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Simultaneous Determination of Palladium(II) and Gold(III) in Mixtures by Third Derivative Spectrophotometry Using 3-Hydroxy-2-methyl-1-phenyl-4-pyridone Ligand

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palladium

A spectrophotometric method has been developed for the determination of microgram amounts of palladium(II). The method is based on the extraction of palladium(II) by a chloroform solution containing 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HX). Palladium(II) was highly extracted with HX from aqueous sulphuric acid media. The extraction took place in the pH range 1.5–3.0. The chloroform layer was applicable for the spectrophotometric determination of palladium(II). Molar absorptivity was 1.89×10^4 mol^{-1} dm^3 cm^{-1} at 345 nm. Use of the third-derivative spectrophotometry enables determination of palladium(II) and gold(III) in their mixture without previous separation. Palladium(II) was thus determined in the concentration range 0.28–8.0 μg cm^{-3} (in the presence of 1.0–8.0 μg cm^{-3} gold), and gold(III) was determined in the range 1–13.0 μg cm^{-3} (in the presence of 1–5 μg cm^{-3} of palladium). The method was successfully applied for the determination of palladium in synthetic mixtures and in Pd-charcoal.

INTRODUCTION

Palladium finds very important and extensive use in alloys, catalysts, and in low voltage electrical contacts. Hence, its recovery, purification and determination are vital processes. Many spectrophotometric methods of determining palladium have been reported.[1–9] However, the existing methods suffer from limitations such as low sensitivity, [1–3,6] high reaction temperature,[5] interferences by many metals, *e.g.*, Rh^{III}, Fe^{III}, Co^{II}, Ni^{II}, Au^{III}, Ru^{III}, Cu^{II}, and Pt^{IV}, [8,9] and the use of masking reagents.[5]

Extraction of palladium from acidic solutions is generally carried out from a hydrochloric acid medium.[10–13] Limited data have been reported on the extraction of palladium from nitric acid[14,15] and sulphuric acid[3,16,17] solutions.

The reagent 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HX) has been used for the extraction and spectrophotometric determination of different ions, *i.e.*, vanadium(V), titanium(IV), hafnium(IV), zirconium(IV) and germanium(IV).[18–22] In continuation of the studies on the analytical application of HX for the determination of metals, we used HX as the extracting and spectrophotometric reagent to determine palladium(II). The extraction of a Pd^{II}-HX complex from sulphuric and perchloric acid solutions was applicable to the spectrophotometric determination of palladium(II).

Many methods have been reported for spectrophotometric determination of palladium[1–9] and gold.[23–26] None of these is entirely specific to palladium and to gold in the same sample.

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This paper reports a rapid and simple third-derivative spectrophotometric method for determination of palladium(II) and gold(III) in their mixtures.

The proposed method has been successfully applied to the determination of palladium in synthetic mixtures and in the laboratory palladium-carbon powder.

EXPERIMENTAL

Reagents

The stock solution of palladium(II) chloride (1×10^{-2} mol dm^{-3}) was prepared by dissolving 0.17740 g of $PdCl_2$ (Fluka, Buchs, Switzerland) in 100.0 cm^3 of water acidified with 0.5 cm^3 of concentrated hydrochloric acid. The resulting solution was standardized gravimetrically using the dimethylglyoxime method.[27] Working solutions were obtained by suitable dilution of the stock solution with deionized-distilled water.

Stock solutions of palladium(II) sulphate or palladium(II) perchlorate were prepared by boiling $PdCl_2$ with a small volume of sulphuric (perchloric) acid and evaporating it almost to dryness three times.[28] The precipitate was dissolved in 250.0 cm^3 of 1 mol dm^{-3} H_2SO_4 ($HClO_4$) and the solution was standardized gravimetrically using the dimethylglyoxime method.[27] A working solution was prepared daily by diluting the standard solution with distilled water.

The stock solution of gold(III) chloride (1×10^{-2} mol dm^{-3}) was prepared by dissolving 0.09951 g of $HAuCl_4$ (Merck, Darmstadt, Germany) in 25.0 cm^3 of water. The resulting solution was standardized gravimetrically using the oxalic acid method.[29] A working solution was prepared daily by diluting the standard solution with deionized-distilled water.

Other standard solutions of different metals used to study the effect of diverse ions were prepared by dissolving weighed quantities of their salts in deionized water or in diluted sulphuric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in water. All the chemicals used were of AR grade.

3-Hydroxy-2-methyl-1-phenyl-4-pyridone (HX) was synthesized as described previously.[30] Solutions of HX were prepared by dissolving weighed amounts of HX in chloroform, containing 0.5 % (volume fraction) of ethanol and used without purification or drying.

Apparatus

A Varian double-beam spectrophotometer, Model Cary 3, equipped with 1-cm quartz cells, controlled by Matsuba 386/33DX computer in conjunction with HP Plotter-7574, was used for absorption measurements. The zero-order spectra were recorded at a scan rate of 240 nm min^{-1}. Derivative spectra of different orders were obtained from stored zero-order spectra with a Varian software program.[31,32] The effect of the derivative interval was studied ($\Delta\lambda$ = 1–6 nm), and the $\Delta\lambda$ of 4 nm was selected as the optimum.

For the determination of palladium in the aqueous phase, a Perkin Elmer atomic absorption spectrometer, Model 2380, was used.

A Griffin flask shaker with a time switch served for extraction. The pH of the aqueous phase was measured with a Radiometer PHM 85 precision pH-meter.

Extraction Procedures

To an aliquot of solution containing 4×10^{-5} mol dm^{-3} palladium(II), sulphuric acid and sodium sulphate were added in amounts to achieve the derived acidity (pH = 2.5), ionic strength μ = 0.2 mol dm^{-3}, and the volume was made up to 5 cm^3. The solution was equilibrated with 5.0 cm^3 HX dissolved in chloroform, and both phases were shaken with a mechanical shaker in a 50 cm^3 conical flask for 35 min. After the phases were separated by gravity, their aliquots were used for each experimental point. The spectra of the extract were recorded over the range from 550 to 310 nm against a reagent blank prepared under the same experimental conditions. Absorbance of the organic phase was measured at 345 nm.

Palladium(II) concentrations in the aqueous phase, before and after extraction, were determined spectrophotometrically by the xylenolorange method[33] and by atomic absorption spectrometry (AAS) after suitable dilution. The difference between the initial and final concentration of the metal in the aqueous phase were assumed to be equal to the concentration of the metal in the organic phase.

Analysis of the Real Sample

Determination of Pd in Catalysts. – The method described was applied to the determination of palladium in Pd-charcoal (Merck, Darmstadt, Germany, 10 % Pd). A sample (40.0 mg) of the powdered catalyst was mixed with 20.0 cm^3 of 1 mol dm^{-3} nitric acid. The mixture was heated for about 2 h on a hot plate until dry. The residue was mixed with 50 cm^3 of deionized water, then filtered (using Whatman No. 1 Paper) and washed with three 5 cm^3 aliquots of distilled water. The filtrate solution was diluted with water in a 250.0 cm^3 volumetric flask.[16] Adequate aliquots of sample solution (10–30 μg) of Pd^{II} were analyzed for palladium as described above.

RESULTS AND DISCUSSION

Optimum Conditions for Extraction of Palladium

The extraction of palladium(II) with 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HX) was carried out over the pH range 0.3–6.5. The acidity was adjusted with H_2SO_4, $HClO_4$ or HCl. Quantitative extraction of palladium(II) occurred at pH = 1.5–3.0 at constant ionic strength μ = 0.2 mol dm^{-3} (pH adjusted with sulphuric or perchloric acid). From the hydrochloric acid solution, palladium(II) was extracted quantitatively at pH > 3.3 (Figure 1). The efficiency of extraction (E) was 98.5 %. Among the three suitable acids, sulphuric acid was chosen because of its inertness against redox reaction and complexation.

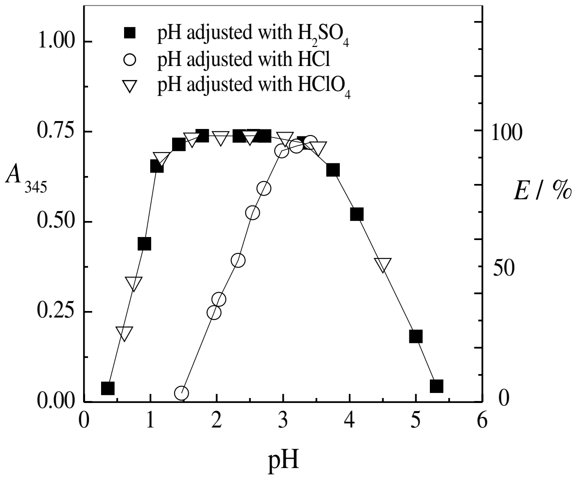

Figure 1. Dependence of Pd^{II}-HX complex absorbance and palladium(II) extraction on the pH; $c(Pd^{II})$ = 4 × 10^{-5} mol dm^{-3}, c(HX) = 1.6 × 10^{-3} mol dm^{-3}.

Varying the shaking period from 5 to 75 minutes showed that at least 25 minutes of shaking is needed for equilibration of the Pd^{II}-HX complex extraction.

The effect of HX concentrations in the organic phase on palladium(II) extraction from the aqueous phase at optimum acidity was also studied. For the quantitative extraction from sulphuric acid solutions, the mole ratio of HX to Pd^{II} had to be at least 10.

To test the feasibility of developing a palladium recovery process based on the HX reagent, the back-extraction properties of the Pd^{II}-HX complex in chloroform were studied using various mineral acids as the stripping reagent. The palladium, extracted at optimum conditions, could be stripped quantitatively with ≥ 0.5 mol dm^{-3} H_2SO_4 or ≥ 0.5 mol dm^{-3} $HClO_4$.

Spectrophotometric Measurements

The absorption spectra of the Pd^{II}-HX complex in the chloroform medium were measured against a reagent blank. The absorption maximum of the extracted complex was at 345 nm, whereas the blank showed a very low absorbance. The optimum pH range for a constant absorbance in the organic layer was found to be between 1.5–3.0 (pH adjusted with H_2SO_4 or $HClO_4$), at constant ionic strength μ = 0.2 mol dm^{-3} (Figure 1). Therefore, in subsequent studies a pH of 2.5 adjusted with H_2SO_4 was maintained throughout the experiment. The absorbance of the organic phase was stable for at least 1.5 h.

The system obeyed Beer's law over the range 0.3––8.0 µg cm^{-3} of palladium(II). The molar absorptivity was 1.89 × 10^4 mol^{-1} dm^3 cm^{-1}, and the corresponding Sandell's sensitivity was 5.1 × 10^{-3} µg cm^{-2}.

The composition of the complex of palladium(II) with HX was established by the log-log plot of the distribution ratio *versus* HX concentration, at a fixed pH. It showed a mole ratio of 1:2 with respect to HX (Figure 2a). The composition was verified by Job's continuous variation method (Figure 2b).

To assess the usefulness of the proposed method, the effects of diverse ions that often associate with palladium were studied. Palladium(II) was then determined as the Pd^{II}-HX complex under the optimum conditions, as described in the given procedure. The tolerance of the method to foreign ions was investigated with solutions containing 4.26 µg Pd^{II} per cm^{-3} and various amounts of foreign ions. The tolerance limit was taken to be the amount that caused a ±2 % change in absorbance. Sulphate, nitrate, acetate, perchlorate and phosphate were tolerated in the Pd^{II} to anion mole ratio exceeding 1:2500. The results showed that the anionic complexing agents such as SCN interfered. Most metal ions did not interfere. The most serious interferents were iron(III), titanium(IV), gold(III) and iridium(IV). Interference of iron(III), copper(II) and vanadium(V) could be minimized by their reduction with ascorbic acid (Table I).

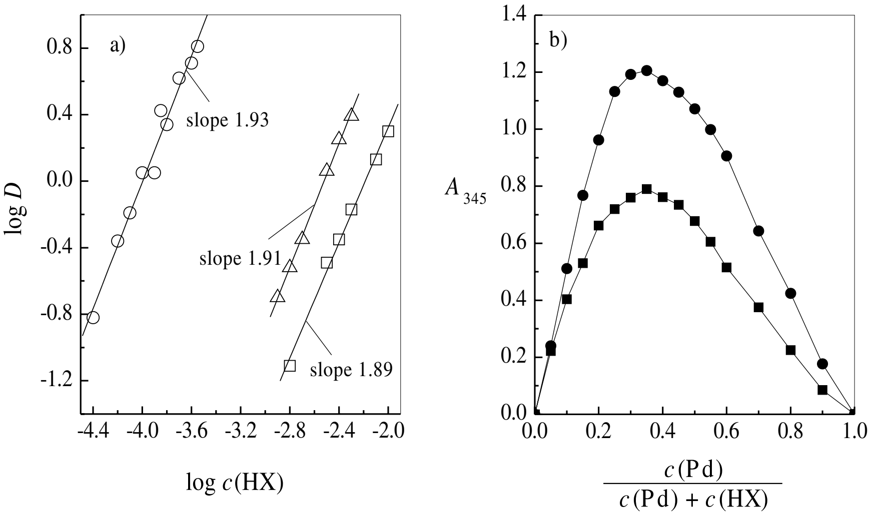

Figure 2. Determination of the composition of the extracted Pd-HX complex by slope analysis (a) and Job's method (b). a) $c(Pd^{II})$ = 4 × 10^{-5} mol dm^{-3}, pH = 2.5 (○), 0.78 (△), 0.6 (□); b) pH = 2.5, $c(Pd^{II})$ + c(HX) = 2.5 × 10^{-4} mol dm^{-3} (■), $c(Pd^{II})$ + c(HX) = 3.0 × 10^{-4} mol dm^{-3} (●).

TABLE I. Effect of foreign ions on the spectrophotometric determination of palladium(II) with HX dissolved in chloroform; c(Pd^{II}) = 4×10^{-5} mol dm^{-3}, c(HX) = 1.6×10^{-3} mol dm^{-3}

Foreign ions	Tolerance limit [Ion] / [Pd^{II}]
Sulphate, nitrate, acetate, perchlorate, phosphate, Na^{I}, K^{I}, NH_4, Ca^{II}, Mg^{II}	2.5×10^3
Ni^{II}, Mn^{II}, Cd^{II}, Co^{II}, Ni^{II}, Zn^{II}, Pb^{II}	1×10^3
Chloride, Cr^{III}	250
In^{III}, Bi^{III}, Zr^{IV}	50
Ag^{I}	25
Fe^{III}, Cu^{II}, V^{V}	10(a)
Bromide, citrate, tartarate	5
Os^{VIII}, U^{VI}, Pt^{IV}	1
Thiocyanate, Ti^{IV}, V^{V}, Ir^{IV}, Au^{III}	<1

(a) 0.1 mol dm^{-3} ascorbic acid present.

Reaction of Gold(III) with HX

Gold(III) reacts with HX at low concentrations of sulphuric or hydrochloric acid, giving a complex that is extractable with chloroform. The obtained colourless organic phase had maximum absorption at 365 nm. The extractability and absorbance of the metal complex were affected by the choice of sulphuric or hydrochloric acids. The extraction was highest from hydrochloric acid solution at pH = 2.25–2.75, or sulphuric acid solution at pH = 1.4–2.75. It was shown that at least 20 minutes of shaking was needed for equilibration of the Au^{III}-HX complex extraction. The absorbance of the organic phase was stable for 90 minutes. For maximum absorbance, the mole ratio of HX to Au^{III} had to be at least 6.

The complex system conformed to Beer's law over the range 0.95–18 μg cm^{-3} of gold(III). The molar absorptivity at 365 nm was 1.65×10^4 mol^{-1} dm^3 cm^{-1}. The photometric sensitivity of the method, as defined by Sandell, was 0.012 μg Au^{III} cm^{-2}. The reproducibility of the measurements, expressed as standard deviation, is 0.5 to 2%, depending on the gold(III) concentration.

Simultaneous Determination of Palladium and Gold in Mixtures by Third Derivative Spectrophotometry

The zero-order spectra of isomolar solutions of the Pd^{II}-HX complex and Au^{III}-HX complex in chloroform (curves 1 and 2) and of their mixture (curve 3) are shown in Figure 3a. Since the absorption spectra of Pd^{II}-HX and Au^{III}-HX complexes overlap, their determination in mixture by conventional spectrophotometry was difficult. In order to resolve this problem, derivative spectrophotometry was used. A study of the first-, second-, third-, and fourth-derivative spectra of the Pd^{II}-HX complex revealed that the third-derivative spectra gave results with the highest sensitivity and lowest detection limits.

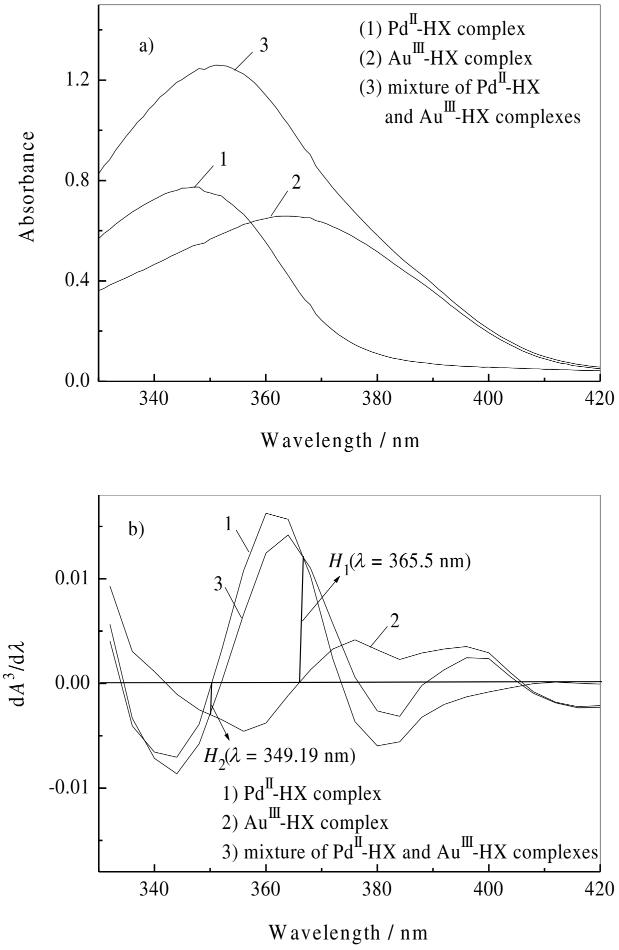

Figure 3. Zero-order (a) and third-derivative spectra (b) of Pd^{II}-HX complexes, Au^{III}-HX complexes and their mixture; pH = 2.5, c(HX) = 1.6×10^{-3} mol dm^{-3}, c(Pd^{II} or Au^{III}) = 4×10^{-5} mol dm^{-3}.

The third-derivative spectra of the complexes and their mixture are shown in Figure 3b. It can be seen that the third-derivative spectra of the mixture of both metal complexes are not sufficiently resolved to generate two distinct peaks. Therefore, the zero-crossing measurement technique was utilized for resolving the mixture of the said complexes. Palladium(II) and gold(III) can be determined using the absolute value of the total derivative spectrum at a wavelength corresponding to the zero-crossing point of the component. The heights H_1 and H_2, in the third-derivative spectra of mixtures corresponding to values taken at 365.5 nm (zero-crossing point of the gold complex) and at 349.19 nm (zero-crossing point of the palladium complex) are proportional to palladium(II) and gold(III) concentrations, respectively. Calibration graphs for simultaneous determination of palladium and gold using HX were obtained from H measurements in third-derivative spectra for standards containing between 0.28 and 8.0 μg cm^{-3} of palladium(II) in the presence of 3.9 and 8.0 μg cm^{-3} of

TABLE II. Equations for calibration graphs and the correlation coefficient for the determination of palladium(II) and gold(III) in mixtures with HX using third-derivative spectrophotometry[(a)]

Determination of palladium with Au as interference[(b)]		
$\frac{\gamma(\mathrm{Au})_i}{\mu\mathrm{g\ cm^{-3}}}$	Regression equation[(c)]	Correlation coefficient
–	$D = -1.79 \times 10^{-4} + 3.73 \times 10^{-3}\ C$	0.998
3.9	$D = -1.09 \times 10^{-4} + 3.61 \times 10^{-3}\ C$	0.994
8.0	$D = -1.09 \times 10^{-4} + 3.61 \times 10^{-3}\ C$	0.994
Determination of gold with Pd as interference[(d)]		
$\frac{\gamma(\mathrm{Pd})_i}{\mu\mathrm{g\ cm^{-3}}}$	Regression equation[(c)]	Correlation coefficient
–	$D = 2.72 \times 10^{-4} - 4.71 \times 10^{-4}\ C$	0.996
2.2	$D = 2.72 \times 10^{-4} - 4.71 \times 10^{-4}\ C$	0.989
5.0	$D = 1.61 \times 10^{-4} - 4.30 \times 10^{-4}\ C$	0.996

[(a)] γ(Pd) = 0.28–8 μg cm^{-3}, γ(Au) = 1–15 μg cm^{-3}.
[(b)] λ = 365.5 nm.
[(c)] D, derivative value; C, concentration (C / μg cm^{-3}).
[(d)] λ = 349.19 nm.

gold(III). Similarly, calibration graphs were prepared for standards containing between 1 and 15 μg cm^{-3} of gold(III) in the presence of 2.2 and 5.0 μg cm^{-3} of palladium(II). The equation for each graph and the correlation coefficients are summarized in Table II. It can be seen that the slopes had similar values when palladium was analyzed in the presence of various amounts of gold, implying that the interferences of gold were completely removed. In the determination of gold(III) in the presence of small amounts of palladium(II), the slope also conformed with the equation for the calibration graph without palladium(II). However, in the presence of a higher amount palladium(II), the slope was different, indicating that mutual interference occurred.

The value of the signal in derivative spectrophotometry depends precisely on the shape of the basic spectra.[31] Spectra of sharp peaks are preferred, in which the signal value after differentiation increases with the derivative order, contrary to spectra of flat peaks, for which the signal decreases. The value of the sharp peak derivative is then several times greater than that of the broad peak. The error in the zero-crossing point method is connected with the determination of the crossing point of the straight line with the derivative spectrum. Because of the derivative values on the steep side, the derivative zeroing points of the interfering substance may undergo small shifts with a change in the sample composition.

The zero-order absorption spectra of the Au^{III}-HX complex were broad compared to the zero-order absorption spectra of the Pd^{II}-HX complex. The zero-order absorption spectra of the Pd^{II}-HX complex were narrower. Accordingly, the derivative spectra of the Pd^{II}-HX complex were sharp and the derivative spectra of the Au^{III}-HX complex spectra had flat peaks. We suppose that the determination of the crossing point of the straight line (curve 1, Figure 3b) and the lower derivative values on the flat curve (curve 2, Figure 3b) were the cause of different slopes in the determination of gold(III) in the presence of higher amounts of palladium.

Six successive measurements were carried out with the standard solution containing 3.2 μg cm^{-3} of palladium(II) and 7.1 μg cm^{-3} of gold(III). Relative standard deviation for the third derivative method of palladium was 0.9 % and that for gold was 1.6 %. The precision of gold determination is lower than that of palladium.

Application of the Method to Real Samples and Synthetic Mixtures

The method was applied to the determination of palladium in certain synthetic mixtures corresponding to its alloys and in activated charcoal. The values determined were in good agreement with the certified values (Table III).

CONCLUSION

3-Hydroxy-2-methyl-1-phenyl-4-pyridone (HX) was used as the reagent for the extraction of palladium(II) from sulphuric acid media and for the spectrophotometric determination of palladium in the organic phase.

TABLE III. Determination of palladium in some synthetic alloys and in Pd-charcoal[(a)]

Sample	Specialty	Found / %	
		Pd	Au
Alloy 1: Pd 95.5 %, Ru 4.5 %	High resistance to oxidation and corrosion	94.8 ± 0.8	–
Alloy 2: Pd 72 %, Ag 26 %, Ni 2 %	Improvement in hardness and in resistance to mechanical wear	72.1 ± 1.2	–
Alloy 3: Pd 60 %, Au 40 %	Jewellery alloy	59.4 ± 0.9[(b)]	38.9 ± 1.6[(b)]
Alloy 4: Pd 34 %, Au 10 %, Co 22 %, Ni 34 %	Low melting dental alloy	33.7 ± 0.9[(b)]	9.2 ± 1.8[(b)]
Pd-charcoal: Pd 10 %, C 90 %	Hydrogenation and dehydrogenation	9.7 ± 0.56	–

[(a)] Average of four determinations. [(b)] Third-derivative spectrophotometry.

The important features of the method described here are that: i) it permits simultaneous determination of palladium(II) and gold(III) in their mixtures without previous separation, ii) a low reagent concentration is required, iii) the method is applicable to the analysis of palladium(II) in synthetic mixtures with a composition corresponding to its alloys and in Pd-charcoal.

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SAŽETAK

Istovremeno određivanje paladija(II) i zlata(III) u smjesi derivacijskom spektrofotometrijom trećeg reda uporabom 1-fenil-3-hidroksi-2-metil-4-piridona

Vlasta Vojković i Vinka Drušković

Opisana je metoda za određivanje mikrogramskih količina paladija(II). Metoda se bazira na postupku ekstrakcije paladija(II) s 1-fenil-3-hidroksi-2-metil-4-piridonom (HX) otopljenim u kloroformu. Paladij(II) se najbolje ekstrahira iz sumporno kiselih otopina. Kvantitativna ekstrakcija je u pH rasponu od 1,5–3,0. Organska faza može se primijeniti za spektrofotometrijsko određivanje paladija(II). Molarna apsorptivnost iznosi $1{,}89 \times 10^4$ mol^{-1} dm^3 cm^{-1}, pri 345 nm. Primjenom derivacijske spektrofotometrije moguće je istovremeno određivanje paladija i zlata u njihovoj smjesi bez prethodnog odvajanja ovih dvaju elemenata. Paladij(II) je moguće odrediti u rasponu koncentracija 0,28–8,0 $\mu\text{g cm}^{-3}$ (u prisutnosti 0.5–8 $\mu\text{g cm}^{-3}$ zlata), a zlato(III) u intervalu 1,5–13,0 $\mu\text{g cm}^{-3}$ (u prisutnosti 1–5 $\mu\text{g cm}^{-3}$ paladija). Metoda je uspješno primijenjena na određivanje paladija u sintetskim smjesama i u paladijevom katalizatoru na aktivnom ugljenu.