Short communication

Determination of palladium(II) as a chloro complex by capillary zone electrophoresis

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Abstract

A novel method of separating and determining palladium as the chloro complex $PdCl_4^{2-}$ in the presence of rhodium(III), ruthenium(III), osmium(III) and iridium(III) chloro complexes by capillary zone electrophoresis (CZE) is described. On-column direct UV detection was achieved at 214 nm and the detection limits were lower than 20 ppb. By adding a suitable long-chain cationic surfactants, 0.2 mM cetyltrimethylammonium bromide, to the carrier electrolyte to create a layer of positive charges at the capillary wall and by reversing the polarity of the CZE system (cathodic injection and anodic detection scheme), analyte anions were caused to migrate in the direction of the electroosmotic flow, and thus the analysis time (3.0 min) was shortened. The effect of sample stacking on the plate number was investigated.

1. Introduction

Owing to its extremely high separation efficiency, capillary electrophoresis (CE) has proved to be a powerful tool for the determination of inorganic ions and inorganic ion complexes. As long ago as 1967, Hjérten [1] demonstrated the first application of CE to inorganic cations, namely the separation of bismuth and copper cations. Sixteen years later, Tsuda et al. [2] separated copper and iron cations. In 1987, Huang et al. [3] described the separation of rubidium, potassium, sodium, lithium and alkylamines. It is only in the last few years that CE has rapidly expanded to encompass various classes of ions. In 1992 Jones and Jandik [4] listed 129 ionic species found to be separable by CE, including inorganic and organic anions,

short-chain anionic surfactants, Group I and II metals, some transition metals (manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead) and some lanthanides.

However, relatively little attention has been devoted to separating and determining the platinum group metals ruthenium, rhodium, palladium, osmium, iridium and platinum. As we know so far only Buchberger et al.'s work [5] relates to the separation of cyanide complexes of palladium(II) or platinum(II) and some non-platinum group metals, cadmium(II), zinc(II), cobalt(II) and cobalt(III). The difficulty in the determination of platinum group metals by CE is that they exist in the form of metal complexes in water, which are stable in solutions of high ligand concentration, which leads to a high ionic strength and great Joule heating.

In this paper, the separation and determination of Pd(II) as chloro complexes are de-

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scribed for the first time. We found the following advantages of determination of platinum group metals as chloro complexes by CZE. First, chloride complexes of platinum group metals are the basis of the qualitative and quantitative analysis of platinum group metals [6] and platinum group metals are usually dissolved in $HCl-HNO_3$, so it is important to determine platinum group metals as chloro complexes. Second, we found that the separation and determination of Pd chloro complexes by CZE in the optimum system gave excellent results i.e., a good detection limit and linear range, compared with the above-mentioned method [5]. Third this method can determine Pd(II) in the presence of Rh(III), Ru(III), Os(III) and Ir(III) chloro complexes and Cu(II), Ni(II), Fe(II), Co(II) and a large amount of Cl^-.

2. Experimental

2.1. Instrumentation

The CE system employed as a Quanta 4000 (Waters Chromatography Division of Millipore, Milford, MA, USA) with a negative power supply. Direct UV detection was achieved with the use of a Zn lamp and a 214-nm optical filter. Waters AccuSep fused-silica capillaries (52.2 cm × 75 μm I.D.) were used throughout. Data acquisition was carried out with a Maxima 820 chromatography workstation (Waters) with a system interface module connecting the CE system to the station. Collection of electrophoretic data was initiated by a signal cable connection between the Quanta 4000 and the system interface module.

2.2. Reagents and carrier electrolytes

All chemicals were of analytical-reagent grade. A palladium(II) stock standard solution (1.00 mg/ml) was prepared by dissolving 0.1000 g of palladium metal in aqua regia, fuming the solution to dryness with hydrochloric acid and diluting to 100 ml with 1 M hydrochloric acid. The stock standard solution was diluted to 10.00 μg/

ml Pd with deionized water. Further dilution was carried out as required by using a solution containing at least a 200-fold stoichiometric excess of Cl^- to ensure sufficient chloride to form the Pd(II) chloro complex. Rh(III), Ru(III), Os(III) and Ir(III) stock standard solutions (100 μg/ml) were prepared by exactly weighing on an analytical balance the appropriate salt, $(NH_4)_2OsCl_6$, which required the addition of 5.0 g of ascorbic acid as reducing agent for dissolution, $(NH_4)_2Rh(H_2O)Cl_5$, $(NM_4)_2Ru(H_2O)Cl_5$ and $(NH_4)_3IrCl_6 \cdot H_2O$ (Aldrich), then dissolving them in 20 ml of 6 M HCl and finally diluting to 100 ml with deionized water.

Carrier electrolytes of 50 mM HCl-KCl (50 mM Cl^-) containing 0.2 mM cetyltrimethylammonium bromide (CTAB) were prepared by mixing appropriate volumes of 50 mM HCl containing 0.2 mM CTAB and 50 mM KCl solution containing 0.2 mM CTAB, and then if necessary titrating with KOH solution to achieve the required pH. The electrolyte was prepared daily, degassed and filtered through a 0.45-μm membrane prior to use.

2.3. Procedure for electrophoresis

Gravity injection was used. A 3-min capillary purge was performed prior to all injections. The purge was accomplished by a 12–15 p.s.i. vaccum applied to the receiving electrolyte vail. The sample was injected at the cathode and the detector was placed 7.25 cm from the receiving electrolyte end. The electroosmotic flow μ_{eo} was determined from the migration time of formamide.

3. Results and discussion

3.1. Effect of pH on electrophoretic mobility

Fig. 1 shows the effect of pH on electrophoretic mobility μ_e of Pd(II) chloro complex for 50 mM HCl-KCl carrier electrolyte containing 0.2 mM CTAB. The pH range is from 2.80 to 5.95 because the electric current hardly changes within this range, and thus the effect of
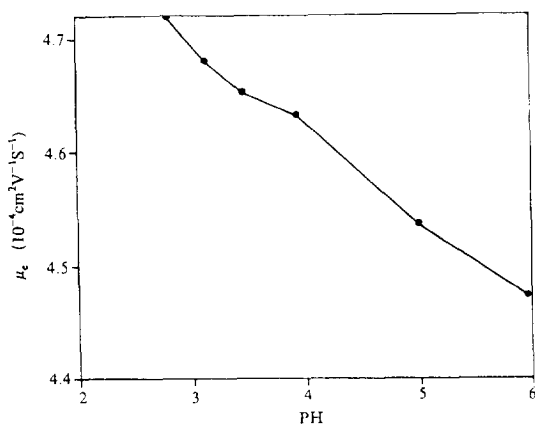
Fig. 1. Effect of pH on the electrophoretic mobility μ_e of the Pd(II) chloro complex. Carrier electrolyte, 50 mM HCl–KCl containing 0.2 mM CTAB at different pH values; untreated fused-silica capillary, 52.2 cm × 75 μm I.D.; applied voltage. 15 kV.

electric current can be eliminated. Fig. 1 shows that the electrophoretic mobility decreases with increasing pH. The $PdCl_4^{2-}$ complex slightly hydrolyses with increasing pH. The hydrolysates are complicated, and may be $PdH_2OCl_3^-$, $PdOHCl_3^{2-}$, etc. The average number of Cl^- ligands decreases with increasing pH, so the effective electrophoretic mobility of the Pd(II) complex decreases. This conclusion was further confirmed by the following experiment.

3.2. Influence of the concentration of Cl^- on migration time, plate number and peak area

We found that the Cl^- concentration of the carrier electrolyte influences the migration time

of the Pd(II) chloro complex. Considering that zones do not travel at the same velocity for different Cl^- concentrations of the carrier electrolyte, we corrected the peak area for the differences in zone velocity to obtain the actual influence of concentration of Cl^- on peak area. We refer to the general peak area, with units of peak response (μV s), as the temporal peak area, S_t. The correction involves simply multiplying the temporal peak area S_t by the zone velocity. Thus the influence of zone velocity on peak area is eliminated. We refer to the corrected peak area, with units of the peak response (μV cm), as the spatial peak area, S_1. A similar correction for band width was made by Huang et al. [7] to analyse the contributions of the various factors to band width.

From Table 1, the Cl^- concentration of the carrier electrolyte influences the migration time, peak height, plate number and temporal peak area, but hardly influences the spatial peak area. Generally, increasing the concentration of carrier electrolyte increases the migration time owing to the decreased electroosmotic mobility [8]. For the Pd(II) chloro complex, with increasing Cl^- concentration of the carrier electrolyte, the electroosmotic mobility also decreases, but the migration time decreases. The decreased migration time is due to the change in the degree of complexation: the average ligand number and effective negative charge of the Pd(II) chloro complex increase with increasing ligand Cl^- concentration, which results in an increase in the effective electrophoretic mobility. Therefore, it can be concluded that the larger the degree of

Table 1
Influence of Cl^- concentration (C) of carrier electrolyte on migration time (t), peak height (H), plate number (N), temporal peak area (S_t) and spatial peak area (S_1) of Pd(II) chloro complex

C (mM)	t (min)	H (μV)	N (×10^{-4})	S_t (μV s)	S_1 (μV cm)
5	4.220	349	0.54	2752	489
10	4.130	655	1.9	2728	495
25	3.838	1025	4.7	2511	490
50	3.327	1409	8.8	2198	495

Conditions: voltage, 15 kV; carrier electrolyte, HCl–KCl of different concentrations containing 0.2 mM CTAB at pH 3.0; capillary, 52.2 cm × 75 μm I.D.

complexation of Pd(II) with Cl⁻, the larger the effective electrophoretic mobility becomes, which is the same conclusion as in the above discussion about the effect of pH on electrophoretic mobility.

Whereas the effect of Cl⁻ concentration on migration time is small, it significantly and favourably influences the plate number: with increasing Cl⁻ concentration, the peak becomes higher and narrower, but the spatial peak area remains almost unchanged. The reason is sample stacking, which is a powerful technique in narrowing the analyte zone length and increasing the number of theoretical plates in capillary ion analysis (CIA). Sample stacking (concentration of the analyte zone) is the process that occurs when a voltage is applied along a capillary tube containing a sample plug with an electric resistivity higher than that of the surrounding carrier electrolyte. From our recent work [9], the "stacking force" (ΔE) is the difference between the field strength along the sample zone E_1 and running carrier electrolyte E_2:

$$\Delta E = E_1 - E_2 = \frac{V}{l_0 + \dfrac{L}{\rho_0/\rho_2 - 1}} \qquad (1)$$

where V is the applied voltage, L is the total length of the capillary, l_0 is the initial length of introduced sample zone, ρ_0 is the electric resistivity of the introduced sample solution and ρ_2 is the electric resistivity of the running carrier electrolyte. From Eq. 1, the smaller is ρ_2, the greater the "stacking force" becomes. The electric resistivity of a strong electrolyte solution is inversely proportional to the solution concentration. Therefore, a general increase in plate number was observed with increasing concentration of Cl⁻ of the carrier electrolyte. Obviously an increasing Cl⁻ concentration in the carrier electrolyte has several advantages: the migration time decreases and the peak height and plate number increase.

3.3. Selection of optimum conditions

Based on the above analyses, it is in a solution of low pH and high chloride concentration that

the Pd(II) chloro complex is stable and not easy to hydrolyse, which requires the chloride concentrations of both the sample solution and the carrier electrolyte to be high. Moreover, to prevent the band from spreading, the chloride concentration of the carrier electrolyte must be higher than that of the sample solution owing to the "stacking effect'. However, the increase in the chloride concentration and the decrease in the pH of the carrier electrolyte are subject to limits because a solution of low pH and high chloride concentration has a high ionic strength, which results in high conductivity, large current and large Joule heating. Based on the experimental results, 50 mM HCl–KCl carrier electrolyte at pH 3.0 was selected as the optimum condition. Further, 0.2 mM CTAB, which was also determined by experiment, was added in carrier electrolyte to cause the electroosmotic flow to move in the same direction as PdCl₄²⁻ (towards the anode).

3.4. Limits of detection and quantitative analysis

Based on a peak height of twice of the baseline noise, the detection limit was determined for hydrostatic injection, where the sample was raised by 10 cm for 20 s. The detection limit of PdCl₄²⁻ was 20 ppb for 50 mM KCl–HCl carrier electrolyte containing 0.2 mM CTAB at pH 3.0. Quantitative determination using hydrostatic injection can be carried out on the basis of a linear relationship between peak area and sample concentration. The linear range was two orders of magnitude above the limit of detection (the correlation coefficient for the calibration curve is 0.9998). The relative standard deviation of the peak area for PdCl₄²⁻ was 3.1% ($n = 8$).

Our experiments showed that PdCl₄²⁻ can be determined in the presence of 20 ppm of Ir(III), Os(III), Rh(III) and Ru(III), 100 ppm of Cu(II), NI(II), Fe(II) and Co(II) and a large amount of Cl⁻ (see Fig. 2). The cations Cu(II), Ni(II), Fe(II) and Co(II) do not influence the determination of Pd since they travel in the opposite direction to the cathode, and so Fig. 2 does not contain the peaks of Cu(II), Ni(II),
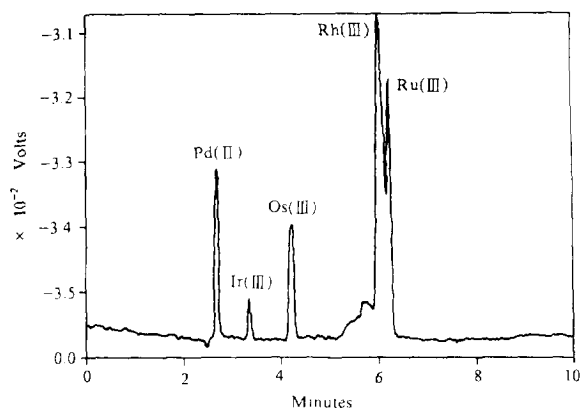
Fig. 2. Electropherogram for the determination of Pd(II) in the presence of 20 ppm each of Ir(III), Os(III), Rh(III) and Ru(III) chloride complexes and 100 ppm each of Cu(II), Ni(II), Fe(II) and Co(II). Carrier electrolyte, 50 mM HCl–KCl containing 0.2 mM CTAB at pH 3.0. Applied voltage 17 kV. Other experimental conditions as in Fig. 1.

Fe(II) and Co(II). At pH 3.0, Ir(III), Os(III), Rh(III) and Ru(III) chloro complexes easily hydrolyse and they migrate more slowly than the Pd(II) chloro complex (see Fig. 2), so they also do not influence the determination of Pd. Studies are currently being carried to improve the separation selectivity of platinum group metals, such as the simultaneous determination of Pd(II) and Pt(II) as chloro complexes. The potential application of the method, such as in the precious metal mining industry and in the control of waste water from synthetic rubber plants, is great.

Acknowledgement

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