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Determination of platinum, palladium, osmium, iridium, rhodium and gold as chloro complexes by capillary zone electrophoresis

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Abstract

The influence of pH, concentration of chloride in the background electrolyte, temperature, cetyltrimetylammonium, and other factors on the capillary zone electrophoresis of platinum group metals has been investigated. A high efficiency of the separation of Os(IV), Pt(IV), Ir(III), Pd(II), Au(III), Rh(III) and reduction of the analysis time to 5–6 min under the optimal conditions was achieved at elevated temperature. The possibility of simultaneous determination of Pt(II) and Pt(IV), or Os(IV) and Os(III) has also been demonstrated. The stability constants of chloro complexes of Pd(II) 1:n (Pd: Cl), n=2, 3, 4 and their mobilities were determined at ambient and elevated temperatures. In case of Pd(II) it was shown that the increase of the efficiency with temperature can be explained by changes of the stability constants of chloro complexes.The determination of platinum group metals in some real samples was made and compared to that of inductively coupled plasma atomic emission spectrometry. Detection limits achieved were in the range 0.1–0.6 ppm.

Keywords: Buffer composition; Metal complexes; Platinum-group metals; Chloro complexes

1. Introduction

There is an increasing interest in metal-containing agents in medicine, especially platinum and platinum-group elements (PGEs) [1]. The most common analytical methods for the determination of PGEs are UV–visible spectrophotometry [2–5] and HPLC [6–9]. However, a low selectivity of these methods remains a serious drawback. Moreover, the analysis time is long, and a time-consuming sample processing is required.

Owing to its extremely high separation efficiency, capillary zone electrophoresis (CZE) has proved to be a powerful tool also for the determination of inorganic ions and complexes. However, relatively little attention has been paid to separation and determination of PGEs. Buchberger et al. [10] studied the separation of cyanide complexes of palladium(II) or platinum(II). In the study of Motomizu et al. [11], 4-hydroxy-3-nitrosonaphthalene-1-sulfonic acid was used as a ligand for the determination of Pd(II) in the presence of Co(II) and Fe(II). However, the determination of the platinum group metals as chloro complexes might have several advantages. Platinum metals are usually dissolved in 'aqua-regia'. Thus, it might be advantageous to determine these metals as chloro complexes without any long pre-treatment of samples.

Recently, several studies dealing with the determination of PGEs as chloro complexes have been reported. Zhang et al. [12], determined palladium(II)

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in the presence of Rh(III), Ru(III), Os(III) and Ir(III) chloride complexes. Basaj et al. studied the CZE determination of Au(III) [13], as well as Pt(IV) and Pd(II) [14]. However, the problem of selective and rapid determination of all PGEs in their mutual presence by CZE remains topical, and it was the aim of this work to study the CZE separation of chloro complexes of PGEs.

2. Experimental

2.1. Instrumentation and procedure for electrophoresis

CZE measurements were carried out using SpectraPhoresis 2000 (Thermo Bioanalysis, CA, USA) with untreated fused-silica capillary, 44.5 cm×75 μm I.D. (Avery Dennison, MA, USA), length up to the detector window was 36.8 cm. A reversed polarity mode of the CZE system (cathodic injection and anodic detection) was used. If not stated otherwise, applied voltage was −11 kV, and the temperature was maintained at 55°C. Direct detection at 214–230 nm was used throughout the work.

Prior to use the capillary was washed for 5 min with 0.1 *M* NaOH at 25°C. Between each run the capillary was flushed with 0.2 *M* HCl for 0.5 min, followed by flushing with pure water for 1 min, and the running buffer solution for 1.5 min. Applying this procedure the migration times of analytes were constant. The pre-washing of the capillary by only water and buffer gives a permanently decreasing of the migration times. On the other hand, washing of the capillary by a solution of dimethylformamide (0.1%) led to increased migration times. At the end of daily work, the capillary was flushed with 0.2 *M* HCl and then with water for 2 min. If not stated otherwise, the samples were injected by hydrodynamic injection for 2 s.

The electroosmotic flow was determined from the migration of the mesityl oxide, MsO (4-methyl-3-penten-2-one). However, it is known that complex chlorides of platinum(IV) and palladium(II) form two compounds with the structure $(C_6H_9OPdCl)_2$ and $C_6H_{10}Cl_2OPt$ with MsO [15]. We found that at concentration of chloride >30 m*M* in the background electrolyte these substances move together with the electroosmotic flow and give a peak. The migration time of this peak is equal to that of MsO. If the concentration of chloride ions in the background electrolyte is reduced the distortion of MsO peak and the occurrence of the second peak with a higher migration time were observed. So, for example, using 60 m*M* $NaClO_4$ in the electrolyte in the presence of platinum(IV) or palladium(II), MsO gives two peaks on the electropherogram.

2.2. Chemicals

Os(IV), Rh(III) and Ir(III) standard stock solutions (5 m*M*) were prepared by weighing $(NH_4)_2OsCl_6$, $(NH_4)_3RhCl_6 \cdot 1.5\ H_2O$, and $(NH_4)_3IrCl_6 \cdot H_2O$ salts, respectively. They were obtained from Johnson, Mattey (London, UK). The salts were dissolved in 1 *M* HCl and diluted up to 100 ml adding 1 *M* HCl. The stock solution of Pd(II) was prepared by dissolving 0.02381 *M* of metal in 15 ml 5.692 *M* HCl and diluted to 200 ml distilled water. The working solutions were prepared by diluting of the stock solutions with double-distilled water or with the solution of potassium chloride (200 mg l^{-1}). The platinum(IV) stock solution was prepared by dissolving platinum metal (2.8428 g) in aqua regia 1:9 (HNO_3:HCl), double fuming the solution to dryness with hydrochloric acid and diluting to 100 ml with 0.2 *M* HCl. The solution of Pt(II) was prepared by heating 5.2 ml of stock solution of Pt(IV) with 1.64 ml 0.8% solution of hydrazinium hydrate up to 40°C and dissolved in 100 ml 0.2 *M* HCl. Standard solution of $AuCl_3$ was prepared by dissolving of anhydrous Au(III) chloride (Safina, Prague, Czech Republic), and then the solution was diluted to the concentration equal to 200 μg ml^{-1} with 0.2 *M* HCl.

All other chemicals were of analytical grade purity and were obtained from Lachema (Brno, Czech Republic). Double-distilled water from quartz still Heraeus (Hanau, Germany) was used for preparation of the solutions used in this study.

Carrier electrolytes were prepared by mixing appropriate volumes of 100 m*M* KCl (or NH_4Cl), water, and 0.1 *M* HCl. The background electrolyte (BGE) was prepared daily, filtered through a 0.45-μm filter prior to use and degassed in the ultrasonic bath for 2 min.

3. Results and discussion

3.1. Optimization of the separation conditions

3.1.1. Electrolyte selection

It is well known that chloride complexes of PGEs are stable in acid solutions and under a large excess of chloride ions [16]. This feature determines the selection of the electrolyte for the CZE. A mixture of an alkali metal chloride and hydrochloric acid can serve as an appropriate choice. However, one should take into account that a high concentration of chloride and a low pH leads to a high ionic strength and thus high conductivity and the production of a strong Joule heat.

In Fig. 1 the distribution diagram of Pt(IV) species depending on pH is indicated. It should be noted that only $[PtCl_6]^{2-}$ ionic form of platinum predominates in solutions with pH below 4. And, therefore, the ratio of concentration $[PtCl_6]^{2-}$ and $[PtCl_5(H_2O)]^-$ is practically constant in pH range 0–4. A similar picture is observed for distribution of palladium(II) complexes in hydrochloric solution. Gold in the pH range from 1–4 forms mainly $[AuCl_4]^-$ complex [13]. From these data it can be concluded that the pH of the BGE cannot be higher than 3–4. Distribution of platinum metals species depends not only on pH of the solution but also on the concentration of chlorides. So, at pH 3 palladium(II) is basically in the form of $[PdCl_3]^-$ and $[PdCl_4]^{2-}$ in a wide range of chloride concentration (Fig. 2A). This results in a broadening of the palladium peak and the dependence of the migration time on the concentration of chlorides in the electrolyte. Fig. 3 displays the dependence of effective mobility, μ_{eff}, of palladium(II) on the concentration of chlorides in the electrolyte. Decreasing the concentration, the effective mobility of palladium(II) decreases owing to the predominant formation of $[PdCl_3]^-$, $[PdCl_2]$, etc. In Fig. 4 the distribution diagram of rhodium(III) species vs. the concentration of chloride is presented. $[RhCl_5]^{2-}$ predominates at high chloride concentration. However, at this concentration of chloride the current is undesirably high. Hence, for rhodium(III) it is possible to expect less reproducible and effective determination, and a more narrow range of linearity of the calibration plot. Osmium, iridium, platinum and gold ions give mainly one

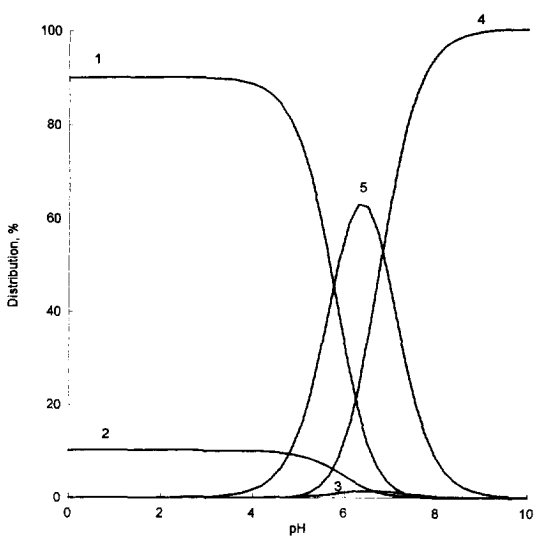

Fig. 1. Distribution of Pt(IV) species in chloride solution as a function of pH. 1=$PtCl_5^-$; 2=$PtCl_6^{2-}$; 3=$PtCl_4(OH)^-$; 4=$PtCl_4(OH)_2^{2-}$; 5=$PtCl_5(OH)^{2-}$.

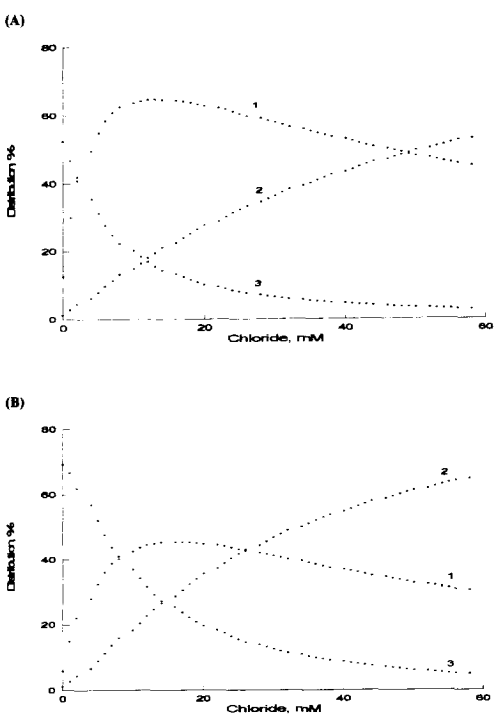

Fig. 2. Distribution of Pd(II) species in chloride solution vs. chloride concentration. (A) at 25°C, (B) at 55°C. 1=$PdCl_3^-$; 2=$PdCl_4^{2-}$; 3=$PdCl_2$. Concentration of Pd(II) 0.15 m*M*, pH=3.2.

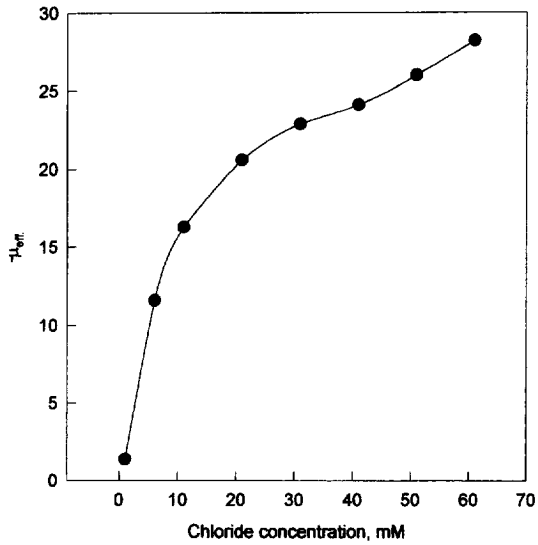

Fig. 3. Effective mobility of palladium(II), $\mu_{eff.}$, as a function of chloride concentration.

ionic complex form at 100-fold excess of chloride in solution. One can expect a more efficient determination in this case. Thus, the concentration of chloride in BGE should be as high as possible. All

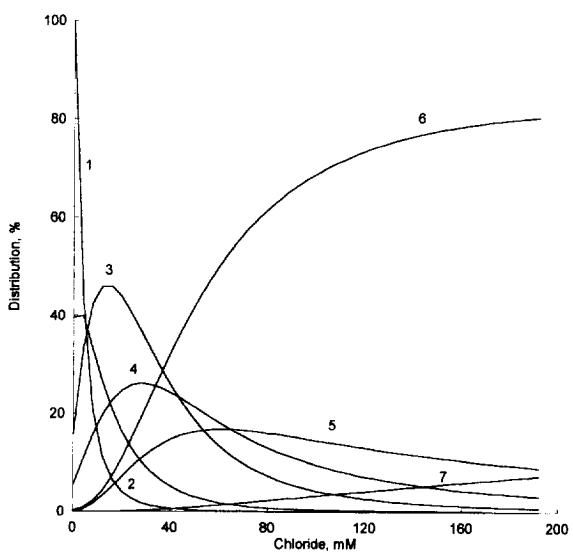

Fig. 4. Distribution of rhodium(III)–chloride species in chloride solution at pH 3. Concentration of rhodium(IV) 1 m*M*. 1=Rh^{3+}; 2=$RhCl^{2+}$; 3=$RhCl_2^+$; 4=$RhCl_3$; 5=$RhCl_4^-$; 6=$RhCl_5^{2-}$; 7=$RhCl_6^{3-}$.

distribution diagrams in this work were calculated using CELET computer program [17].

3.2. Influence of cetyltrimethylammonium bromide (CTMAB)

Hu et al. [12] used CTMAB as an electrolyte additive to modify the capillary surface and to reduce the analysis time. We have found, however, that CTMAB forms a precipitate with palladium(II) chloride at ratio of concentration Pd (II):CTMAB equal to 1:1 and higher. Probably, a bromide complex of palladium $[Pd(H_2O)_2Br_2]$ [16] is formed with considerably low solubility. The solutions containing 0.07 m*M* palladium(II) were prepared by dilution of the initial solution of palladium(II) by a solution of potassium chloride with a concentration of 200 ppm. Excessive turbidity of the solution with a ratio of concentration Pd and CTMAB=1:1 was observed, and at the ratio of concentration Pd:CTMAB=1:3 a precipitate was detected. The decreased palladium(II) concentration in solution, containing CTMAB was also confirmed spectrophotometrically. Moreover, by using the electrolyte containing CTMAB (0.2 m*M*) a sorption of palladium on the walls of capillary was observed. Our results show, in contrast to those of Zhang et al. [12], that the addition of bromides of cationic surfactants to the BGE it is not suitable for CZE analysis of platinum metals.

3.2.1. Influence of temperature

It is known that increasing temperature can shorten the time of the analysis and in certain cases it can improve the selectivity of the determination [16]. We have observed a 3-fold increase of the efficiency of palladium determination by increasing the temperature to 55°C and the simultaneous reduction of the analysis time (Table 1). This can be explained by change of stability constants of chloro complexes of palladium(II). From dependence of the effective mobility palladium(II) vs. the chloride concentration in BGE, formation constants of chloro complexes and mobilities of $[PdCl_3]^-$, and $[PdCl_4]^{2-}$ were determined (Table 2). The computer program CELET [17] has been used for the calculations. Good agreement of calculated values with literature data was received. Similarly constants at of 55°C were

Table 1
The influence of the separation temperature on the determination of 25 ppm palladium(II)

Temperature (°C)	Average current (μA)	Migration time (min)	Peak height (μV)	Efficiency (TP $m^{-1} \cdot 10^{-3}$)
15	50	5.3	2600	7.3
25	56	4.8	3700	10.5
35	62	4.4	4900	16
45	69	4.1	6000	21
55	77	3.8	7000	26

Carrier solution 30 m*M* KCl and 1 m*M* HCl, detection at 230 nm.
TP m^{-1}: Theoretical plates per meter.

determined. Change of the constants of chloro complexes when increasing the temperature results in predominance of the form $[PdCl_4]^{2-}$ (Fig. 2a and b). The predominance of only one form of the metal ions in the solution results in an increase of the efficiency of the determination. For PGEs which under the experimental conditions produce mainly one ionic form (iridium, gold, osmium), the increase of the temperature has a considerably lower effect.

However, the increase of temperature results in an increase of the current, and, hence, high Joule heat. At the temperature of 60°C and above also strong drift of the baseline was observed. At high temperature, probably, thermostation of the capillary is not sufficient. At 60 m*M* potassium chloride (pH 3.0, HCl) and voltage 11 kV, and temperature 55°C the average value of the current was about 140 μA and detached power about 1.3 W. At these conditions the reproducibility of the migration times was 0.3–1.1%. The reproducibility of peak area was 1–7%, so, about the same as at room temperature.

The reduction of the separation voltage reduces the drift of the baseline, but considerably increases the duration of the analysis (from 5 min at 55°C up to 22 min at 25°C). At voltages less than 8 kV the strong reduction of the efficiency of the determination of platinum metals (Fig. 5) is observed.

3.2.2. *Influence of sample injection time*

The increase of the injection volume of the sample can increase the sensitivity of the determination. On the other hand, at large injected volumes reduction of the efficiency and the selectivity of the determination was observed. The results obtained are summarised in Table 3. The injection time 2 s was chosen as the optimal one. The similar results were received applying electrokinetic injection.

3.3. *CZE determination of platinum metals*

On the basis of above mentioned results the following experimental conditions were chosen: concentration of chloride of 60 m*M* (pH 3), temperature 55°C, voltage −11 kV, hydrostatic injection of

Table 2
The determined efficient mobilities and stability constants of some chloro complexes of palladium(II) using general least squares CELET program [17][a]

Species	μ_{eff}		Log β	
	25°C	55°C	25°C	55°C
$[PdCl_2]$	0	0	7.75±0.03 (7.76)[b]	7.9±0.07
$[PdCl_3]^-$	−18.1±0.3	−26.9±0.5	10.26±0.02 (10.20)[b]	10.3±0.05
$[PdCl_4]^{2-}$	−38.0±0.5	−39.6±0.3	11.49±0.02 (11.50)[b]	11.9±0.04

Carrier electrolyte: 60 m*M* KCl and 1 m*M* HCl, detection at 214 nm.
[a] The computation is based on minimization of the sum, *U*, of squares of residuals ($\mu_{eff,exp} - \mu_{eff,calcd}$), $U = \Sigma(\mu_{eff,exp} - \mu_{eff,\ calcd})^2 = \min$, where $\mu_{eff,exp}$ are experimental and $\mu_{eff,\ calcd}$ calculated values of effective mobilities. The summation is done over all experimental points. For details cf. [17].
[b] Numbers in parenthesis means reference data [16].

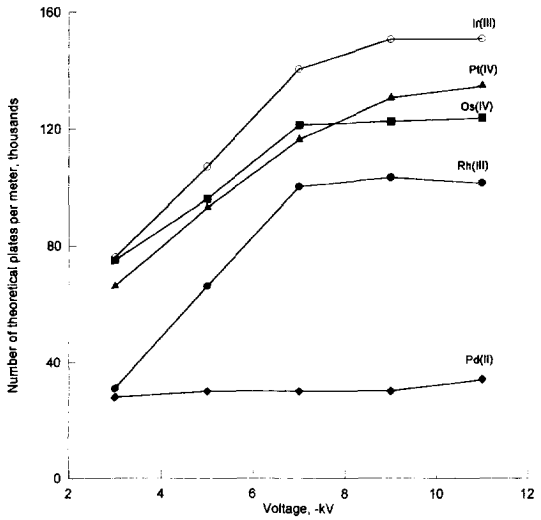

Fig. 5. The number of theoretical plates as a function of separation voltage for Ir(III), Pt(IV), Os(IV), Rh(III), and Pd(II). Experimental conditions: BGE 60 m*M* KCl (pH 3.1), temperature 55°C, hydrostatic injection during 2 s.

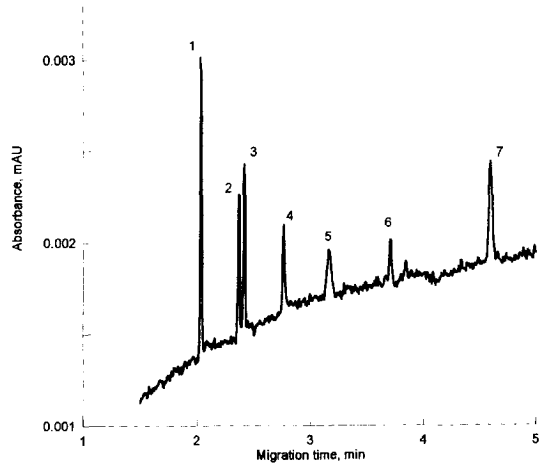

Fig. 6. Separation of platinum group metal as chloro complexes. Peaks: (1) Pt(II) (10 ppm), (2) Os(IV) (3 ppm), (3) Pt(IV) (2 ppm), (4) Ir(III) (5 ppm), (5) Pd(II) (4 ppm), (6) Pt(IV) (hydrolysis product), (7) Rh(III) (2 ppm). Separation conditions: BGE 60 m*M* KCl (pH 3.1), temperature 55°C, voltage −11 kV, electrokinetic injection 2 s at 5 kV, detection at 214 nm.

sample during 2 s. Under these conditions it is possible to determine selectively and expressively all PGEs (Fig. 6). The analytical characteristics are given in Table 4. Pt(IV) gives two peaks, that correlates with data of the work [14]. Hydrolysis of platinum(IV) salts begins at the concentration of hydrogen ions less than 0.1 *M*. However, the kinetics of the process are slow [16]. Thus, for solutions of platinum(IV) with concentration ≈0.1 poorly reproducible results during one day were observed.

Some reductants, for example ascorbic acid, are able to reduce platinum metals in their chloro complexes. In Fig. 7 electropherograms of osmium (IV) solutions obtained in the presence and absence of ascorbic acid were compared. In this case 2 g of ascorbic acid were added to the solution of Os(IV) of concentration 500 mg l^{-1} to prepare an Os(III) solution. In Fig. 8 the electropherogram of the solution of a mixture of Pt(II) and Pt(IV), prepared two weeks before analysis, is presented. It is shown, that in this solution not only chloro-complexes of platinum in appropriate oxidation degrees are present, but also the products of the hydrolysis. However, under the experimental conditions the peaks of Pt(II) are not very reproducible. A possible explanation is that chloro complexes of Pt(II) in solution hydrolyse easier than those of Pt(IV), which is in agreement with the literature [16]. Hydrolysis of

Table 3
The influence of injection time on the determination of Os(IV) (2 ppm) and Pt(IV) (4 ppm)

Injection time (s)	Resolution (R_s) of peak Os and Pt	Peak height of Os (mm)	Efficiency (Os), (TP $m^{-1} \cdot 10^{-3}$)
0.5	1.88	5	147
1.0	1.76	10	135
2.0	1.50	15	80
4.0	1.04	22	52
6.0	0.4	25	12

Carrier solution 60 m*M* KCl and HCl (pH=3.1), temperature 55°C, detection at 214 nm.
TP m^{-1}: Theoretical plates per meter.

Table 4
Metrological characteristics of the determination of platinum metals by capillary zone electrophoresis

Element	LOD ($\mu g\ ml^{-1}$)	Linear range of the calibration plots, ($\mu g\ ml^{-1}$)	
		Using peak height	Using peak area
Os(IV)	0.5	1–30	1–250
Pt(IV)	0.2	1–40	1–300
Ir(III)	0.6	1–40	2–300
Pd(II)	0.2	1–60	1–250
Rh(III)	0.1	1–25	1–50

Carrier solution 60 m*M* KCl and 1 m*M* HCl, temperature 55°C, detection at 214 nm.

such substances begins at pH 5–7 at room temperature (in hot solutions at pH 3) and, therefore, this may occur under the conditions of the experiment.

With 60 m*M* KCl concentration of the BGE, Au (III) hardly interferes with the determination of palladium(II). However, because migration time of palladium strongly depends on the chloride concentration in the electrolyte, we have attempted to change the conditions of the determination with the aim of minimizing this influence. In Fig. 9 electropherograms of PGEs and gold(III) at various concentration of chloride in the electrolyte (appropriate amount of sodium perchlorate was added to the electrolyte to maintain constant ionic strength) are shown.

The ratio of threshold mutual interfering influence of Os(IV) and Pt(IV) is 1:10 or 10:1. The determination of Pt(IV), Os(IV), Ir(IV), Pd(II), Au(III), Rh(III) is not interfered with by most of the transition metals as they move in the opposite direction (towards the cathode). Interfering influence of nitrate (showing large absorbance at the wavelength of detection and frequently present in PGE sample solution) was investigated. The nitrate peak was observed before the peaks of PGEs. Therefore, nitrate does not interfere with the determination of Os (3 ppm) and Pt (2 ppm) up to the concentration 1250 $mg\ ml^{-1}$. Concentration of chloride in the sample solution, higher than that in the background electrolyte results in appreciable decrease of the efficiency and the selectivity of the determination.

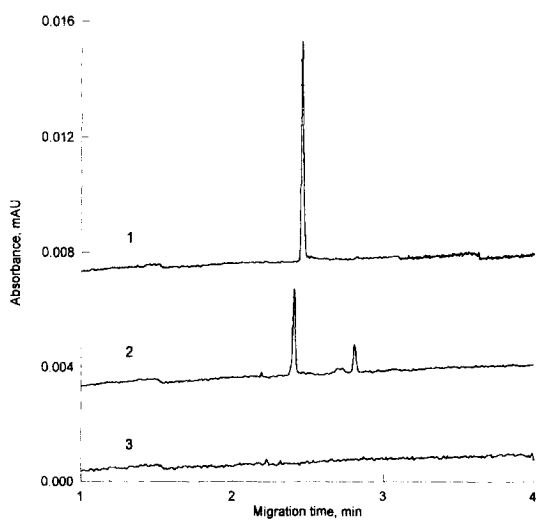

Fig. 7. Effect of ascorbic acid on the separation of Os(IV). (1) Os(IV) 10 ppm, (2) Os(IV) 10 ppm+0.04 $g\ l^{-1}$ ascorbic acid, (3) 0.04 $g\ l^{-1}$ ascorbic acid. Separation conditions: BGE 60 m*M* KCl (pH 3), temperature 55°C, voltage −11 kV, hydrostatic injection during 2 s, detection at 214 nm.

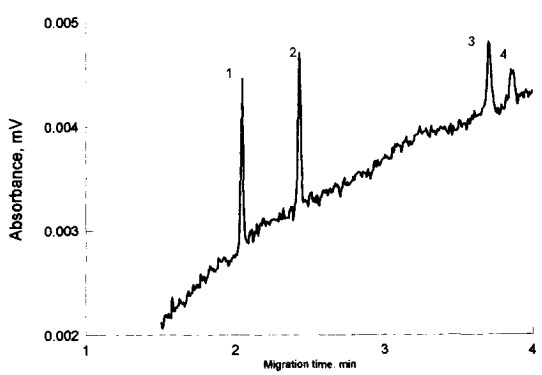

Fig. 8. Effect of Pt solution aging — electropherogram of the solution of a mixture of Pt (II) (20 ppm) and Pt(IV) (5 ppm), prepared two weeks before analysis at pH 3. Peaks: (1) $[PtCl_4]^{2-}$, (2) $[PtCl_6]^{2-}$, (3) $[Pt(OH)Cl_5]^{2-}$, (4) $[Pt(OH)Cl_3]^{2-}$. Separation conditions same as in Fig. 6.

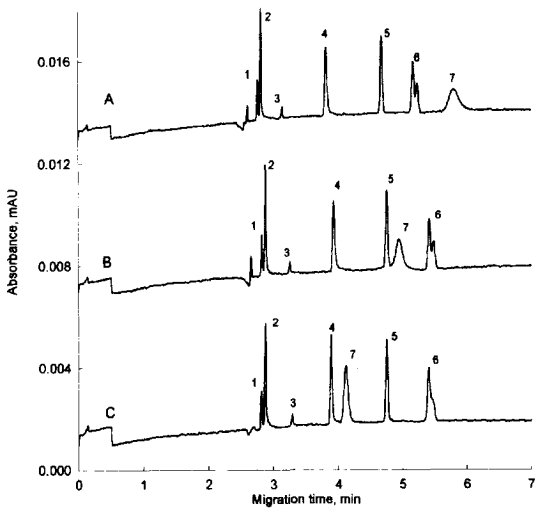

Fig. 9. Separation of 2 ppm Os(IV) (1), 2 ppm Pt(IV) (2), 2 ppm Ir(III) (3), 15 ppm Au(III) (4), Pt(IV) (5), 3 ppm Rh(III) (6), 4 ppm Pd(II) (7) at different chloride concentrations. Separation conditions: temperature 55°C, voltage −11 kV, BGE: (A) 10 m*M* KCl, 1 m*M* HCl, 40 m*M* $NaClO_4$; (B) 20 m*M* KCl, 1 m*M* HCl, 30 m*M* $NaClO_4$; (C) 30 m*M* KCl, 1 m*M* HCl, 20 m*M* $NaClO_4$.

Before analysis of such samples removal of large excess of chloride is recommended. In our system, the concentration of chloride in the sample solution up to 2–3 m*M* did not influence the determination of PGEs.

3.4. Applications

An example of a drug containing platinum, is Ribocarbo-L, from Ribosepharm (Haan, Germany), containing carboplatin which is used to cure some cancer diseases. We accomplished the quantitative determination of platinum in two samples of carboplatin. The preparation of the samples was made as follows.

Sample 1: To 5 ml of the liquid drug solution containing (on passport data) 50 mg of carboplatin 6 ml of HCl (conc.) and 2 ml HNO_3 (conc.) were added. The solution was evaporated to dryness in a PTFE plate. The dry residue was dissolved in 100 ml of 0.2 *M* HCl.

Sample 2: 3 ml of a solution of the sample containing 30 mg of carboplatin and 15 ml HNO_3 (conc.) was evaporated in a PTFE plate up to the volume of about 3 ml. Then 0.5 ml 70% $HClO_4$ was solution evaporated up to 0.5 ml. Finally, the solution was transferred to glass flask and diluted to 100 ml with 0.1 *M* HCl.

Table 5
Results of the determination of platinum in selected samples

Sample	Result of the determination (ppm)		
	Given	CZE	ICP-AES
1	262.7	260±5	247±6
2	157.64	155±6	163±10
3	16 000	15 600±300	16 200±700

Carrier electrolyte 60 m*M* KCl and 1 m*M* HCl, temperature 55°C, detection at 214 nm.
ICP-AES: Unicam 7000, power 1.0 kW, coolant flow 12 l min^{-1}, sample uptake 1.0 ml min^{-1}, spectral line 214.423 nm.

Sample 3: The content of platinum in the solution for platination Platinovací Roztok dle Lummer Kurlbauma (Laboratorní přístroje, Prague, Czech Republic) was analysed as well. The sample was diluted 1:1000 with distilled water before the analysis. The results of the analysis by CZE method were compared to whose obtained by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Table 5).

A satisfactory agreement of the results obtained by CZE with the nominal values was obtained and CZE results are also in a good agreement with those of a standard ICP-AES procedure [18,19].

4. Conclusions

This CZE method for the separation and determination of all PGEs in chloride medium is quite efficient and fast and it yields results in good agreement with those of ICP-AES. The detection limits obtained without any preconcentration step are comparable to those of ICP-AES and or atomic absorption spectroscopy.

Acknowledgments

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