SOME IMPORTANT PARAMETERS FOR ELECTROCHEMICAL BEHAVIOUR OF PALLADIUM(II) IN THE PRESENCE OF CHELATE LIGAND DIMETHYLGLYOXIME

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Abstract

The procedure for the voltammetric determination of palladium(II) involves an adsorptive accumulation of palladium(II)-DMG complex on a stationary mercury electrode, followed by a stripping voltammetric measurement of reduction current of adsorbed palladium(II) chelate complex. The optimum conditions for the analysis of palladium(II) included pH (3.5 - 4) and an accumulation potential between 0 and - 0.3 V (vs. Ag/AgCl). The peak current is proportional to the Pd-DMG concentration and increases linearly with a preconcentration time.

Keywords: Palladium determination, Adsorption stripping voltammetry, Dimethylglyoxime, Adsorption time

Introduction

The interest in the determination of extremely low concentration of palladium(II) in environmental samples has rapidly increased during the last years. Although there are strict requirements in the durability of catalyst material [1], its emission into the environment cannot be avoided. To study the influence of palladium(II) in the environment, reliable information about its concentrations in the ng/g range is needed [2-3].

The difficulties in the determination of palladium(II) by some conventionally electrochemical methods are not yet overcome [4-5]. Therefore, it is expected that the electroanalytical techniques analogous to the stripping method are advantageous in improving the quantitation of palladium(II). Further increase in the sensitivity and the selectivity of advanced voltammetric methods, e.g., differential pulse polarography (DPP), square wave voltammetry (SWV) and stripping voltammetry (SV), can be achieved by a modification of the electrode [6-8] and/or an enhanced adsorption of the analyte [9-14].

On the basis of the data published by Wang and Varughese [10] and considering our previous investigations [2,14], we optimised some parameters of importance for adsorptive stripping voltammetry (AdSV). The determination of palladium(II) in different solid samples by this method is also presented herein.

Experimental

A palladium standard stock solution (1.00 mg/ml) was prepared by dissolving palladium(II) chloride (Merck) in 6 mol/L HCl, and standardised gravimetrically by precipitation with dimethylglyoxime (DMG). Working Pd(II) solutions were prepared by dilution of the standard solution with 0.01 mol/L HCl. An ethanolic solution of 0.1 mol/L DMG was prepared by dissolving DMG (butane-2-3-dione dioxime, Merck) in absolute ethanol. As supporting electrolyte an acetate buffer of pH 3.6 was used. It was prepared by mixing the appropriate amounts of 0.1 mol/L acetic acid and 0.1 mol/L sodium acetate. A combined glass electrode and a pH meter were used for the pH measurement. All reagent were of analytical purity or suprapure quality. Deionized water was additionally purified using the Milli - Q system.

Voltammetric measurements were performed using a microprocessor controlled polarograph (PARC M 374) equipped with a Static Mercury Drop Electrode (SMDE, PAR M 303). An Ag /AgCl /3M KCl was used as a reference electrode and a platinum wire as an auxiliary electrode. Oxygen was eliminated by purging with pure argon gas (99.9 %) for 5 min. Voltammograms were recorded after 2 min of adsorptive preconcentration of palladium chelate with stirring (750 rpm) at - 0.3 V. Before the measurement the solution was equilibrated (stirrer off) for 15 s. Measurements were made in a DPP mode with a polarizing voltage of 8 mV/s scanned in a negative (cathodic) direction.

Silver and silver alloy samples are dissolved in HNO₃ (1:1). The solution is then evaporated to a smaller volum (approx. 5 mL) and transferred into an appropriate measuring flask. An aliquot is partly neutralised by ammonia, and palladium determined by the method of standard additions.

Alloys of platinum samples (0.1-0.2 g) are dissolved in aqua regia (HCl+HNO₃, 3+1). The solution is heated on a water bath to remove nitrogen oxides, acidified with conc. HCl, and then left to evaporate to near dryness. Affter quantittative transfer to a measuring flask, an aliquot of the solution is pipetted into the cell and palladium determined as described above.

Results and discussion

Investigation of the reduction process of Pd-DMG complex [14] showed that the voltammetric peak height depends on pH , the concentration of DMG and buffer composition, the scan rate, and the presence of surface active substances [2].The adsorptive stripping response was evaluated with respect to the concentration of the supporting electrolyte and the preconcentration potential. The optimum concentration of the supporting electrolyte (acetate buffer) is 0.1 mol/L and the optimum pH value is 3.5 ± 0.5. Pd-DMG complex is strongly adsorbed on the Hg electrode between pH 3 and 6. The optimum potential range for its accumulation is between 0 and - 0.35 V with respect to the Ag/AgCl electrode [2, 14]. Current response during the reduction of the Pd-DMG complex depends on their equilibrium concentration on the electrode surface [14].

Voltammetric curves recorded in 0.1 mol/L acetate buffer at pH 3.6 are shown in Fig. 1. Curve a in the Figure 1 shows that the voltammetric peak of DMG is not appearing in observed potential area. If palladium is added in the solution (curve b), one obtains a voltammetric peak at a potential of - 0.55 V. Its height is considerably dependent on the preconcentration time. Finally, one can see that the shape of the voltammetric peak (curve c) is asymmetric. That is important for processes which proceed from an adsorptive state of the analyte. The reduction process is completely irreversible. This is also, evident from curve d of the same figure. This curve is recorded in anodic direction.
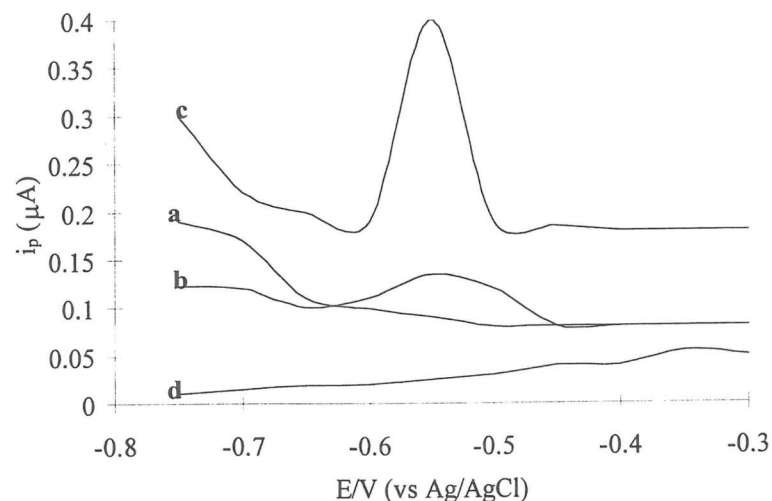

Figure 1. Peak current - peak potential dependence in 0.1 mol/L acetate buffer (pH 3.6); a) 1×10^{-4} mol/L DMG; b) a + 10 μg Pd^{2+}/L at deposition time 15 s ; c) b at deposition time of 120 s and d) c in anodic direction.

Figure 2 shows voltammetric curves obtained in an acetate buffer of pH 3.6 at different preconcentration times. It can be seen that after 15 seconds even in 10 μg Pd/L (curve c) an outstanding peak which can be very precisely measured was obtain. This peak is markedly higher if the preconcentration was carried out for two minutes (curve d).
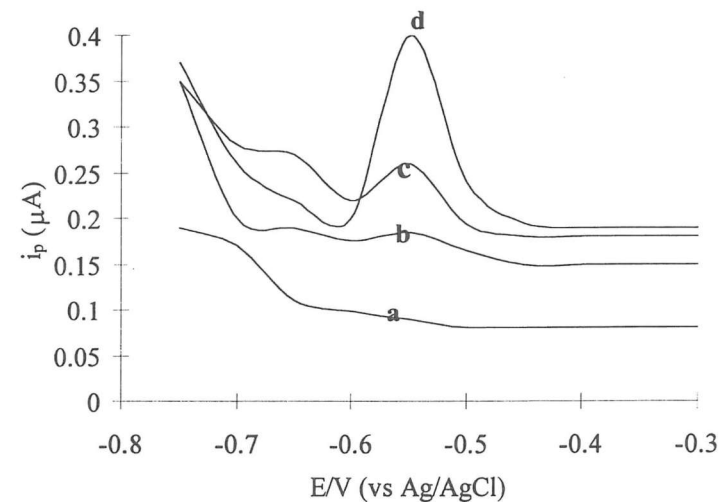

Figure 2. Dependence of the peak height on preconcentration time in 0.1 mol/L acetate buffer (pH 3.6) , 1×10^{-4} mol/L DMG (a) and (b) - (d) 10 μg Pd^{2+}/L at different accumulation times; b) 0 s, c) 15 s , and d) 120 s at –0.3V; electrode area: 2.6 mm^2

At the same time it is particularly dependent on the adsorptive preconcentration time. The dependence of the peak current of Pd-DMG complex on the preconcentration time was studied in solutions containing various palladium concentrations and the results are shown in Fig.3. At a low concentration of palladium (curve a) it takes more than 5 min. for the peak current to level off. For higher concentration of palladium (curve b), the peak current increases as the preconcentration time increases and starts to level off about 3 min.
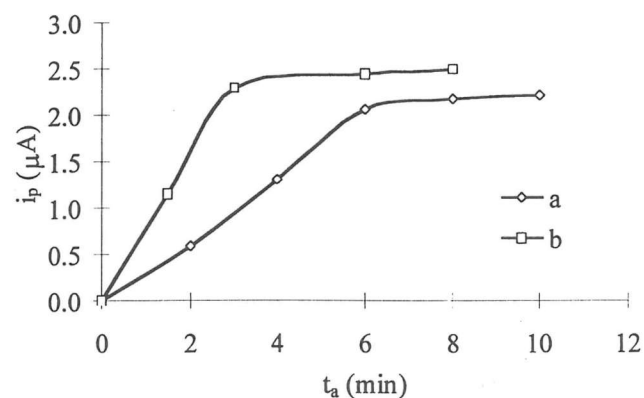
Figure 3. Peak current dependence on preconcentration time in 0.1 mol/L acetate buffer of pH 3.6, 1×10^{-4} mol/L DMG; a)15 μg Pd^{2+}/L , b) 25 μg Pd^{2+}/L; electrode area : 2.6 mm^2

Table 1. Palladium contents in some silver and platinum samples

Sample	Pd (μg/g)	Average (μg/g) and std.dev.	Relative std.dev. (%)
Silver (wire)	< 0.05	---	---
Platinum (wire)	5.48	4.98 ± 0.4	8.2
	5.20		
	4.93		
	4.39		
	4.38		

Apparently, higher concentration gradient enhances the diffusion of Pd-DMG complex toward the stationary electrode during the accumulation and thus, reaches the equilibrium state faster. Since a longer preconcentration time gives a better sensitivity but, based on these experimental conditions, the preconcentration time of two minutes was chosen to obtain the linear response in all the subsequent work.

High sensitivity, selectivity and simplicity of the voltammetric method and the linearity between the peak current and the concentration of Pd(II) were utilized to analyse some samples, e.g., silver and platinum. Amount of palladium in pure silver wire (99.99 % Ag) was below the limit of detection (LOD) of the voltammetric procedure (Tab.1). Five replicate analysis of a platinum wire give an average of 4.98 mg Pd/kg and a relative standard deviation (RSD) of 8 %. But, the high uncertainty of the final result originates mainly from the sample dissolution step [2]. Results obtained by NAA showed a similar level of Pd in commercial platinum [15-16]. For the analysis of complex samples of unknown type and concentration of interfering compounds, an evaluation based on multiple standard addition is recommended. By the method of standard addition one can control the linear response, that is applicable condition for determination of Pd(II) in the sample solution.

In summary, the present study suggests that stripping voltammetry of palladium(II) based on accumulation of palladium chelate complex can be used to determine trace amounts of palladium in samples of some precious metals. The detection limit of this method is 50 ng/g Pd after 120 s preconcentration period. Applying this method a quite well reproducibility of the individual experimental parameters and the accuracy of the analytical results are obtained. Therefore, the proposed method can be used as a suitable practical application for Pd(II) determination with high sensitivity, selectivity and simplicity.

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ELECTROCHEMICAL STUDY OF 3,5 – DIMETHYLPYRAZOLE-PENTACYANOFERRATE (II) COMPLEXES AT GLASSY CARBON ELECTRODE.

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ABSTRACT

Electrochemical oxidation of 3,5 dimethylpyrazole-pentacyanoferrate (II) complexes at glassy carbon electrode has been determined from analyses of voltamperometric curves at different pH values. The complex species formed are dependent on the pH media. Voltammograms display only a well-defined wave but the peak potentials shift to less positive values as the pH medium increases. The possible mechanisms of the reaction have been discussed.

Key words: glassy carbon electrode; pyrazole complexes