ± 0.07	138 ± 4
Cu (mg/l)	3.3 ± 0.1	3.64 ± 0.05	29.1 ± 0.5
Zn (mg/l)	17.2 ± 0.4	39.9 ± 0.7	293 ± 5
Fe (mg/l)	5.76 ± 0.06	8.2 ± 0.2	1159 ± 9
Mn (mg/l)	13.32 ± 0.04	25.0 ± 0.5	157 ± 2
Ca (mg/l)	1235 ± 20	2629 ± 25	10914 ± 160

capacity of the road dust. However, the 1 M hydrochloric acid was sufficient to exhaust the buffer capacity and reduce the pH of the extract below 1. This was accompanied by lively gas evolution when adding the extractant to the dust. Due to the constant pH the element concentrations in the 20 and 100 mM extracts are quite similar. Most elements occur in the low milligram per liter range with exception of Ca (about 1 g/l) as well as Pt and Hf in the low microgram per liter range. Pt-concentrations are below the detection limits for the Pt(II)- and Pt(IV)-species of the developed speciation method. Consequently, no Pt-peak could be detected in unspiked extracts. The dramatic decrease of the pH in the 1 M extract is well documented by the rising concentrations of Pb, Cu, Zn, Fe and Mn. The Hf content increased also. This is probably the main reason for a small Pt-peak in the void at the chromatographic separation of the 1 M extract. Surprisingly, the Pt-concentration is lower compared to the neutral extracts.

4. Conclusion

With the described modifications of the method from Nachtigall et al. an on-line coupling to ICP-MS could be realised with the advantage of Pt-specific detection and 10-fold decreased detection limits. Matrix effects at the analysis of spiked road dust extracts were low although these extracts contain huge amounts of other elements. Due to the high UV-absorption of these matrix compounds the characterisation of the Pt-species in the spiked extracts is not possible with the HPLC-UV-method. The stability of the Pt(II)-chloro complex in 20 mM HCl is critical but no problem when freshly prepared stock solutions and dilutions are used. The known HfO-interference does not affect the quantification of the separated species because the Hf elutes with the void. A mathematical HfO-correction was developed for determination of total Pt in the extracts.

The total Pt-concentrations in the hydrochloric acid extracts from road dust were below the detection limits of the developed speciation method for the single species. Therefore, it is necessary to optimise the extraction methods for Pt-species from road dust. In particular, a higher selectivity of the extractant towards Pt is desired to increase the Pt amounts in the extract relatively to the amounts of other elements. This aim may

be reached by the application of so called platinophilic complexing agents like EDTA and thiourea. Pt(II) is a soft ion with higher affinity, for example, to sulphur containing ligands while Pt(IV) as a hard ion is preferably bound by ligands with oxygen containing functional groups like EDTA.

Acknowledgements

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