Spectrophotometric determination of the platinum metals VIII.* Highly sensitive extraction determination of palladium with 4-(2-pyridylazo)resorcinol in the presence of cetylpyridinium bromide

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The formation of the red chelates of palladium with 4-(2-pyridylazo)-resorcinol in the presence of the cationogennic tenside cetylpyridinium bromide is used to develop a highly sensitive extraction spectrophotometric method for the determination of Pd(II). The best results ($\varepsilon_{540\,nm} = 9.16 \times 10^4$ dm^3 mol^{-1} cm^{-1}, $S = 1.16 \times 10^{-3}$ μg Pd(II) cm^{-2}, determination of mass concentrations to 1.9 μg Pd(II) cm^{-3} were obtained with extraction of a solution of palladium(II) salt using a chloroform solution of a mixture of PAR—CPB, where the coloured product is stable for 7 h.

Образование краснокрашенных хелатов палладия с 4-(2-пиридилазо)-резорцинолом в присутствии катионогенного тензида бромида цетилпиридиния было использовано для разработки высокочувствительного экстракционного спектрофотометрического метода определения Pd(II). Наилучшие результаты ($\varepsilon_{540\,нм} = 9{,}16\ 10^4$ дм^3 моль$^{-1}$ см$^{-1}$, $S = 1{,}16\ 10^{-3}$ мкг Pd(II) см$^{-2}$, определяемость вплоть до концентраций 1,9 мкг Pd(II) см$^{-3}$) были получены при экстрагировании растворов солей палладия(II) хлороформовым раствором смеси ПАР—БЦП, в котором окрашенный продукт устойчив в течение 7 часов.

Of the known and described reactions of Pd(II) with the reagent 4-(2-pyridylazo)resorcinol (PAR), the red chelates [1], formed in solutions with pH > 4 are employed in analytical applications and are stable in aqueous medium.

Addition of a third component participating in the formation of the coloured product leads to an improvement in the optical properties of the system. The cationogennic tenside, benzyldimethyltetradecylammonium chloride (Zephiramin, $TDBA^+Cl^-$) [1] or the presence of an organic base, *e.g.* diphenylguanidine [2], has

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been found to be useful, where the analytical application usually involves extraction of the ternary coloured product into an organic solvent.

In the use of another cationogennic tenside, cetylpyridinium bromide (CPB), in the study of analytical conditions for the determination of Pd(II) with PAR, we found that procedures involving either extraction of the binary complex of Pd(II) with the reagent into a chloroform solution of the tenside or direct extraction of a Pd(II) solution using a chloroform solution of the mixed reagent PAR—CPB are useful. The latter procedure has both high sensitivity and increased stability of the colouration of the measured product.

Experimental

The solution absorbance was measured using a Unicam SP 800 recording spectrophotometer (Pye-Unicam, Cambridge), with a cuvette with an internal thickness of 1.00 cm. The pH values of the solutions were measured using an N-512 pH-meter (Mera-Elmat, Wrocław) with a combined SAgP-201 W electrode.

The stock 1×10^{-3} M-Pd(II) solution was prepared by diluting a 10 % solution of $PdCl_2$ (Safina, Vestec). The palladium content was found gravimetrically after precipitation with biacetyldioxime.

The stock 5×10^{-4} M-reagent solution of PAR (H_2L) was prepared by dissolving the substance $C_{11}H_8N_3NaO_2 \cdot H_2O$ (Lachema, Brno) in distilled water. The reagent solution prepared in this way is stable in the light for 10 h at most.

The stock 5×10^{-3} M-CPB solution was prepared by dissolving the substance (Lachema, Brno) in a 20 vol. % methanol solution and dilution with distilled water. The purity of the substances was verified by elemental analysis and the bromide content was found argentometrically.

All the other chemicals used were of anal. grade purity.

The pH of the solutions was adjusted using 0.2 M-acetate buffer (Walpole).

The effect of the other platinum metals on the determination of palladium was determined using aqueous solutions of the salts $(NH_4)_3IrCl_6$, $(NH_4)_2IrCl_6$, $(NH_4)_2Ru(H_2O)Cl_5$ (all from Johnson, Matthey and Co., London) or $RhCl_3 \cdot 4H_2O$ and $H_2PtCl_6 \cdot 6H_2O$ (Safina, Vestec).

Results

Palladium forms several complexes in aqueous solution with PAR reagent, in dependence on the pH of the medium [1]: at $pH < 4$ a green chelate is formed, which is unstable and not useful analytically. At $pH > 4$ a red chelate is formed with composition $(Pd(HL)H_2O)^+$, $(Pd(L)H_2O)^0$, and $(Pd(L)OH)^-$ The authors [1] have proposed utilizing the formation of the anionic chelate for the determination of Pd(II) as the red ion associate $(Pd(L)\ OH)^-$ $(TDBA\ micelles)^+$ in the presence of a cationogennic tenside, zephiramine after extraction into $CHCl_3$ at a wavelength of 540 nm (Table 1).

Table 1

Conditions for the extraction determination of Pd(II) with PAR in the presence of tensides

pH_{opt} Aqueous phase	Tenside	Extractant	E/%	$S\ 10^3$ / μg cm^{-2}	$\varepsilon_{540\ nm} \cdot 10^-$ / dm^3 mol^{-1} cm^{-1}	Determination concentration range ϱ(Pd(II))/(μg cm^{-3})	
6—11	$TDBA^+Cl^-$	$CHCl_3$	—	—	3.29	≤2.0	[1]
5.1	CPB	—	—	4.10	2.69	0.5—4.78	[3]
5.0 ± 0.2	CPB	$CHCl_3$	99.89	1.16	9.19	0.2—2.12	
5.0 ± 0.2	CPB	$CPB + CHCl_3$	99.80	1.22	8.75	0.2—1.91	
5.0 ± 0.2	CPB	$PAR + CPB + CHCl_3$	100.00	1.16	9.16	0.2—1.91	

S — Sandell sensitivity.

A detailed study of the effect of another cationogennic tenside, CPB, on Pd—PAR chelates has indicated [3] that the red product formed in the medium of acetate buffer can be used for determination of palladium (Table 1). The maximum colour formation for the red product in aqueous solution Pd—PAR—CPB ($\lambda(\varepsilon_{max} = 540$ nm) is attained at pH 4.9 to 5.3 after 25 min standing of the reaction mixture at room temperature and the colour is then stable for at least 2 h. Study of the product composition under these conditions using the Job method at constant tenside concentration $c_{CPB} = 1 \times 10^{-3}$ mol dm^{-3}, $c_{Pd+PAR} = 1 \times 10^{-4}$ mol dm^{-3}, pH = 5.1, λ/nm: 530, 540, 550, and 580, where a further less marked maximum appears in the spectrum, and at $\lambda = 600$ nm, indicated that the product composition is $x(Pd) : x(PAR) = 1 : 2$. The red product formed can be used in aqueous medium to determine ϱ up to 4.78 μg Pd(II) cm^{-3} (Table 1).

The red product, Pd—PAR—CPB, can be extracted into $CHCl_3$; the optimal pH value of the aqueous phase is from 4.8 to 5.2 (an acetate buffer). The $\varepsilon_{540\,nm}$ value in the extract is then more than 2.5 times higher than in the procedure employing zephiramine (Table 1). It follows from the comparison of the absorption spectra of the dye alone, of the red Pd—PAR complex and of the Pd—PAR—CPB species that PAR alone is also extracted into $CHCl_3$, both in the presence and in the absence of CPB (Fig. 1, curves *1*, *4*). The binary complex of palladium with PAR is also extracted (Fig. 1, curve *2*), but in the presence of the tenside the absorbance value increases considerably for the absorption maximum of the extract of the Pd—PAR—CPB product at a wavelength of 540 nm.

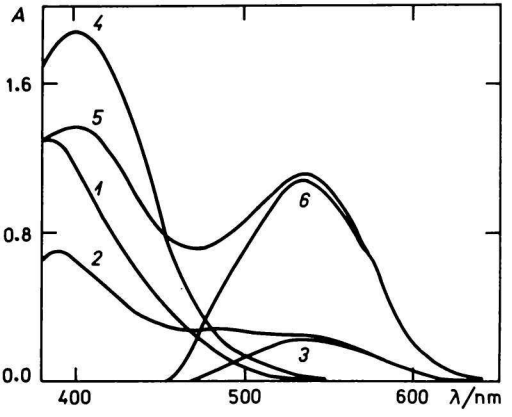

Fig. 1. Absorption spectra of Pd—PAR and Pd—PAR—CPB after extraction into $CHCl_3$. $c_{Pd} = 1 \times 10^{-5}$ mol dm^{-3}, $c_{PAR} = 5 \times 10^{-5}$ mol dm^{-3}, $c_{CPB} = 1 \times 10^{-3}$ mol dm^{-3}, pH = 5.0 (acetate buffer), measured against $CHCl_3$.
1. PAR; *2.* Pd—PAR; *3.* differences between *2* and *1*; *4.* PAR—CPB; *5.* Pd—PAR—CPB; *6.* difference between *5* and *4*.

Extraction times for the Pd—PAR—CPB product from 1 to 5 min are useful; at longer extraction times, the absorbance value decreases. Study of the time stability of the extract, separated from the aqueous phase after standing for 5 min, indicated that the absorbance value begins to decrease slightly after 20 h. It was further found that, at a pH value adjusted to 5 with acetate buffer, the absorbance of the product formed in the organic phase is highest and is constant for PAR concentrations in the aqueous phase of $c_{PAR} = 4 \times 10^{-5}$ to 1×10^{-4} mol dm^{-3} and tenside concentrations greater than 1×10^{-3} mol dm^{-3}. The effect of the ionic strength of the aqueous phase on the absorbance of the extract was studied for NaCl and $NaNO_3$ in the range $I = 0.1$ to 0.5 mol dm^{-3}. The presence of $NaNO_3$ led to turbidity at the lowest concentrations. Heating on a boiling water bath led to dissolution of the turbidity, but a precipitate formed again on cooling. The effect of NaCl in the given concentration range appeared as a marked decrease in the absorbance of the extract: almost to half of the original value for $I_{NaCl} =$ 0.5 mol dm^{-3}. The detection concentration range was found from the calibration graph to be from 0.2 to 2.12 μg Pd(II) cm^{-3} (Table 1; the slope of the regression straight line, $b = 0.879$, the intersept, $a = -0.013$, the standard deviation estimate for the scatter around the regression straight line, $s_{x,y} = 0.035$ for nine points of the calibration curve, each point is the average of ten experimental values). The Job method was used at a constant concentration $c_{CPB} = 1 \times 10^{-3}$ mol dm^{-3} to find a x(Pd):x(PAR) ratio for the complex in the chloroform extract of 1:2 ($c_{Pd+PAR} =$ $= 5 \times 10^{-5}$ mol dm^{-3}, pH = 5.0, λ/nm = 520, 540, 550, and 580).

In the study of interferences from other ions, the effects of selected platinum metals were followed, in addition to the influence of Cl^- and NO_3^- described above. Under the optimal conditions for the determination of palladium ($c_{Pd} = 1 \times$ $\times 10^{-5}$ mol dm^{-3}, pH = 5.0, $c_{PAR} = 5 \times 10^{-5}$ mol dm^{-3}, $c_{CPB} = 1 \times 10^{-3}$ mol dm^{-3}) the extraction was carried out from aqueous solutions with x(Pd):x(M) ratios of 5:1, 2:1, 1:2, 1:4, and 1:10, allowing the solutions to stand for 25 min prior to the extraction. The Pd:M ratios at which there is no interference from M are given in Table 2.

Table 2

Interferences from some ions

M	Substance used	x(Pd):x(M)
Pt(IV)	H_2PtCl_6	1:4
Ir(III)	$(NH_4)_3IrCl_6$	1:1
Ir(IV)	$(NH_4)_2IrCl_6$	2:1
Ru(III)	$(NH_4)_2Ru(H_2O)Cl_5$	2:1
Rh(III)	$RhCl_3$	2:1

As the use of a tenside has been found advantageous for some extraction spectrophotometric determinations, *e.g.* Septonex in $CHCl_3$ [4], a chloroform solution of CPB with a tenside concentration of $(c_{CPB})_0 = 1 \times 10^{-3}$ mol dm^{-3} was prepared and its use for the extraction of the binary red Pd—PAR complex was studied. It was found that experimental conditions, such as the pH of the aqueous phase, range of PAR concentrations in the aqueous phase, extraction time, and stability period of the extract are identical to those for extraction of the Pd—PAR—CPB coloured associate formed in aqueous medium. Study of the effect of the tenside concentration in the organic solvent on the absorbance of the extract indicated that, in contrast to the previous procedure, a much lower $(c_{CPB})_0$ value can be used to attain a high extraction efficiency: in study of the concentration range 2×10^{-4} to 1.4×10^{-3} mol dm^{-3} it was found that 90 % extraction is attained at $(c_{CPB})_0 = 2 \times 10^{-4}$ mol dm^{-3}. To attain the highest extraction efficiency a concentration of $(c_{CPB})_0 = 1 \times 10^{-3}$ mol dm^{-3} was used. Evaluation of the calibration curve indicated that the determination concentration range is from 0.2 to 1.91 μg Pd(II) cm^{-3} (Table 1; $b = 0.821$, $a = 2.8 \times 10^{-4}$, $s_{x,y} = 0.011$).

As the dye is also extracted into the chloroform solution, preparation of the reagent by dissolving both PAR and CPB in the organic phase was studied. First the dependence of the absorbance of the Pd—PAR—CPB extract on the dye concentration in the organic phase $(c_{PAR})_0$ at constant tenside concentration $(c_{CPB})_0$ was studied: 25 cm^3 of aqueous solution of palladium with $c_{Pd} = 1 \times 10^{-5}$ mol dm^{-3} were adjusted to pH 5 and shaken for 1 min with 10 cm^3 of a chloroform solution of a mixture of PAR with CPB ($(c_{CPB})_0 = 1 \times 10^{-3}$ mol dm^{-3}; 4×10^{-5} mol dm$^{-3} < (c_{PAR})_0 < 1.8 \times 10^{-4}$ mol dm^{-3}). After separation of the organic phase, the absorbance of the extract was measured against a chloroform solution of a mixture of PAR—CPB.

It followed from the results that the absorbance value of the extract differential curve increases to a concentration of $(c_{PAR})_0 = 1.2 \times 10^{-4}$ mol dm^{-3} and then no longer changes. The optimum PAR concentration was selected as $(c_{PAR})_0 = 1.25 \times 10^{-4}$ mol dm^{-3}. The most suitable tenside concentration in the organic solvent was found analogously ($(c_{PAR})_0 = 1.25 \times 10^{-4}$ mol dm^{-3}; 0.2×10^{-3} mol dm$^{-3} < (c_{CPB})_0 < 1.4 \times 10^{-3}$ mol dm^{-3}). It has been found that the absorbance of the Pd—PAR—CPB extract is almost independent of the tenside concentration, similar to the extraction of the binary Pd—PAR system into a chloroform CPB solution. As previously, the formation of the Pd—PAR—CPB product is dependent on the time of standing of the mixture after extraction: for complete complex formation, the extract after 1 min shaking must be left to stand at laboratory temperature for 25 min; the absorbance of the extract is then stable for 7 days, while the absorbance of the differential curve of Pd—PAR—CPB after extraction into $CHCl_3$ and the product of the reaction of the Pd—PAR chelate after extraction into a chloroform solution of CPB is stable for a maximum of 2 h.

The calibration curve was again measured for this latter procedure and found to be linear from $\varrho(\mathrm{Pd(II)}) = 0.2—1.91$ μg cm^{-3} (Table 1, $b = 0.859$, $a = 2.1 \times 10^{-4}$, $s_{x,y} = 0.021$).

These results for the utilization of the extraction of the red chelate of palladium with PAR reagent in the presence of cationogennic tenside CPB or the formation directly in the organic phase reflect the broad applicability of tensides. The presence of tensides in the spectrophotometric determination of metals with various chromogennic reagents in aqueous medium leads not only to an improvement in the spectral characteristics of the method, but also in improved solubilization. The inverse micelles of the tenside [5] in the organic reagent the properties of which depend on the micellar structure with a hydrophilic core and lipophilic surface oriented into the solvent consist of a smaller number of tenside units than in aqueous medium and thus higher efficiency of extraction of the coloured product is attained at lower values $(c_{\mathrm{CPB}})_0$. The marked increase of the $\varepsilon_{540\,\mathrm{nm}}$ value for the described reaction of palladium with PAR in the organic solvent reflects the ability of the inverse micelles not only to extract ion associates of charged chelates with the tenside, but also to solubilize uncharged chelates, which is accompanied by a shift in the complexation equilibria in favour of quantitative extraction of the product into $CHCl_3$. This could be in agreement with the determined different mole ratio of $x(\mathrm{Pd}):x(\mathrm{PAR})$ in the coloured product in aqueous medium in the absence of tenside [1] compared to our results.

Procedure

An amount of 10 cm^3 of $CHCl_3$ solution containing a mixture of PAR and CPB with concentrations $(c_{\mathrm{PAR}})_0 = 1.25 \times 10^{-4}$ mol dm^{-3} and $(c_{\mathrm{CPB}})_0 = 1 \times 10^{-3}$ mol dm^{-3} is mixed with 25 cm^3 of a palladium solution containing 5 to 30 μg Pd(II) cm^{-3} and adjusted by addition of acetate buffer to pH = 5; the mixture is shaken for 1 min and then left to stand for 25 min at laboratory temperature. After separation of the organic phase, the absorbance of the extract is measured at $\lambda = 540$ nm against a chloroform solution of PAR—CPB.

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