Determination of Palladium Traces by Differential Pulse Polarography after Preconcentration by Extraction with Quaternary Ammonium Salts

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The samples with the complicated matrix containing organic substances have to be mineralized by wet combustion in the mixture of acids. Palladium is then extracted from the HCl medium with quaternary ammonium salts into toluene and reextracted by alkaline NH_4NO_3 solution which is the base electrolyte for polarographic determination. During the adjustment of the sample the preconcentration of palladium takes place. The determination limit is 2.5 μg dm^{-3} in 100 cm^3 of the sample. The determination is practically selective with respect to other metals, the determination limit is worsened only by the presence of cadmium.

Palladium is often used as catalyst in different organic productions. With respect to its high price its losses in the form of low-concentrated waste may be economically important. The determination of palladium in these samples requires the method with low determination limit and at the same time with a very good selectivity. The palladium concentration which is necessary to be determined usually makes 0.1—10 mg dm^{-3} in several cm^3 of the sample which often contains many organic substances. For the determination of low palladium concentration the AAS and spectrophotometry methods are typical [1]. The standard spectrophotometric method [2] enables to determine palladium in the concentration 5—20 mg dm^{-3} and is very selective with respect to other metals; the newer methods [3—5] reach lower determination limit, however, the selectivity is worse. The determination in real samples by AAS is not possible directly especially when the content of salts is high. The determination in most methods is disturbed by the complicated organic matrix.

In the medium of amines palladium offers the well developed polarographic wave; therefore in the determination with differential pulse polarography (DPP) *e.g.* ammoniacal medium is used, when the complex $[Pd(NH_3)_4]^{2+}$ is formed [6]; the peak being within the range of potentials *ca.* - 0.8 V *vs.* SCE, the determination limit being 50 µg dm^{-3} The acid medium is unfavourable for the DPP method, palladium is, however, well extracted from the acid medium into the organic solvents [7—9] both by tertiary and quaternary amines, especially in the presence of halide ions as the complex anion. With respect to the high stability of the complex $[Pd(NH_3)_4]^{2+}$ ion [10] and to the mechanism of the extraction by amino reagents it is obviously possible to reextract palladium by ammonia solution suitable for the determination by DPP method.

EXPERIMENTAL

10 % palladium(II) chloride solution (Safina, CSFR) was used as a source of palladium the solutions of which in HNO_3 were prepared by the *Jorgensen* method [11]. The standardization of stock solutions of palladium was made by the usual dimethylglyoxime method [1]. The trioctylmethylammonium chloride solutions (Adogen 464, General Mills, USA) in toluene were purified by the multiple washing with the solutions of hydrochloric acid, sodium hydroxide, and distilled water. All other chemicals were of anal. grade and were used without further purification.

Polarographic measurements were made with polarograph PA-3 in connection with static mercury drop electrode SMDE-1 (Laboratorní přístroje, Prague). The polarographic records were scanned by the DPP method within the range of potentials from - 0.55 V down to - 1.1 V *vs.* SCE, the rate of potential change was 2 mV s^{-1}, the modulation amplitude 100 mV, the controlled drop time was 2 s and there was used the drop of maximal possible size.

In the work, model samples of palladium solutions as well as real industrial waste waters were used. These contained great amount of inorganic salts (NaCl) and unspecified organic substances which did not enable direct determination of palladium. Such samples were mineralized by the mixture of acids H_2SO_4—HNO_3—$HClO_4$. The sample of volume 10 cm^3 was slowly dropwise added to 2 cm^3 of H_2SO_4 heated to about 180 °C. Simultaneously the necessary amount of the mixture HNO_3—$HClO_4$ (φ_r = 1 1) was dropwise added. After the decomposition has been finished, the excess of acids was evaporated and fumed and solid rest was dissolved in HCl with suitable concentration.

RESULTS AND DISCUSSION

For the choice of optimum conditions of the extraction and reextraction in the sense of sufficient recovery of the decrease in volume, the conditions of extraction and reextraction of palladium were studied. Fig. 1 shows the dependence of distribution ratio of palladium on the HCl concentration. Its course is explainable by the formation of $[PdCl_4]^{2-}$ complex with increasing of HCl concentration and at the same time by concurrent extraction of overstoichiometric acid [12]. The optimum concentration is $c(HCl) \approx 0.5$ mol dm^{-3}. With respect to the great affinity to the salts of amines the negative effect on extraction recovery of palladium is exerted also by other acids present in macroconcentrations. Fig. 2 shows the dependence of distribution ratio of palladium on the concentration of HNO_3, H_2SO_4, and $HClO_4$, respectively, that enables to determine which concentration of these acids may be tolerated. The content of H_2SO_4 is obviously not critical but the extraction is strongly suppressed by HNO_3 and more remarkably by $HClO_4$.

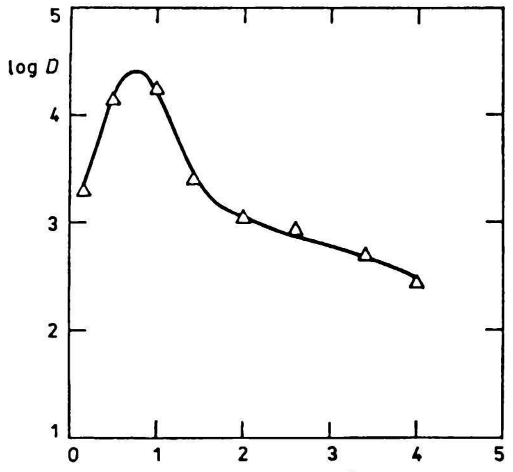

Fig. 1. Dependence of palladium distribution ratio on the concentration of HCl in aqueous phase; in toluene phase ρ(Adogen 464) = 100 g dm^{-3}.

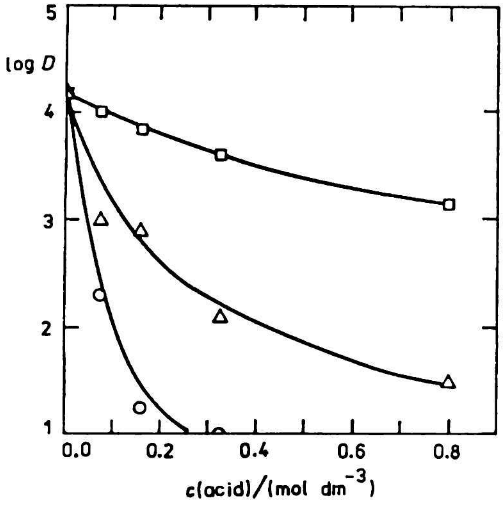

Fig. 2. Influence of addition of inorganic acids into 0.5 M-HCl phase on the palladium extraction (in toluene phase ρ(Adogen 464) = 100 g dm^{-3}). □ H_2SO_4; △ HNO_3; ○ $HClO_4$.

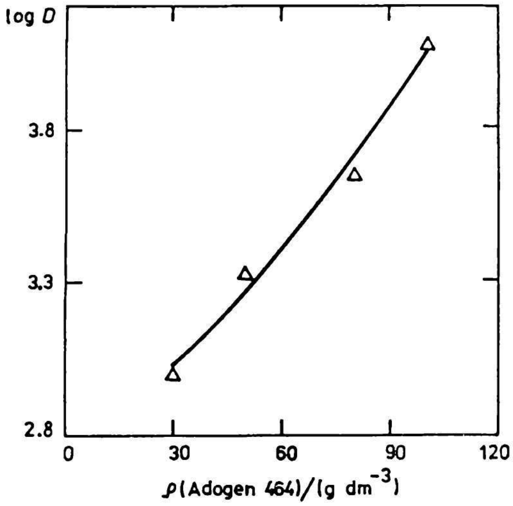

Fig. 3. Dependence of palladium distribution ratio on the concentration of Adogen 464 in toluene (aqueous phase: 0.5 M-HCl).

The palladium distribution ratio is sufficiently high within the range of concentration of Adogen 464 from 30 up to 100 g dm^{-3} (Fig. 3). Additional increase in the reagent concentration leads to the difficulties in the separation of phases.

In the assumed volume ratio of phases 10 : 1 the extraction recovery takes 99 % at the distribution ratio 1000. For the quantitative separation, the following conditions are necessary for the organic phase: 10 cm^3 of Adogen 464 (ρ = 100 g dm^{-3}) in toluene, and for the aqueous phase: 100 cm^3 of the sample in HCl with concentration 0.5 mol dm^{-3}.

The extraction is rapid, 1 min of shaking is sufficient. If the sample is mineralized, it can contain H_2SO_4 up to the concentration 0.8 mol dm^{-3}

Table 1. Reextraction Recovery of Palladium as the Function of the NH_4NO_3 Concentration for Different Phase Ratio at $c(NaOH) = 0.5$ mol dm^{-3}

$c(NH_4NO_3)$	Reextraction recovery/%	
mol dm^{-3}	$V_{org}/V_{aq} = 1$	$V_{org}/V_{aq} = 2$
0.5	98.0	96.0
2.5	99.0	98.0
4.5	99.4	99.0
5.5	99.4	99.0
7.5	94.0	88.0
9.5	93.0	87.0

Table 2. Reextraction Recovery of Palladium as the Function of the NaOH Concentration for Different Phase Ratio at $c(NH_4NO_3) = 5$ mol dm^{-3}

$c(NaOH)$	Reextraction recovery/%	
mol dm^{-3}	$V_{org}/V_{aq} = 1$	$V_{org}/V_{aq} = 2$
0.25	99.5	99.0
0.5	99.5	99.0
1.0	99.5	99.0
1.5	99.0	98.0
2.5	94.0	88.0
5.0	92.0	85.0

(maximum 4 cm^3 of concentrated H_2SO_4 may remain in the rest). If the mineralized mixture reaches the temperature of evaporation of H_2SO_4, the HNO_3 and $HClO_4$ are practically fully decomposed.

Palladium is extracted as $(R_4N)_2PdCl_4$, the reextraction is connected with the formation of cationic complex $[Pd(NH_3)_4]^{2+}$ which is nonextractable by quaternary ammonium salts. For the reextraction the solutions of NH_4NO_3 and NaOH were chosen since these are from the point of view of the DPP method purer than the commercial NH_4OH solution of analytical reagent purity (Lachema, Brno). The results of determination of optimum reextraction solution are given in Tables 1 and 2. For the reextraction NH_4NO_3 solution of the concentration 5 mol dm^{-3} with addition of NaOH of concentration 0.25 to 1 mol dm^{-3} is suitable.

For polarographic determination the reextraction solutions do not require any other adjustment besides the removal of oxygen through bubbling by inert gas. With respect to the expected selectivity in the determination after mineralization of organic substances and after the extractional and reextractional separation of inorganic substances the parameters of the DPP measurement were chosen so that the possibly greatest signal might be obtained. The dependences of the peak heights on the palladium concentration were measured as follows:

1. By palladium additions to the solution the composition of which corresponds with the optimum for the reextraction and which was not in contact with organic phase - the pure calibration line for DPP;

2. by palladium additions to the reextraction solution which was in preliminary contact with organic phase the simulation of influence of organic phase at 100 % recovery;

3. by application of the whole procedure of extractional and reextractional adjustment of the sample.

In all cases the linearity is preserved within the whole studied range of concentrations. Slopes of lines were about 3 μA dm^3 mg^{-1} and standard deviations of signal for the whole procedure were about 0.7 μA and 0.1 μA in concentration range 0.18—1.8 mg dm^{-3} and 2.25—22.5 mg dm^{-3}, respectively. The contact of ammoniacal reextractional solution with organic phase was expressed besides the moderate decrease of slope by the worsened reproducibility of measurements, which is probably caused by the presence of surface-active substances in the reagent. This influence is decreased by the purification of organic phase. From the repeated measurements the value of standard deviation in minimum and maximum concentration of observed range as well as the residual deviation around regression line was determined. The agreement of variances was confirmed by the F-test. The determination limits (Table 3) are determined as the concentration from which the relative standard deviation makes ≤ 10 %. The determination limit defined in this way includes also errors of the used apparatus and is thus various for different concentration ranges. The increase in determination limit in the direction *1*→*3* and *2a*→*3a* is caused by growing complexity of experiment.

Supposing that the initial amount of palladium prior to the extraction is in the volume 100 cm^3, the concentration determination limit makes about 2.5 μg dm^{-3}.

The selectivity of determination may be judged from extraction data [12]. From the medium of HCl with the concentrations 0.5—1 mol dm^{-3} only Pd^{2+},

Table 3. Determination Limits of Palladium in the Solution under Described Conditions

Experiment	Concentration range	Determination limit	Minimum deter. quantity *
	mg dm^{-3}	mg dm^{-3}	μg
1	2.08—20.8	0.10	0.50
2	2.08—20.8	0.28	1.35
3	2.25—22.5	0.48	2.18
2a	0.037—0.37	0.02	0.11
3a	0.18—1.80	0.05	0.24

* The assumed volume of reextraction solution 5 cm^3.

Ag^+, Tl^+, Bi^{3+}, and Sn^{4+} are extracted well, *i.e.* the distribution ratio $D > 1$ for similar reagents and concentrations as in this work. More weakly ($D \approx 1$) are extracted Fe^{3+}, Cd^{2+}, Pt^{4+}, and Cu^{2+} and thus at the ratio of phases $V_{org}/V_{aq} = 1 : 10$ only nearly 10 % of these metals will be extracted. On the basis of formation of cationic complexes in the ammoniacal medium the effective reextraction may be assumed for Cd^{2+}, Ag^+, and Pt^{2+}.

Total selectivity is determined also by the selectivity of polarographic determination. From literature data [13] the interference of Cd^{2+} may be assumed, however, no conclusions may be drawn for the used electrolyte. Because of that there were measured the DPP records of reextraction solutions with the addition of metals Ag^+, Sn^{4+}, Tl^+, Bi^{3+}, Fe^{3+}, Fe^{2+}, Cd^{2+}, Pt^{2+}, and Cu^{2+}, respectively, the concentration of which made 10^{-5} mol dm^{-3}. Only Cd^{2+} offers the peak at the potential near the palladium peak. By the application of the whole procedure it has been found that about 40 % of Cd^{2+} will be separated together with the palladium. Their peaks will be distinguished well on the DPP record if the modulation amplitude 25 mV is used, however, the sensitivity of determination is decreased moderately in this case.

THE RECOMMENDED PROCEDURE

The palladium sample with the content > 0.25 μg of palladium is adjusted so that the concentration of HCl may be 0.5—1 mol dm^{-3} and the sample volume may be ≈ 100 cm^3. It is extracted for 1 min by the solution of Adogen 464 (ρ = 100 g dm^{-3}) in toluene with the volume 10 cm^3. After the separation of phases palladium is reextracted from organic phase for 1 min into 5 cm^3 of the NH_4NO_3—NaOH solution with concentration 5—0.5 mol dm^{-3}. Aqueous phase is used directly for determination by the DPP method.

After the removal of diluted oxygen through bubbling by inert gas the DPP curve is recorded within the potential range − 0.55 V down to − 1 V *vs.* SCE at the drop time 2 s, the rate of potential change 2 mV s^{-1}, the amplitude modulation 100 mV (in the presence of Cd^{2+} 25 mV). The determination is made by the method of standard addition.

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