Spectrophotometric determination of platinum metals. V.*
Determination of palladium with Pyrogallol Red

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A new spectrophotometric method for the determination of palladium with Pyrogallol Red is described. Its high sensitivity is dependent on the presence of micellar system of 1-carbethoxypentadecyltrimethylammonium bromide, which leads to the maximum colour formation in acid solutions (pH 5.5) in a shorter time interval than in the absence of tenside. The ternary palladium−dye−cation-active tenside system obeys the Beer law over the range 0.20—3.70 µg ml^{-1} Pd(II), with sensitivity index according to Sandell $S = 4 \times 10^{-3}$ µg cm^{-2} and a molar absorptivity of $\varepsilon' = 2.6 \times 10^4$ l mol^{-1} cm^{-1} at the maximum of the differential curve at 620 nm.

Описывается новый спектрофотометрический метод определения палладия с пирогалловым красным. Его большая чувствительность зависит от присутствия мицеллярной системы 1-карбэтоксипентадецилтриметиламмонийбромида, приводящего к образованию максимального окрашивания в кислых растворах (pH 5,5) за более короткое время, чем в отсутствии поверхностно активных веществ (ПАВ). В третичной системе палладий–краситель–катионное ПАВ закон Бера соблюдается в пределах 0,20–3,70 мгк мл$^{-1}$ Pd(II) с показателем чувствительности по Сэнделлу $S = 4 \times 10^{-3}$ мкг см$^{-2}$ и молярным коэффициентом поглощения $\varepsilon' = 2,6 \times 10^4$ л моль$^{-1}$ см$^{-1}$ при максимуме на дифференциальной кривой при 620 нм.

In the further study of the use of some triphenylmethane dyes for the spectrophotometric determination of the platinum metals [1, 2] the reactions of platinum metal ions with Pyrogallol Red in the presence of cation-active tenside were studied, as well as the effect of the presence of the cation-active tenside. Tensides of the tetraalkylammonium or pyridinium type have recently been found to be useful for markedly increasing the sensitivity of metal−dye colour reactions and for improving the contrast between measured solutions. Of the studied

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* Part IV: J. Šabartová, M. Herrmannová, M. Malát, and L. Čermáková, *Chem. Zvesti 34*, 111 (1980).

reactions, the complexing reaction of palladium with Pyrogallol Red (PG) was found to be most useful, especially in the presence of 1-carbethoxypentadecyl-trimethylammonium bromide.

Experimental

Apparatus

The absorbances of the solutions were measured using a Unicam SP 800 (Pye-Unicam, Cambridge) or Spekol (Zeiss, Jena) spectrophotometer using 1.00 cm cuvettes. The pH of the solutions was measured using a PHM 62 (Radiometer, Copenhagen) or Acidimetr 325 (Druopta, Prague) instrument. Reactions at increased temperatures were studied in a U 10 thermostat (Medingen, GFR).

Reagents

The stock 1×10^{-3} M palladium solution was prepared by diluting a 10% solution of $PdCl_2$ (anal. grade) containing 0.06 g Pd(II) per ml (Kovohutě, Vestec); the palladium content was controlled gravimetrically with biacetyl dioxime.

The stock 2×10^{-4} M solution of Pyrogallol Red was prepared by grinding 0.0210 g of the commercial indicator (Lachema, Brno) with ethanol in a mortar and diluting with distilled water so that it contained 20% ethanol. Purified Pyrogallol Red was used for the study of the composition of the complex. The commercial PG was purified as follows: The substance was dissolved in a Na_2CO_3 solution, the solution was filtered and precipitated with HCl $(1+1)$. The suspension was heated to 80°C with constant stirring, the green-brown crystals formed were filtered off from the hot solution, washed with water, and dried in the air at 100°C. The preparation was finally several times recrystallized from ethanol and dried to a constant weight.

The stock 5×10^{-3} M solution of 1-carbethoxypentadecyltrimethylammonium bromide (CPTB) was prepared by dissolving Septonex (Slovakofarma, Hlohovec) in distilled water; the purity of this substance complied with Czechoslovak pharmacopoeia.

The remaining chemicals were of anal. grade. The pH value was adjusted using phosphate buffer described by Sørensen, Walpole acetate buffer, hydrochloric acid or sodium hydroxide.

Methods

The composition of the Pd(II)−PG binary complex was found by the Job method of continuous variations and by the mole ratio method. The composition of the ternary Pd(II)−PG−CPTB system was found by the triangular method described by *Babko* [3], *i.e.* the method of continuous variations applied to a three-component system, by the "cross-section" method [3, 4], and by the Job method of continuous variations with a constant excess of the third component.

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Determination of Pd(II) with PG

Into a 50 ml volumetric flask is pipetted 10 ml of phosphate buffer (pH 6.5), 30 ml of a 2×10^{-4} M solution of PG, and a sample solution containing 20—100 µg Pd(II); the mixture is diluted with distilled water to the mark and left to stand for 70 min at laboratory temperature. The absorbance is measured at 600 nm against a blank.

Determination of Pd(II) with PG in the presence of CPTB

10 ml of acetate buffer (pH 5.5), 15 ml of 2×10^{-4} M PG, and 5 ml of 5×10^{-3} M CPTB are pipetted into a 50 ml volumetric flask, followed by·a sample solution containing 10—180 µg Pd(II) and the mixture is diluted with distilled water to the mark. The mixture is left to stand at laboratory temperature for 20 min and then the absorbance is measured at 620 nm against a blank.

Results and discussion

Pyrogallol Red forms complexes which are not very strongly coloured with Pd(II) in neutral media (pH 6—7). Their formation is not accompanied by marked maxima, but rather by a decrease in the absorbance of the dye and a marked broadening of the absorption band to longer wavelengths (Fig. 1, curves 1—3). On the basis of a detailed study, optimum conditions were found for utilization of this reaction for the spectrophotometric determination of palladium at the wavelength of the maximum of the differential curve ($\lambda = 600$ nm) (Table 1).
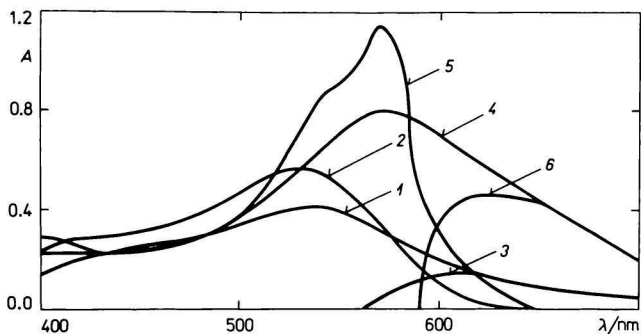

Fig. 1. Absorption spectra of the Pd(II)−PG and Pd(II)−PG−CPTB systems.
$c_{Pd} = 2 \times 10^{-5}$ M; $c_{PG} = 4 \times 10^{-5}$ M; $c_{CPTB} = 5 \times 10^{-4}$ M.
1. Pd−PG; 2. PG; 3. difference between 1 and 2; 4. Pd−PG−CPTB; 5. PG−CPTB; 6. difference between 4 and 5.
1—3: pH 6.5, measured after standing 70 min at laboratory temperature vs. water; 4—6: pH 5.5, measured after standing 20 min at laboratory temperature vs. water.

Table 1

Optimum conditions for the determination of Pd(II) with PG

System	pH	$\lambda_{max(dif)}$ nm	ε' $l\ mol^{-1}\ cm^{-1}$	Concentration range $\mu g\ ml^{-1}$	S $\mu g\ cm^{-2}$	a	b	$s_{x.y}$
Pd(II)–PG	6.5	600—620	1.4×10^4	0.41—2.16	0.008	0.060	0.078	0.008
Pd(II)–PG–CPTB	5.5	620	2.6×10^4	0.20—3.70	0.004	0.025	0.022	0.002

$\lambda_{max(dif)}$ — the wavelength of the difference curve maximum.
ε' — molar absorption coefficient at the difference curve maximum.
S — sensitivity index.

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The presence of the cation-active tenside CPTB (cetylpyridinium bromide behaves similarly) results in both bathochromic and hypsochromic shifts of the maximum of the differential curve, a more suitable pH region for the formation of the coloured system, and a shorter time for maximal colour formation in the solution: in weakly acid media (pH 5—6) at laboratory temperature a blue-purple colour is formed after 15 min, which is stable for at least 48 h. The presence of CPTB has a marked effect in the concentration interval $c_{CPTB} = 3$ to 9×10^{-4} M, corresponding to the region of formation of the micelles of this tenside [5]. The spectra for the Pd(II)—PG—CPTB system are given in Fig. 1 (curves 4—6). Under optimum conditions for the formation of the coloured Pd(II)—PG—CPTB system ($c_{PG} = 6 \times 10^{-5}$ M, $c_{CPTB} = 5 \times 10^{-4}$ M, pH 5.5, $\lambda = 620$ nm) the calibration curves were measured and the results were treated by the linear regression method; the results are given in Table 1 together with the values of the apparent decadic absorption coefficients ε', the sensitivity index of the colour reactions S, expressed according to Sandell, the parameters of the regression straight line a and b, and the

Table 2

Interference of foreign ions in the determination of palladium

Foreign ion	Salt	Pd(II): ion ratio in the reaction[a]	
		Pd—PG	Pd—PG—CPTB
Ru(III)	$(NH_4)_2Ru(H_2O)Cl_5$	1:1	1:5
Rh(III)	$RhCl_3 \cdot 4H_2O$	1:5	1:5
Os(IV)	$(NH_4)_2OsCl_6$	1:1	1:1
Ir(III)	$(NH_4)_3IrCl_6 \cdot H_2O$	1:1	1:2
Ir(IV)	$(NH_4)_2IrCl_6$	1:1	1:1
Pt(IV)	$(NH_4)_2PtCl_6$	1:5	1:5
Ni(II)	$Ni(NO_3)_2 \cdot 6H_2O$	—	1:100
Co(II)	$CoSO_4 \cdot 7H_2O$	1:5	1:100
Ba(II)	$Ba(NO_3)_2$	1:20	1:1000
Ca(II)	$Ca(NO_3)_2 \cdot 4H_2O$	1:20	1:1000
Mn(II)	$MnSO_4$	1:20	1:1000
Mg(II)	$Mg(NO_3)_2$	1:50	1:1000
Zn(II)	$Zn(NO_3)_2 \cdot 4H_2O$	1:5	1:100
Ag(I)	$AgNO_3$	1:5	1:10
Na(I)	$NaNO_3$	1:1000	1:1000
K(I)	KNO_3	1:1000	1:1000
NO_3^-	$KNO_3, NaNO_3$	1:1000	1:1000
Cl^-	KCl	1:200	1:200
Br^-	$NaBr$	1:200	1:200
SO_4^{2-}	Na_2SO_4	1:1000	1:1000
CO_3^{2-}	Na_2CO_3	1:200	1:100

a) At the given concentration the foreign ion does not interfere.

estimate of the standard deviation of the scatter around the regression straight line $s_{x,y}$. For comparison, the same values for the binary system $Pd(II)-PG$ are given in Table 1.

The spectrophotometric determination of palladium is disturbed by some ions in the presence of CPTB and acetate buffer; however, their content with respect to that of palladium can sometimes be much greater than in the absence of CPTB. Table 2 gives a summary. In both cases, the following ions interfere in a ratio of Pd: metal of 5:1: Au(III), Fe(II), Fe(III), Cu(II), Al(III), and Pb(II).

The determination of palladium as the described ternary system was found to be useful in the analysis of a palladium−silver alloy [6].

An attempt was also made to determine the composition of the studied systems. The composition of the binary system found by the given method indicates the formation of two complexes with Pd:PG ratios of 1:1 and 1:2 (pH 6.5, $\lambda = 600$ and 620 nm). The Babko triangular method for the evaluation of the ternary system yields ratios of Pd:PG:CPTB of 1:1:2 or 1:2:2, as indicated in Fig. 2 (overall concentration of Pd(II), PG, and CPTB 1×10^{-4} M, pH 5.5, $\lambda = 620$ nm, measured after standing 20 min after mixing components). These ratios were also confirmed by the "cross-section" method. It was found the Job plots at a constant excess of the third component ($c_{CPTB} = 5 \times 10^{-4}$ M) that the Pd:PG ratio is 1:1 or 1:2. The presence of more than one complex is also indicated by the shape of the absorption spectra, given in Fig. 3, recorded under optimal conditions for the
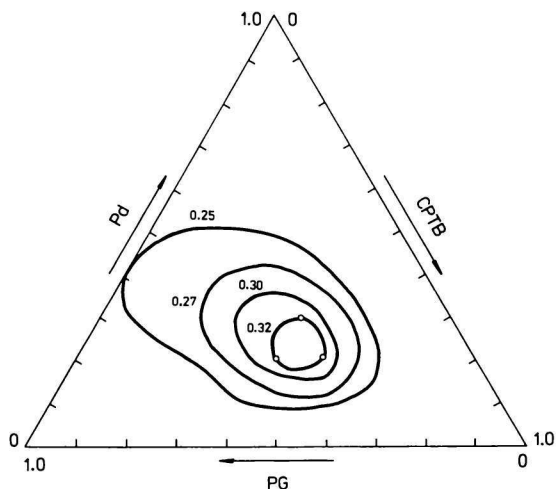

Fig. 2. Continuous variation method applied to the ternary $Pd(II)-PG-CPTB$ system.
Overall concentration of Pd(II), PG, and CPTB: 1×10^{-4} M; pH 5.5; $\lambda = 620$ nm, measured after standing 20 min after mixing components.
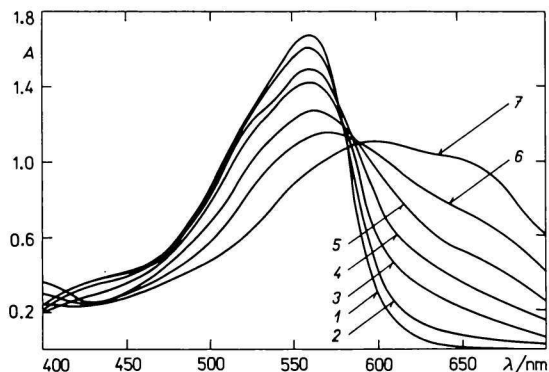
Fig. 3. Absorption spectra of the Pd(II)−PG−CPTB ternary system.
$c_{PG} = 6 \times 10^{-5}$ M; $c_{CPTB} = 5 \times 10^{-4}$ M; pH 5.5, measured after standing 20 min at laboratory temperature *vs.* water; c_{Pd} ($\mu g\ ml^{-1}$).
1. 0.00; *2.* 0.42; *3.* 1.25; *4.* 1.84; *5.* 2.49; *6.* 3.53; *7.* 4.67.

formation of the ternary Pd(II)−PG−CPTB complex for increasing metal concentration (calibration curve spectra).

The described determination of palladium with Pyrogallol Red in the presence of 1-carbethoxypentadecyltrimethylammonium bromide is a further indication of the usefulness of employing micelle systems of cation-active tensides for the spectrophotometric determination of metals.

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