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Speciation of platinum–chloro complexes and their hydrolysis products by ion chromatography Determination of platinum oxidation states[1]

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Abstract

A method for the separation and determination of tetrachloroplatinate, $PtCl_4^{2-}$, and hexachloroplatinate, $PtCl_6^{2-}$, applying UV absorption detection was developed and statistically validated. Independent and specific Pt quantification was possible by off-line inductively coupled plasma mass spectrometric determination. Special attention was paid to storage and stability of species standards and their suitability for calibration. The species purity of standard solutions was determined and the hydrolysis kinetics were investigated. Qualitatively, a number of Pt(II) and Pt(IV) complexes formed by hydrolysis from tetra- and hexachloroplatinate were detected. First applications of the methods are described. © 1997 Elsevier Science B.V.

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1. Introduction

1.1. Platinum in the environment — demand for analytical procedures

Increasing platinum concentrations have been detected in environmental samples since the mid-1980s [1]. Catalytic converters used in cars are a major source, which has been established in several studies [2–5]. The average emissions of common three-way catalytic converters are in the order of ng Pt/km. They were determined using laboratory-based car engines [6,7]. Although platinum is emitted mainly in the elemental form as Pt(0) attached to alumina particles [8], in tunnel- and air-dust samples several percent of the total platinum content were soluble [9,10].

In 1986, Rosner and Hertel [11] discussed the health risk of platinum emissions from catalytic converters. The general toxicity of platinum compounds was described based on the literature available. It has to be noted, that generally toxic effects are not necessarily correlated with the total content of an element but have to be ascribed to the concentration of individual species in the sample. For example, the chloro complexes of platinum are potent sensitizing agents causing severe allergic reactions [12,13], while the insoluble platinum dioxide is rather non-toxic. In order to judge the actual health risk of the environmental platinum and to

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understand its transformations, methods for the determination of platinum species have to be developed. Messerschmidt et al. [14,15] applied gel permeation chromatography and isotachophoresis combined with adsorptive voltammetric measurements to platinum speciation in grass, and Lustig et al. [10] characterized the transformations of different platinum compounds in soil using extraction procedures.

In order to study the bioavailability of platinum emissions from catalytic converters, a model substance was synthesized [16]: aluminium oxide particles with diameters <5 μm were coated with 3 to 5% nanocrystalline, elemental platinum. The substance was tested in studies with rats, either being inhaled or instilled as a suspension into the lung. Apart from the determination of the total platinum content in solutions, tissues and excrements, speciation techniques are required to elucidate the species involved in the platinum uptake and to explain the observed physiological effects.

Surprisingly, the model substance showed a rather large solubility in some solvents [17]. Several percent of the total platinum content were oxidised and chemically dissolved in the presence of oxygen and ligands like chloride. In physiological sodium chloride solution, a variety of platinum–chloro complexes was expected to form. An analytical method was needed to characterize the species involved in this first step of the bioavailability study. Additionally, their reactions with biological ligands had to be investigated. Ion chromatography was a suitable separation technique for the inorganic and low-molecular-mass species.

1.2. Determination of platinum by ion chromatography

When using ion chromatography for platinum determination, many authors refer to hexachloroplatinate complexes as standards. However, their aim is mostly the determination of the total platinum content instead of the distinction between different platinum species. Rocklin [18] described a method for the determination of several precious metal–chloro complexes using a perchlorate–hydrochloric acid eluent and UV detection. He points out that due to the species-selective nature of ion chromatography, all platinum has to be converted to a single species and recommends aqua regia digestion of samples. Jerono et al. [19] developed a combined procedure consisting of high-pressure acid digestion of biological samples, evaporating of the nitric acid and subsequent Pt determination in diluted hydrochloric acid. They used an anion-exchange column and a perchlorate eluent, according to Rocklin. Shpigun and Pazukhina prepared hexachloroplatinate standards in 6 *M* HCl, where only the higher oxidation state is said to exist. They used sulfosalicylic acid, as eluent, and UV detection [20,21].

Urasa et al. [22] also determined hexachloroplatinate, applying an oxalic acid–trilithium citrate eluent and d.c. plasma atomic emission spectrometric detection. They also described the formation of additional species in 14-day-old standard solutions. The reaction of hexachloroplatinate with cysteine was investigated.

In the present study, a procedure based on the method published by Rocklin [18] is presented for the analysis of several platinum species such as the anionic platinum–chloro complexes and some of their hydrolysis products.

2. Experimental

2.1. Chemicals

Sodium perchlorate and sodium chloride, both of analytical grade, hydrochloric acid (30%), Suprapur, and nitric acid (65%), analytical grade, were purchased from Merck, Darmstadt, Germany. The nitric acid was further purified by sub-boiling point distillation. Potassium hexachloroplatinate and potassium tetrachloroplatinate were obtained from Alfa Johnson Matthey, Karlsruhe, Germany. Stock solutions with a nominal concentration of 500 mg platinum/l were prepared by dissolving the required amount of each platinum complex salt in 1 *M* NaCl, 1 *M* HCl, concentrated HCl and in water. If necessary, ultrasound was used for dispersing the solid. The total platinum concentration was verified by electrothermal atomic absorption spectrometry. Tetra- and hexachloroplatinate in separate stock solutions were kept at least one month before the first analysis in order to reach equilibrium. They

were diluted to the required standard concentration with deionized water immediately prior to measurement to prevent hydrolysis. Pt, In and Lu standard solutions from B Kraft, Duisburg, Germany, 1 g/l each, were used for inductively coupled plasma mass spectrometric (ICP–MS) determinations. Deionized water was prepared applying a Milli-Q water purification system from Millipore, Eschborn, Germany.

2.2. Equipment

For ion chromatographic (IC) determinations, DX 500 chromatography modules from Dionex, Sunnyvale, CA, USA were applied: LC20 chromatography enclosure with 6-port injection valve and 26 μl sample loop, GP40 gradient pump and AD20 absorbance detector. The standard detection wavelength was 215 nm. Polyether ether ketone (PEEK) tubing (0.25 mm I.D.) was used throughout the system behind the injection valve. Two back pressure loops (77 cm×0.25 mm PEEK tubing each) were connected to the AD20 outlet. The whole system did not contain any metal parts. No disadvantageous effects with respect to the corrosive nature of the eluent were observed.

2.3. Software

Data acquisition and evaluation was performed with Dionex PeakNet software, release 4.2. Statistical calculations were made with Statgraphics Plus for Windows version 2.0 from Manugistics, Rockville, MD, USA.

ICP–MS determinations were carried out with a VG PlasmaQuad PQ 2+ from VG Elemental, Winsford, UK. UV spectra were recorded on a UV-2100 UV–Vis recording spectrophotometer, Shimadzu, Kyoto, Japan.

2.4. Sample preparation

A special sample preparation was not needed for chromatographic determinations. Aqueous standard solutions, 0.9% and 1 *M* sodium chloride solution and 0.1 *M* Tris buffer solution were measured directly.

For ICP–MS determinations in IC fractions, the collected volume was made up to 2 ml with the mobile phase before 10 μl of 10 mg/l In and Lu was added as internal standard. Each sample was made up to 10 ml with 1% nitric acid. Standards for calibration were prepared correspondingly to match the matrix of the samples.

2.5. Column

An IonPac AS5 analytical column (250×4 mm) with an IonPac AG5 guard column (50×4 mm) from Dionex was used at room temperature.

2.6. Mobile phase

Eluent A: 42.14 g sodium perchlorate and 5 ml 30% hydrochloric acid were dissolved in deionized water and made up to 1 l resulting in 300 m*M* perchlorate and 48 m*M* hydrochloric acid (pH=1.3). Eluent B: deionized water (pH=5).

2.6.1. Method 1

Tetra- and hexachloroplatinate were separated isocratically within 4 min using 100% eluent A, a flow-rate of 2 ml/min and UV detection at 215 nm.

2.6.2. Method 2

For the determination of both complexes and their hydrolysis products, the following gradient programme was applied (UV detection at 215 nm):

Time (min)	Flow-rate (ml/min)	Eluent A (%)	Eluent B (%)	Gradient
00.00–12.00	0.5	0.5–15.0	99.5–85.0	Linear
12.00–17.00	1.0	15.0–21.3	85.0–78.7	Linear
17.00–17.01	2.0	21.3–60.0	78.7–40.0	Linear
17.01–25.00	2.0	60.0	40.0	(Isocratic)

2.7. k′ values

The system's void time was determined by injecting deionized water. k' Values for the tetrachloro and hexachloro complexes refer to the maximum of the (negative) water peak which is assumed to mark t_0. Since the hardware setup of the chromatographic system was not changed for the determination of the hydrolysis products, the void volume remains constant. The initial flow-rates being 2 and 0.5 ml/min, respectively, t_0(method 2)=4t_0(method 1).

3. Results

3.1. Qualitative investigations

3.1.1. Choice of detection wavelength and eluent

Absorption maxima within the UV region are at 202 and 262 nm for hexachloroplatinate and at 216 nm for tetrachloroplatinate (±1 nm). After chromatographic separation, $PtCl_4^{2-}$ was first detected at 216 nm and $PtCl_6^{2-}$ at 262 nm switching the wavelength after elution of the first peak. This is advantageous for hexachloroplatinate because of the lower background (eluent) absorption at 262 nm. However, in order to avoid switching the wavelength and because tetrachloroplatinate could only be detected at 262 nm with very low sensitivity, 215 nm was chosen as the standard detection wavelength in accordance with Rocklin [18]. At 215 nm both complexes and the hydrolysis products could also be detected with reasonable signal-to-noise ratios.

The platinum–chloro complexes are strongly retained on anion-exchange resins [23,24]. Therefore, a highly effective eluent is required. However, for speciation investigations it had to be considered that no reaction between the eluent and the species occurred. Elding [25] described studies of the hydrolysis of the tetrachloroplatinate ion, which were carried out in a 0.5 *M* perchloric acid medium. Hence, no ligand-exchange reactions were expected using the perchlorate eluent according to Rocklin [18]. Other eluent ions like the ones mentioned above (e.g., citrate) would have been possible ligands. Although perchlorate is a strong oxidizing agent, a significant oxidation of platinum(II) was not observed in our experiments; for example, no $PtCl_6^{2-}$-signal was detected measuring a pure tetrachloroplatinate standard diluted from a stock solution in 1 *M* NaCl.

3.1.2. Separation of tetra- and hexachloroplatinate

The separation of tetrachloroplatinate (t_R=1.31 min, S.D.=0.02 min or 1.5%) from hexachloroplatinate (t_R=2.76 min, S.D.=0.05 min or 1.8%) is shown in Fig. 1. The void time of the system was 0.74 min (S.D.=0.01 min or 1.4%) and hence the capacity factors were calculated as $k'(PtCl_4^{2-})$=0.77 and $k'(PtCl_6^{2-})$=2.73. At t_R=0.96 min (S.D.=0.01 or 1.0%), hydrolysis products were eluted with a capacity factor of k'=0.30. The separation of these hydrolysis products will be described in the following section.

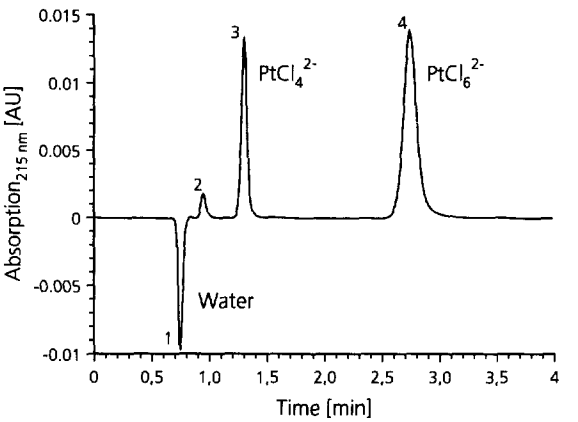

Fig. 1. Separation of tetra- and hexachloroplatinate (Method 1). 2 μg Pt/ml in the form of each species; stock solution in 1 *M* NaCl; eluent: 300 m*M* sodium perchlorate, 48 m*M* hydrochloric acid, flow=2 ml/min. Retention times are: 1 (water) 0.74 min, 2 (hydrolysis products) 0.96 min, 3 (tetrachloroplatinate) 1.31 min, 4 (hexachloroplatinate) 2.76 min.

3.1.3. Determination of hydrolysis products

Apart from the complexes containing only chloride ligands, platinum tetrachloroplatinate and platinum hexachloroplatinate both form a great number of species in diluted aqueous solutions containing chloride. Depending on platinum and chloride concentrations, on the pH and on the temperature, chloride ligands can be exchanged for water molecules. The latter may lose protons resulting in the formation of platinum–hydroxo complexes. For example, at 60°C the equilibrium mixture of $PtCl_4^{2-}$ in 0.5 *M* $HClO_4$ was reported to contain up to 40% of $PtCl(H_2O)_3^+$, but the tetraaquo ion could not be detected [25]. It is obvious from the start that a complete determination of all possible hydrolysis products of the system $PtCl_x^{2-}$/chloride/water cannot be achieved. However, the major compounds that still contain chloride ligands can be observed by UV absorption at 215 nm. In order to develop a method for the separation of several mixed aquo/chloro complexes of Pt(II) and Pt(IV), 500 mg Pt/l stock solutions in water were prepared separately for tetra-

and hexachloroplatinate. At the time of analysis the solutions were three months old and equilibrated. Compared to the bright yellow appearance of $PtCl_6^{2-}$ in 1 *M* chloride solutions, the aqueous solution showed a more intensive, darker yellow colour. $PtCl_4^{2-}$ in chloride solution was pale orange coloured; in pure water the colour turned to dark grey. The platinum(II) complexes were probably reduced to colloid elemental Pt. The dry residue of the solution after evaporating the water was investigated by transmission electron microscopy (TEM) in combination with energy dispersive X-ray analysis (EDX). It revealed particles with sizes between 10 and 25 nm showing a morphology characteristic for colloid metal particles. In more diluted, aqueous solutions of $PtCl_4^{2-}$ (10 μg/ml), solid metal flakes were observed after standing for several months. The formation of elemental platinum in the stock solution could explain the low recovery when the platinum content in eluent fractions of a chromatogram of hydrolysed standards was measured by ICP–MS (see below).

The stock solutions in water were diluted to 10 μg Pt/ml immediately prior to injection into the chromatograph in order to ensure that the analysis represented the equilibrium state in the stock solution. The results are shown in Fig. 2 ($PtCl_4^{2-}$) and

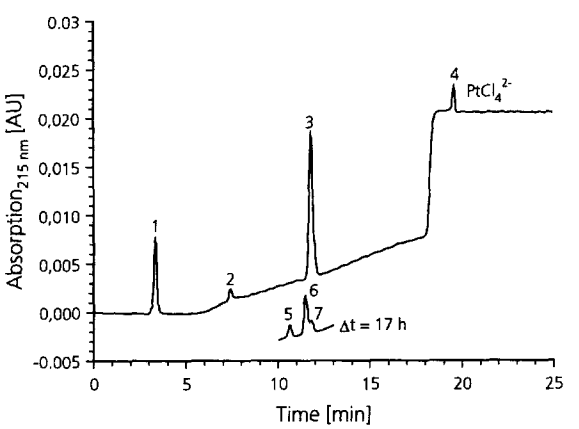

Fig. 2. Example for the separation of $PtCl_4^{2-}$ hydrolysis products (Method 2). Initially 10 μg Pt/ml in the form of tetrachloroplatinate; stock solution in water; separation acc. to method 2 (refer to Section 2 and Table 1). The small section attached below was taken from a chromatogram recorded 17 h after dilution of the stock solution.

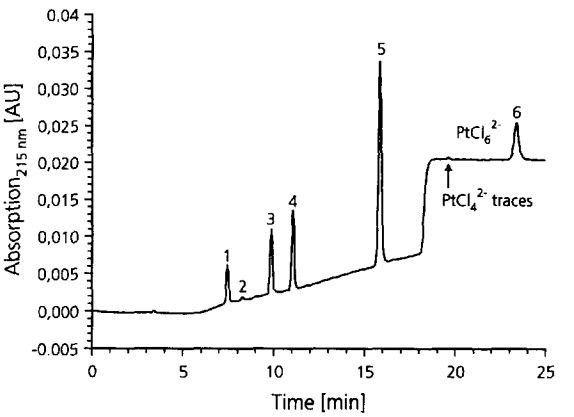

Fig. 3. Example for the separation of $PtCl_6^{2-}$ hydrolysis products (Method 2). Initially 10 μg Pt/ml in the form of hexachloroplatinate; stock solution in water; separation acc. to method 2 (refer to Section 2 and Table 1).

Fig. 3 ($PtCl_6^{2-}$). Table 1 lists all peaks observed with their retention times, reproducibility and capacity factors.

Table 1
List of chloro- and mixed aquo/chloro complexes determined by IC with UV detection at 215 nm according to method 2 (refer to Section 2, Fig. 2 and Fig. 3). Standard deviations for retention times are based on long-term, multi-concentration statistical data; the short-term reproducibility (identical eluent, column, etc.) at a constant concentration is better by a factor of 2 to 10. Capacity factors refer to a void time of 2.97 min.

Peak no.	Retention time (min)	S.D. (min)	Capacity factor, k'	Compound
Tetrachloroplatinate				
1	3.23	0.07	0.09	
2	7.42	–[a]	1.50	
3	11.56	0.29	2.89	
4	19.50	0.03	5.57	$PtCl_4^{2-}$
Hexachloroplatinate				
1	7.12	0.24	1.40	
2	8.01	0.18	1.70	
3	9.40	0.22	2.16	
4	10.66	0.17	2.59	
5	15.61	0.09	4.26	
6	23.17	0.09	6.80	$PtCl_6^{2-}$

[a] Within the range of 6 to 8 min a number of peaks appear with badly reproducible retention times. No clear assignment is possible.

Five hydrolysis products were observed for hexachloroplatinate and three for tetrachloroplatinate. There were, however, no species that were as strongly retained on the column as the mother compounds. For the separation of the hydrolysed species, a relatively weak perchlorate gradient had to be used: Starting with 1.5 m*M* sodium perchlorate and 0.24 m*M* HCl, the concentrations were 64 and 10 m*M*, respectively, after 17 min.

Using an anion-exchange resin, within a first approximation, the retention time should positively correlate with the negative charge of the analytes: the species with the greatest negative charge are eluted with the highest retention times, the cationic and neutral complexes are eluted closely after the void volume of the system. Since the exchange resin used in this study also has a certain cation-exchange capacity [18], the positively charged species are expected to be eluted later than the neutral compounds.

In the chromatograms of Fig. 2 and Fig. 3, signals close to the $PtCl_x^{2-}$ species carrying double negative charge were not detected. Moreover, an acid pH was always maintained (pH 5 in the stock solution, pH 1.3 in the eluent). For these reasons, species with double negative charge other than the mother compounds (hydroxo complexes) were not formed in significant concentrations. The last hydrolysis compounds eluting at 15.61 min (descending from $PtCl_6^{2-}$) and at 11.56 min (descending from $PtCl_4^{2-}$) might be $PtCl_5(H_2O)^-$ and $PtCl_3(H_2O)^-$, respectively. So far no attempt to identify the actual species belonging to the chromatographic signals has been made. However, by comparing the individual chromatograms changes in equilibrium compositions and redox processes can be recognized.

The section inserted in Fig. 2 shows part of a chromatogram measured 17 h after dilution of the stock solution to 10 μg/ml. Obviously, the hydrolysis has continued and new species have been formed. Peak 5 might be assigned to a Pt(IV) species, peak 6 is a new compound and peak 7 would be the remains of signal 3. Unfortunately, the long-term reproducibility of the separation method is relatively large (Table 1), which causes the clear identification of a species eluting closely to another one to be uncertain.

In Fig. 3, traces of tetrachloroplatinate are observed, which is an indication of reduction of chloroplatinates in low concentrated solutions. In an eight-month-old, 1 μg/ml solution derived from a Pt(IV) stock solution in 1 *M* NaCl, three Pt(II) hydrolysis products were determined.

3.2. Quantitative determinations

For reasons outlined in the preceding paragraph, only tetra- and hexachloroplatinate were determined quantitatively.

Measuring the UV absorption is the most convenient way to detect the platinum–chloro complexes. However, using standard solutions containing a known amount of total platinum for the calibration, this method does not give any quantitative information about the individual species concentrations unless the hydrolysis and redox equilibrium existing between these is known. Only the sum of the molar concentrations of the individual compounds containing Pt in the standard equals the total molar Pt concentration added. Dilution, addition of competitive ligands and changes in physical parameters, like temperature, influence the equilibrium concentrations. The kinetics of the changes may, however, be slow.

These difficulties can be overcome by using an element specific detector or a postcolumn derivatization (PCD) technique, thus converting all the different chemical species quantitatively into just one compound after their separation. Both techniques, however, require more experimental effort and are not available in every laboratory. Additionally, the kinetics for the formation of platinum complexes can be rather slow, which is disadvantageous for PCD. Therefore, the simple UV detection was validated applying an independent detection method.

The contents of tetra- and hexachloroplatinate in stock solutions stabilized with 1 *M* NaCl, 1 *M* HCl, concentrated HCl and in water were compared. Off-line ICP–MS detection was used to determine absolute Pt concentrations in eluent fractions. The purity of the $PtCl_x^{2-}$ stock solutions with regard to the Pt oxidation state was investigated. Finally, the time dependence of hydrolysis was determined before the statistical parameters for tetra- and hexachloroplatinate quantification were evaluated.

Table 2
Detection of platinum–chloro complexes by ICP–MS: platinum content of IC eluent fractions. The chromatogram from Fig. 1 was divided into 5 fractions as specified in the collection interval column. The Pt(II) and Pt(IV) concentrations, respectively, were 2 μg/ml each. The total platinum content was determined in each fraction by ICP–MS. 1 *M* NaCl and 1 *M* HCl as complex stabilizing agents were compared to pure water. The standards were mixed and diluted with water exactly 1.5 min before injection into the ion chromatograph. The given values are the mean of two (HCl stock solution and water) or three (NaCl stock solution) consistent replicates.

Fraction	Content	Collection interval		500 mg/l stock solution stabilized with 1 *M* HCl			500 mg/l stock solution stabilized with 1 *M* NaCl			500 mg/l standards in Milli-Q water		
		Start (min)	End (min)	ng Pt	%	Peak area (μAU s)	ng Pt	%	Peak area (μAU s)	ng Pt	%	Peak area (μAU s)
1	Hydrolysis products	0.14	1.14	2.8	1.9		5.3	4.7		65	80.3	
2	$PtCl_4^{2-}$	1.25	1.74	67	46.6	60 400	52	45.9	48 100	5.9	7.3	5140
3		1.85	2.44	<LOD	0		<LOD	0		<LOD	0	
4	$PtCl_6^{2-}$	2.55	3.54	74	51.5	167 000	56	49.4	119 000	10	12.4	22 000
5		3.65	4.14	<LOD	0		<LOD	0		<LOD	0	
Total				143.8	100		113.3	100		80.9	100	

3.2.1. Pt determination by ICP–MS in eluent fractions

In order to relate the peak area determined for $PtCl_4^{2-}$ and $PtCl_6^{2-}$ by UV detection to their concentration (in terms of Pt concentration), eluent fractions were collected after IC separation and platinum was determined by ICP–MS analysis. Table 2 summarizes the results. The highest Pt amounts were determined using the standards diluted from the stock solution in 1 *M* HCl: 67 ng Pt(II) and 74 ng Pt(IV) per injection as $PtCl_4^{2-}$ and $PtCl_6^{2-}$, respectively. According to the following relations, 2 μg Pt/ml standards diluted from the stock solutions in 1 *M* HCl contained approximately 30% more of the respective species than those diluted from the stock solutions in 1 *M* NaCl:

ng Pt(II), HCl: ng Pt(II), NaCl = 1.29

ng Pt(IV), HCl: ng Pt(IV), NaCl = 1.32

At constant chloride concentration, the solution with lower pH was more effective in stabilizing the chloroplatinates. A possible explanation is the relatively higher hydroxide concentration in the NaCl solution, which causes the formation of hydroxo species to a greater extent, thus shifting the equilibrium towards the hydrolysis products. However, within the pH range concerned (pH 0 in the HCl, pH 5 in the NaCl stock solution or approx. pH 2.4 and pH 5 in the respective diluted 2 μg Pt/ml standard solutions), the pH dependence of hydrolysis cannot account for a 30% difference in the species concentrations. Moreover, the relation of the species content of standards diluted from the different stock solutions was dependent on the total platinum concentration (refer to Section 3.2.5), and the amount of Pt in eluent fraction 1 (hydrolysis products) of the stock solution in 1 *M* NaCl does not exceed that of the stock solution in 1 *M* HCl as much as expected (Table 2). Consequently, the sum of all fractions amounted to 21% less for the NaCl than for the HCl stock solutions. This effect was even more significant comparing the stock solution in HCl to that in water: 44% less total Pt was found in the chromatogram of the water stock solution, in which 80% of the total platinum was hydrolysed.

Tetrachloroplatinate was hydrolysed to a slightly greater extent than hexachloroplatinate. This effect was approximately the same in both HCl and NaCl solutions: 46% of the total platinum injected was found in the Pt(II) fraction, 50–52% in the Pt(IV) fraction. These relations have to be slightly corrected, since both the HCl stock solutions contained 1–3% of the respective other oxidation state species (see below).

Table 3
Detection of chloro-complexes by ICP–MS: one point calibration. The platinum content of Pt(II) and Pt(IV) fractions from Table 2 were related to the corresponding peak areas. Three different 500 mg Pt/l stock solutions were compared.

Pt stock solution in	Sensitivity [(μAU s)/ng]	Mean of three [(μAU s)/ng]
Pt(II) as tetrachloroplatinate		
1 *M* HCl	900	
1 *M* NaCl	930	
Water	870	900
Pt(II) as hexachloroplatinate		
1 *M* HCl	2260	
1 *M* NaCl	2130	
Water	2200	2200

The initial goal was to relate the absolute platinum content of the peak fractions to the peak area. The values were calculated for all three stock solutions (Table 3). They correspond well to each other, which means that the sensitivity is independent of the species concentration and the calibration curve for peak area vs. absolute species concentration is linear within the concentration range determined by the three standard solutions (approx. 0.2–2 μg Pt/ml).

3.2.2. Oxidation state purity of species standards

1 μg/ml standard solutions diluted separately from stock solutions of tetrachloroplatinate and hexachloroplatinate in 1 *M* HCl, 1 *M* NaCl, 30% HCl [Pt(II)] and 24% HCl [Pt(IV)[2]] were analysed according to method 1. The results are summarized in Table 4. All standards contained the chloro complex of the other oxidation state except for the $PtCl_4^{2-}$ standard diluted from the 1 *M* NaCl stock solution.

[2]The solubility of potassium hexachloroplatinate in 30% HCl is too small to prepare a 500 mg/L stock solution.

Table 4
Oxidation state purity of species standards. Tetra- and hexachloroplatinate (500 mg Pt/l each) in 1 *M* HCl, 1 *M* NaCl and concentrated HCl were diluted to 1 μg Pt/ml and measured separately in order to determine the content of the other oxidation state species. Listed are the means of two consistent replicates.

Nominal species (stock solution) solution)	Oxid. state state	500 mg/l Pt stock solution in	$PtCl_4^{2-}$ determined			$PtCl_6^{2-}$ determined		
			Peak area (μAU s)	Normalized to maximum peak area observed[a] (%)	Estimation of Pt(II) fraction[b] (%)	Peak area (μAU s)	Normalized to maximum peak area observed[a] (%)	Estimation of Pt(IV) fraction[b] (%)
$PtCl_4^{2-}$	II	1 *M* HCl	40 000	100	96.9	3090	2.9	3.1
$PtCl_6^{2-}$	IV	1 *M* HCl	550	1.4	1.2	107 000	100	98.8
$PtCl_4^{2-}$	II	1 *M* NaCl	25 300	63.3	100	<*LOD*	0	0
$PtCl_6^{2-}$	IV	1 *M* NaCl	270	0.7	1.0	64 700	60.4	99.0
$PtCl_4^{2-}$	II	30% HCl	24 500	61.2	67.5	29 600	27.6	32.5
$PtCl_6^{2-}$	IV	24% HCl	600	1.5	1.6	95 700	89.3	98.4

[a] Read vertically.
[b] The estimated values for the Pt(II) and Pt(IV) fractions add up to 100% in the same row. Estimations are based on the calibration factors from Table 3. They are not quantitatively applicable, however, since UV detection sensitivity remains not necessarily constant.

An estimation of the relative Pt(II) and Pt(IV) contents was made based on the mass calibration factors from Table 3. Although there is some uncertainty remaining for reasons of changing UV detection sensitivity, it can be concluded that the average purity of the species standards was between 97 and 100%. It follows that the species standards were stable as far as redox processes are concerned. An extreme exception was the $PtCl_4^{2-}$ standard in 30% HCl. Obviously, Pt(II) was oxidized in concentrated hydrochloric acid, confirming the statement made by Shpigun and Pazukhina [20] that precious metal chlorides exist in the form of their higher oxidation states in 6 *M* HCl. When analysed, the 30% HCl stock solution used here was obviously not yet equilibrated; further change of colour was still observed later. However, the Pt(IV) solution in 24% HCl contained approximately 1.6% Pt(II).

3.2.3. Kinetics of platinum–chloro complex hydrolysis

The stock solutions used for these experiments had reached equilibrium with respect to hydrolysis. A good long-term reproducibility of signal intensity was observed (refer to Section 3.2.5) and hence the concentrations of the species were constant and at a high level. In order to obtain information about the concentration stability of freshly diluted chloro complex standards, the peak areas of tetra- and hexachloroplatinate were determined at several timepoints analysing aliquots from a solution initially containing 1 μg Pt/ml in the form of each species (without corrections for redox processes and hydrolysis in the stock solutions). Fig. 4 shows the plot of peak area vs. time.

The reaction leading to the decrease in the pure chloro complexes is the first substitution of a chloride ligand by a water molecule according to

$$PtCl_x^{2-} + H_2O \rightarrow PtCl_{x-1}(H_2O)^- + Cl^-$$

Due to the excess of water, this reaction should follow pseudo first order kinetics:

$$\text{Peak area}(t) = Ae^{-kt} + c$$

The residual, c, represents the equilibrium concentration of the chloro complex. $A+c$ equals the peak area for $t=0$, while $c/(A+c)$ is the relative equilibrium concentration. The data of Fig. 4 was successfully fitted to this model. The determined parameters and statistical data are compiled in Table 5.

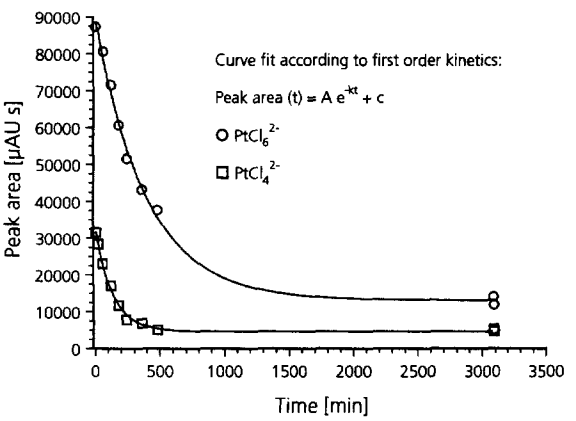

Fig. 4. Hydrolysis kinetics of chloroplatinates in water. Initial concentrations: 1 μg Pt/ml in the form of each species; HCl concentration resulting from stock solution: 4 m*M*.

The half-times for tetra- and hexachloroplatinate are 90 and 230 min, respectively. Hence, Pt(II) is reduced to half its concentration 2.6 times faster than Pt(IV). According to Fig. 4, equilibrium is reached after approx. 9 h for Pt(II) and 30 h for Pt(IV). For practical reasons, it is necessary to know how much decrease in concentration has to be expected during average sample preparation times. Assuming a delay of 3 min between dilution of the stock solution with water and the start of the analysis, according to the kinetic data 98% of the initial tetrachloroplatinate concentration and 99% of the initial hexachloroplatinate is still present. This systematic deviation is acceptable. There is, however, a rather large amount of uncertainty with respect to the reaction constants.

After the equilibrium was reached, 16 and 14.5% of the initial $PtCl_4^{2-}$ and $PtCl_6^{2-}$ concentration were detected.

3.2.4. Statistical validation

In order to point out some basic priciples for the use of species standards of inorganic complexes for calibration, two different stock solutions of tetra- and hexachloroplatinate are compared here: 500 mg/l Pt in the form of each species in 1 *M* HCl and in 1 *M* NaCl. It applies to all calibration data, that the respective total platinum concentrations were related

Table 5
Hydrolysis kinetics of chloroplatinates. Tetra- and hexachloroplatinate taken from the stock solutions in 1 *M* HCl were diluted with water at $t=0$ to give a 1 μg Pt/ml solution of each species. Chloride concentration was 4 mmol. At specified points of time the solution was analyzed by IC (Method 1). Peak area decrease with time was fitted to a first order kinetics model: peak area$(t)=A\,e^{-kt}+c$ (Fig. 5). Data was averaged from four experiments.

	$PtCl_4^{2-}$		$PtCl_6^{2-}$	
	Mean ($n=4$)	R.S.D. (%)	Mean ($n=4$)	R.S.D. (%)
Reaction constant k (min^{-1})	0.0076	21	0.0030	28
Half time $t_{1/2}=\ln 2/k$ (min)	90		230	
A (μAU s)	29 200	7	78 400	4
Residual c (μAU s)	5570	14	13 300	5
Correlation coefficient, r	0.998	0.2	0.996	0.3

to the peak areas of the two species. A correction for the loss of $PtCl_x^{2-}$ by hydrolysis or redox processes was not made. Since all data refers to the same equilibrium in the stock solutions, multiplication by a constant factor should be sufficient to correct this systematic error. Again Pt(II) and Pt(IV) were kept separately before dilution, which took place immediately before analysis.

The limit of detection (LOD) was estimated calculating the standard deviation (S.D.) of the baseline signals. It was defined as three times this S.D.. Accordingly, the limit of quantification (LOQ) was calculated as six times the S.D. of the blank signals. Detection and quantification were both limited by the signal height rather than by the peak area (i.e. the peak width). The values calculated are listed in Table 6. Obviously, LOD and LOQ are approximately the same for tetra- and hexachloroplatinate: 9 or 7 (LOD) and 18 or 14 (LOQ) ng Pt/ml in the form of each species. These concentrations were calculated using calibrations based on stock solutions in HCl, since these contained the highest species

Table 6
Statistical parameters for the determination of chloroplatinates by IC

Limit of detection (LOD) and limit of quantification (LOQ)

	ng Pt/ml in the form of the species specified[a]				
	Stock solution in 1 *M* NaCl			Stock solution in 1 *M* HCl	
	LOD (ng Pt/ml)	LOQ (ng Pt/ml)		LOD (ng Pt/ml)	LOQ (ng Pt/ml)
$PtCl_4^{2-}$	13	26	$PtCl_4^{2-}$	9	18
$PtCl_6^{2-}$	13	25	$PtCl_6^{2-}$	7	14

Reproducibility of peak area (n = number of determinations)

	25 ng Pt/ml		1000 ng Pt/ml	
	n	R.S.D. (%)	n	R.S.D. (%)
$PtCl_4^{2-}$	15	6.2	11	0.68
$PtCl_6^{2-}$	14	7.1	9	0.50

[a] From a three minutes, horizontal part of the method 1 baseline (sampling rate: 5 Hz) the standard deviation (S.D.) of 900 absorption heights was determined ($n=5$ replications). The LOD is defined as three times, the LOQ as six times this S.D.. The height units were converted to concentration values by regression analysis of height calibration curves between 0.01 and 0.25 μg Pt/ml.

concentrations observed. Therefore the values were taken as good estimations of the lowest obtainable LOD and LOQ. Limits of detection for Pt using data obtained from stock solutions in 1 *M* NaCl were naturally greater due to the lower species concentration.

The average short time reproducibility for the signals of both species was 6–7% R.S.D. at the limit of quantification. At 1 μg Pt/ml the R.S.D. of the peak areas reduced to 0.5–0.7%.

3.2.5. Calibration

Signals that are suitable for quantitative evaluation were obtained within a concentration range of at least four orders of magnitude. However, calibration curves were not always linear, without exception, within the complete concentration range. Since a linear relationship was obtained relating the peak area to the total platinum content of peak fractions (refer to Section 3.2.1), the deviation from linearity observed here must have been caused by actual concentration changes of the species.

Using the 500 mg/l chloroplatinate stock solutions in 1 *M* NaCl, linearity of calibration curves was observed for both species within 0.01–1 μg Pt/ml as well as within 1–50 μg/ml (Table 7). A linear regression model could also be used within the high concentration range for calibrations based on the stock solutions in 1 *M* HCl. Within 0.01–1 μg Pt/ml, the optimum curve fit was achieved applying a polynomial model ($n=2$). A linear fit in this range did not work at all (Fig. 5). While in the high concentration range the calibration data resulting from the HCl stock solutions corresponded to that from the NaCl stock solutions, using the HCl stock solutions resulted in relatively higher species concentrations within the low concentration range, as can be concluded from the slopes (b) in Table 7.

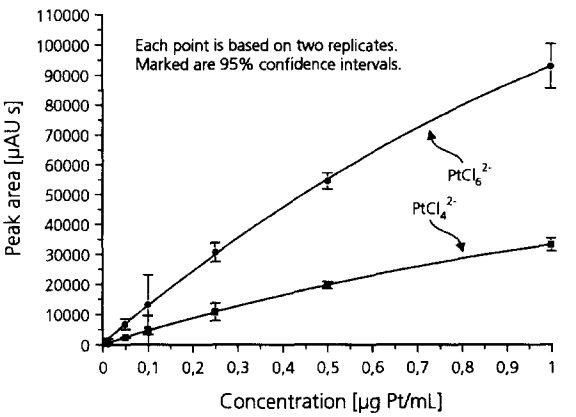

Fig. 5. Calibration curve for low concentrations of $PtCl_4^{2-}$ and $PtCl_6^{2-}$. Stock solutions in 1 *M* HCl.

From a theoretical point of view, the application

Table 7
Calibration data for the determination of chloroplatinates by IC. Calibration: peak area (y) (μAU s) vs. Pt concentration (x) (μg/ml). Units: a=μAU s, b=μAU s/(μg/ml), c=μAU s/(μg/ml)^2. Errors in %. Values in brackets are not significantly different from zero.

Species	a	Error	b	Error	c	Error	r
Stock solution in 1 *M* NaCl, 1–50 μg Pt/ml, linear fit $y=a+bx$							
$PtCl_4^{2-}$	(2440)	35	23 200	0.2			1.0
$PtCl_6^{2-}$	(19 900)	36	53 000	0.6			0.9999
Stock solution in 1 *M* NaCl, 0.01–1 μg Pt/ml, linear fit $y=a+bx$							
$PtCl_4^{2-}$	(310)	36	24 400	1.0			0.9997
$PtCl_6^{2-}$	(890)	34	60 600	1.2			0.9997
Stock solution in 1 *M* HCl, 1–50 μg Pt/ml, linear fit $y=a+bx$							
$PtCl_4^{2-}$	12 900	6.8	22 200	0.2			1.0
$PtCl_6^{2-}$	(54 500)	18	56 900	0.8			0.9999
Stock solution in 1 *M* HCl, 0.01–1 μg Pt/ml, polynomial fit $y=a+bx+cx^2$							
$PtCl_4^{2-}$	(180)	58	45 300	1.5	−12 400	5.2	0.9999
$PtCl_6^{2-}$	(580)	76	126 000	2.3	−33 700	8.2	0.9998

[a] The relative standard error (%) is calculated as the standard deviation of the coefficient divided by the square root of the sample size and divided by the coefficient itself.

of a "force zero" curve fit algorithm can be discussed since the signal without the analyte is also zero when an interfering matrix does not have to be considered (absence of overlapping peaks). There is, however, always a contribution of baseline noise to each peak area which might become significant for integration of detector signals at low concentrations.

In this study, an intercept (a in Table 7) was always calculated. In addition to the correlation coefficient and the standard errors of the curve fit parameters, the intercept was used to judge the goodness of fit: the goal was to minimize a. Since the statistical evaluation revealed almost all intercepts to be not significantly different from zero, they can be disregarded anyway when transforming peak areas to concentrations with this calibration data.

In order to quantify the long-term stability of the calibration, the means of the calibration data obtained on five different days within a period of five months were calculated ($PtCl_4^{2-}$, low concentration range, identical NaCl stock solution, linear fit): a = 13.8 μAU s (R.S.D. = 1800%), b = 23 700 μAU s/(μg/ml) (R.S.D. = 4.1%) and r = 0.998. Obviously, recalibration is only necessary after essential changes in the hardware of the system. The stability of the stock solution was proved by these results, too.

3.3. First applications

The need for the determination of platinum–chloro complexes occurred within the context of platinum emissions from automobile catalytic converters. The model substance (Pt on alumina) described in Section 1 was extracted with 0.9% sodium chloride solution. Both tetra- and hexachloroplatinate had been formed and were detected in the solution. Since this medium resembles the matrix of the chloro complex stock solutions, good quantitative results for the total platinum content were obtained without any correction factors.

In further model experiments, the reaction of the chloro complexes with biomolecules like bovine serum albumin (BSA) was investigated. After incubating hexachloroplatinate with BSA at pH = 7.4 in 0.1 *M* tris(hydroxymethyl)aminomethane (Tris)/0.9% NaCl buffer solution, the proteins were separated from the low-molecular-mass (LMM) species by gel permeation chromatography (Tris buffer as eluent). In the LMM fraction, the platinum species were subsequently determined by IC. Only tetrachloroplatinate but no hexachloroplatinate was detected and hence the reduction of hexachloroplatinate by BSA was observed.

While the buffer solutions could be measured without dilution, interferences in IC determinations occurred with high hydrochloric acid concentrations in synthetic sample mixtures (1 *M* HCl). Irreproducible peaks made the determination of tetrachloroplatinate impossible.

4. Summary and conclusion

Ionic platinum species occurring in aqueous solutions of tetra- and hexachloroplatinate were determined. Since there is an obscure number of complexes even in this simple Pt(II), Pt(IV), water, chloride (and hydroxide) system, the species detectable by UV absorption at 215 nm after IC separation were described only qualitatively. Apart from $PtCl_4^{2-}$ and $PtCl_6^{2-}$, five Pt(IV) and three Pt(II) hydrolysis products were observed.

Tetra- and hexachloroplatinate were also determined quantitatively. The detection limit for both species amounts to approx. 8 ng Pt/ml. The dynamic range is about four orders of magnitude. Using stock solutions in 1 *M* NaCl, a linear curve fit is possible within the whole range. A polynomial fit in the low concentration range is necessary with stock solutions in 1 *M* HCl. As a general rule, the calibrated concentration range should not exceed 1.5 to 2 orders of magnitude.

Due to the occurrence of hydrolysis and possible substitution reactions with other possible ligands, special attention was paid to the characterization of the species standards. However, after the stock solutions had reached equilibrium, they were stable for at least five months.

Hydrolysis can be disregarded up to three minutes after diluting the stock solution. Only 1 to 2% of the initial species content reacts to form hydrolysed compounds.

The total species content of the standard solutions was analysed by ICP–MS in eluent fractions. A

linear correlation between peak area and platinum mass was obtained within a narrow concentration range (approx. 0.2–2 μg Pt/ml in the form of the individual species). Different total platinum contents of chromatograms from stock solutions with the same nominal concentration but different stabilizing media were found. In concentrated stock solutions in pure Milli-Q water Pt(II) was probably reduced to colloidal platinum after several weeks, which could explain the low recoveries.

The methods developed were applied to NaCl extracts of a catalyst model substance or to gel permeation chromatography (GPC) fractions (Tris buffer). Measurement of the undiluted solutions (0.1 *M* Tris, 0.9% NaCl) was possible. Only high hydrochloric acid concentrations interfered with $PtCl_4^{2-}$ quantification. The application of the platinum species determination will be extended to a number of biological samples, partly in combination with GPC, in order to determine protein-bound platinum and the remaining inorganic species.

Future work will have to deal with the identification of individual species by combining chromatographic techniques with spectroscopic methods. The absolute quantification of the complexes can be improved by using an element specific detector.

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