

Sorption-spectrophotometric method for the determination of Pd(II) in aqueous solutions

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Abstract: The reaction of Pd(II) with 1,8-dihydroxy-2-(pyrazol-5-ylazo)-naphthalene-3-6-disulphonic acid (PACA) sorbed onto Dowex 1-X8 ion-exchange resin was investigated with the aim of developing an absorption-spectrophotometric analytical method for the determination of low Pd(II) concentrations in water. The immobilized reagent formed a 1:1 complex with Pd(II) having an absorption maximum at 650 nm. Parameters, such as pH, wavelength and contact time were optimised for a given amount of the sorbed reagent. The linearity range of absorbance vs. Pd(II) concentration extended from 5×10^{-6} – 5×10^{-5} M, 5×10^{-7} – 5×10^{-6} and 2.5×10^{-8} – 2.5×10^{-7} M when using 10, 100 and 200 ml of sample solution, respectively. With a 200 ml sample, the detection limit was 2.5×10^{-7} M Pd(II). Most metals, except Cu(II), did not interfere when present in up to 100 times the concentration of Pd(II).

Keywords: azo-dyes, immobilization, ion-exchangers, ion-exchange colorimetry, palladium.

INTRODUCTION

Azo-dyes are widely used in analytical chemistry because of their ability to form coloured complexes with many metal ions in water.^{1–6} In recent years they have been employed in sorption spectroscopic test methods more extensively than in conventional spectrophotometry. A great number of sorption-spectroscopic test methods for the determination of metal ions in water, based on the use of these reagents immobilized on ion exchange resins, has been developed.^{1,7–12} Measurement of the resin phase absorbance spectra of a complex has various advantages, since even with a resin layer only 1 mm thick, the sensitivity obtained is much higher than measurement of the corresponding solution. In addition, pre-concentration and selective sorption of the chemical species to be identified may occur simultaneously.

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N-Heterocyclic azo-dyes, such as 1-(2-pyridylazo)-naphthol-2- (PAN), 4-(pyridylazo)-resorcinol (PAR), and their analogues are known to form complexes of very high absorptivity with many metal ions.^{11,12} They have often been used for microdetermination of elements when sorbed on ion exchange resins, either in ion-exchanger colorimetric methods or in the design of chemical optical sensors.^{1,2,5} Mono- and bis-azo-chromotropic acid derivatives with pyrazole or imidazole as the heterocyclic diazo-component belong to the class of organic reagents which contain four nitrogen atoms coupled in a conjugated system of π -bonds. Their reactions with Pd(II), Cu(II) and Ni(II) have great sensitivity over a wide acidity range. Furthermore, Pd(II) forms coloured complexes even in strongly acidic media.¹³⁻¹⁵ Recently, 1,8-dihydroxy-2-(pyrazol-5-ylazo)-naphthalene-3,6-disulphonic acid (PACA) was immobilized with great efficiency onto anion exchange resins.¹⁶ The aim of this work was to develop a simple, spectrophotometric test method for the sensitive and selective determination of low Pd(II) concentrations in water, based on the coloured reaction of Pd(II) with an immobilized dye.

EXPERIMENTAL

Chemicals

All chemicals used were of p.a. grade. The Pd(II) stock solution (1×10^{-3} M), was prepared by dissolving a weighed amount of powdered Pd (EGA-CHEMIE), spectroscopic grade, with aqua regia, followed by fuming the solution to near dryness with a small amount of concentrated HClO₄. The residue was dissolved in 0.5 M HClO₄.¹³ Standard solutions of all metal ions (Cu, Ni, Pb, Hg, Fe, Zn, Cd, Co and Mn) were prepared using distilled water. PACA (Na-salt) was synthesized as described earlier.¹⁴ The dye stock solution (concentration about 1×10^{-3} M, pH 4–5) was passed through a cation-exchange resin in order to be converted into the H-form. The working solutions were buffered using a mixture of phosphoric, acetic and boric acids (an 0.04 M), to which a corresponding amount of 0.2 M NaOH solution was added.

Immobilization procedure

0.5 g of Dowex 1-X8 (50–100 mesh) resin¹⁶ was immersed in 10 ml 5×10^{-5} M PACA at pH 4.2 and left at room temperature for 25 min with occasionally stirring until equilibration. The solution was decanted and the resin with the adsorbed dye was washed with distilled water, air-dried and stored in a glass container until use. The amount of sorbed dye was determined as the difference of its concentration, measured spectrophotometrically, in the contact solution prior and after its sorption.¹⁶ A value of $(7.5 \pm 0.5) \times 10^{-7}$ mol PACA per g of resin was obtained.

Spectrophotometry of the resin phase

Absorbance measurements on the resin phase in a 2 mm cell were carried out by the same procedure as that described earlier.^{8,9} A mixture of the modified resin and sample solution was shaken mechanically. The resin beads were separated from the bulk solution and packed together into a cell by means of a pipette. A reference ion-exchanger layer was inserted in the reference beam to balance the light intensities. The overall absorbance of the sample layer is given by the equation

$$A = A_{RC} + A_{RL} + A_R$$

where A_{RC} represents the net absorbance of the complex species in the solid phase, A_{RL} the absorbance of the free dye in the solid phase and A_R the background absorbance due to light scattering and absorp-

tion by the resin phase itself. A_R , A_{RC} and A_{RL} depended on the packing of the modified resin in the cell. A_{RL} and A_{RC} were obtained directly by measuring the absorbance, with a reference layer containing no sample component and prepared under exactly the same conditions. To avoid the effect of resin packing (A_R), the spectrum of the resin phase containing no coloured species was recorded against bidistilled water.^{8,9} The absorbance at two different wavelengths, one corresponding to the absorption maximum of the coloured species (530 nm for the ligand and 650 nm for the complex) and the other in a region where the resin alone absorbs (750 nm) was measured. Absorbance differences of 0.035 and 0.025 absorbance units, respectively, were obtained and assumed to be constant under similar packing conditions.⁷⁻⁹ The absorbance of the complex or ligand on the resin phase was obtained by subtracting $A_R + A_{RL}$ or A_R , respectively, from the overall absorbance, A .

The solid phase absorption spectra were measured using a Beckman 5260 UV/VIS spectrophotometer. The pH-measurements were made with a Metrohm pH-meter, Model 713.

RESULTS AND DISCUSSION

Absorption spectra and composition of the complex in the resin phase

The reaction between Pd(II) and immobilized PACA was followed in the acidity range between pH 1 and 7. A constant amount (0.5 g) of the resin phase on to which the dye had been presorbed was added to a 10 ml sample solution, containing from 5×10^{-6} to 5×10^{-5} M Pd(II).

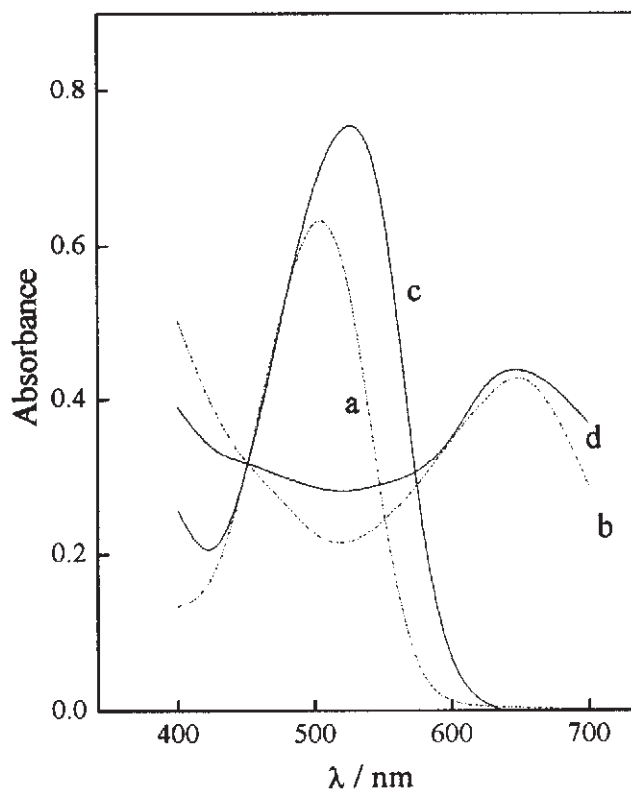


Fig. 1. Absorption spectra of PACA and its Pd(II) complex at pH 4.2. Dotted lines: solution spectra (cell 10 mm). a) 2.5×10^{-5} M PACA; b) 2.5×10^{-5} M Pd-PACA complex. Solid lines: resin spectra (cell 2 mm). c) 7.3×10^{-7} mol of PACA/g resin; d) 1×10^{-6} mol Pd-PACA complex/g of resin. Resin: Dowex 1-X8, 50-100 mesh, Cl⁻ form.

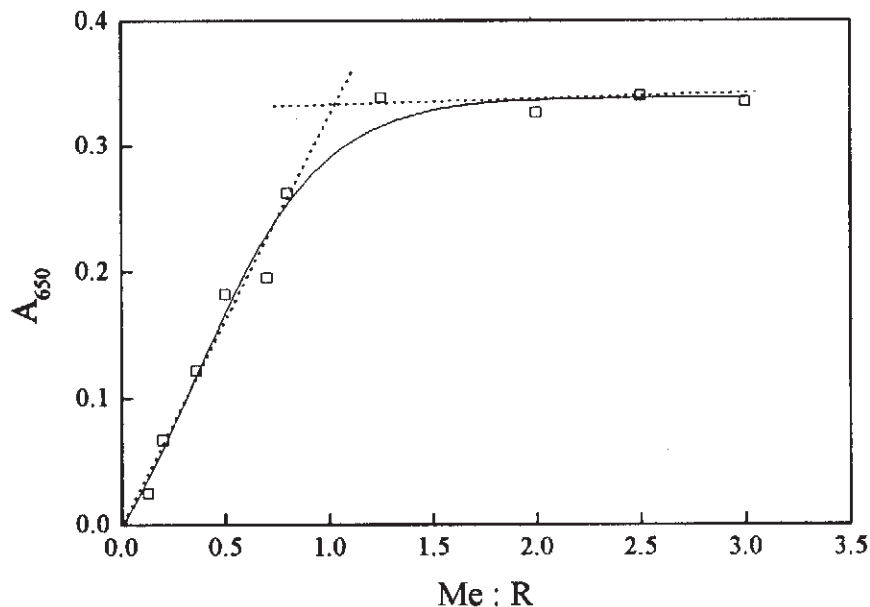


Fig. 2. Mole ratio method applied to the Pd(II) – PACA complex at 650 nm on the anion-exchange resin phase at pH 3 after 50 min of colour development. Resin: Dowex 1-X8, 50–100 mesh, Cl⁻ form, 7.5×10^{-7} mol PACA/g of resin.

The absorption spectra of PACA and its Pd(II) complex after 50 min equilibration of the resin phase with 10 ml of 5×10^{-5} M Pd(II) solution at pH 4.2 is shown in Fig. 1. The absorption spectrum of the sorbed dye does not vary with time and has an absorption maximum between 490 and 520 nm, depending on the acidity of the solution during sorption, whereas the maximum of the dye in solution was at about 500 nm. The absorption maximum of the Pd(II)-PACA complex is at 650 nm, of which wavelength the absorbance of the resin phase can be neglected. This complex was stable in the pH range from 2 to 4. All the spectra were similar to that observed in solution.

The composition of the complex formed in the resin phase was determined by the mole ratio method at pH 3. The reagent concentration was kept constant by prior sorption on to the resin phase (7.5×10^{-7} mol PACA/g of resin), while the Pd(II) concentration in the contact solution changed. To 10 ml of a sample containing Pd(II) in the concentration range from 0.2×10^{-5} M to 1×10^{-4} M was added 0.5 g of the modified resin. The equilibration time was 50 min. The solution was decanted after the equilibration and the absorption spectra of the resin phase were measured. The concentration of the unsorbed Pd(II) was determined by a standard spectrophotometric procedure.^{15,17} The amount of the sorbed Pd(II) was calculated as the difference of its concentration in the solution prior and after the sorption. The results also showed that PACA sorbed on the resin was not desorbed during the measurements. The dependence of the absorbance of the solid phase at 650 nm on the ratio of the amount of PACA (mol/0.5 g of resin) and sorbed Pd(II) (mol

Pd(II)/10 ml of solution) is presented in Fig. 2. The results obtained confirmed the formation of a complex with a stoichiometric ratio PACA; Pd(II) = 1:1, as was also found in solution.^{17,18}

Time dependence of the colour development

The rate of colour development was investigated at various acidities (pH from 0 to 6), by measuring the absorbance of the resin phase at 650 nm, after separation of the resin beads from the solution. To 10 ml of 7×10^{-5} M Pd(II) solution was added 0.5 g of the modified resin. Two types of experiments were performed. In the first series, the contact time between the solution and resin phase was constant at 2 min. The resin phase was separated from the bulk solution and the absorbance was measured as a function of time. In the second series of experiments, the resin beads were stirred with the Pd(II) solution until the absorbance was measured. The results of both series of experiments are presented in Fig. 3. The results show that the rate of complex formation first increased with increasing solution acidity, reaching a maximum at pH 1.7. It is significant to notice, that increasing the acidity above 1 M HClO₄ leads to inhibition of the complex formation due to protonation of PACA functional groups.

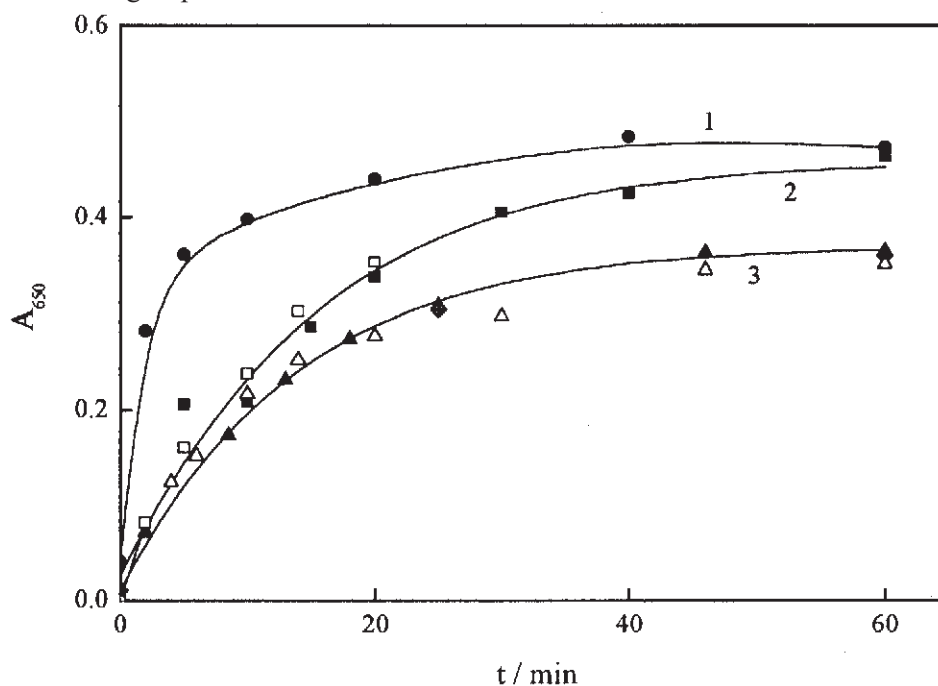


Fig. 3. Time dependence of the colour development in the resin phase separated from 10 ml 7×10^{-5} M Pd(II) solution. Open symbols – solid phase separated after 2 min stirring; Solid symbols – solid phase stirred with the solutions until the measurements. 1–pH 1.7; 2–pH 2.6; 3–pH 4.2 and pH 5.7. Resin: Dowex 1-X8, 50–100 mesh, Cl⁻ form.

It is obvious from Fig. 3 that the time dependence of the absorbance at 650 nm of the resin separated from the solution after 2 min stirring agreed very closely with that for the resin stirred with the solution until the measurements were carried out. Parallel determinations of the Pd(II) concentration in the bulk solution showed that it was completely sorbed onto the resin phase within 2 min. This finding confirms that the sorption of Pd(II) on the resin phase and complex formation between Pd(II) and PACA represent two consecutive reactions. Obviously, the rate of Pd(II) sorption was faster than the rate of complex formation. However, colour development in both cases was almost complete within 40 min. With larger sample volumes, the equilibration time required for quantitative sorption was increased, but the sensitivity was enhanced.

The sorption capacity was determined using the method of saturation at pH values from 2 to 4 by following the dependence of the complex sorbed onto the solid phase on the Pd(II) concentration using a contact time of the Pd(II) solution and the ion-exchanger of 30 min. It was found that the sorbing capacity depended on the amount of sorbed reagent (Table I).

TABLE I. Absorbance of the resin phase (8.2×10^{-7} mol PACA/g of resin) at 650 nm as the a function of the Pd(II) concentration at pH 3

$\mu\text{mol Pd(II)/10 ml}$	0.05	0.18	0.22	0.32	0.43	0.54	0.76
A_{650}	0.032	0.122	0.136	0.195	0.301	0.338	0.326

The results presented in Table I show that 0.5 g of sorbet PACA-Dowex 1-X8 with 4.1×10^{-7} mol PACA maximally sorbed between 4.3×10^{-7} and 5.4×10^{-7} mol Pd(II) from 10 ml of solution, *i.e.*, between 8.6 and 10.8×10^{-7} mol Pd(II) per g of sorbent.

Calibration and precision

Calibration curves were constructed at pH 2 and pH 4. Linear dependencies of absorbance *vs.* Pd(II) concentration were obtained and may be expressed by the equations:

$$A_{650} = (6.45 \pm 0.4) \times 10^3 c$$

and

$$A_{650} = (6.50 \pm 0.2) \times 10^3 c$$

for 10 ml samples, at pH 2 and pH 4, respectively, where c is the concentration of Pd(II) in the sample solutions, in mol dm^{-3} .

The linear concentration range extended from 5×10^{-6} – 5×10^{-5} M Pd(II). The calibration curves were also linear in the concentration range from 5×10^{-7} – 5×10^{-6} M and from 2.5×10^{-8} – 2.5×10^{-7} M for the systems employing 100 ml and

200 ml of sample solution, respectively. The relative detection limit (the concentration that produces an absorbance equal to twice the magnitude of the fluctuation in the background absorbance) for the systems using 10, 100 and 200 ml of sample solution were 5×10^{-6} M, 5×10^{-7} M and 2.5×10^{-7} M Pd(II), respectively. The precision of the method was measured using 10 ml of 5×10^{-5} M Pd(II) sample solution. For ten determinations, the relative standard deviation was 10 %. The limit of detection for the solution spectrophotometric method is 1×10^{-5} M and the linearity range is from 1×10^{-5} to 1×10^{-4} M.

Effect of foreign ions

The effect of foreign ions (Cu, Ni, Pb, Hg, Fe, Zn, Cd, Co and Mn) was investigated for the 10 ml sample system, at pH 2 and pH 4, by the standard procedure. The results are presented in Table II. At pH 2, with the exception of Cu, the investigated metal ions, did not interfere when present at a concentration of up to 100 times the concentration of Pd(II) (the relative error was less than 20 %). Similar results were obtained at pH 4, except the presence of a 100- fold excess of Hg and a 10 fold excess of Cu(II) relative to the Pd(II) concentration interfered. The results show, that it is possible to determine Cu(II) simultaneously, by taking advantage of the pH influence on the complex formation. After Pd(II) was determined by use of the calibration curve at pH 2, the contribution of the Pd(II)-PACA absorbance at pH 4 can be calculated from the calibration graph. The concentration of Cu(II) can then be determined after deduction of the Pd(II) absorbance.

TABLE II. Effect of foreign ions on the determination of 1×10^{-5} M and 5×10^{-5} M* Pd(II)

Ion	Mole ratio to Pd(II)	pH 2			pH 4		
		A_{650}	Pd(II) found 10^5 M	Relative error/%	A_{650}	Pd(II) found 10^5 M	Relative error/%
Pd(II)	1	0.059	1.02	2	0.054	1.06	6
Hg(II)	10	—	—	—	0.058	1.14	14
Hg(II)	100	0.061	1.05	5	0.084	1.65	65
Fe(II)	10	0.064	1.10	10	0.062	1.22	22
Zn(II)	100	0.058	1	0	0.060	1.18	18
Mn(II)	100	0.057	0.98	-2	0.058	1.14	14
Cd(II)	100	0.064	1.10	10	0.060	1.18	18
Pb(II)	10	0.068	1.17	17	0.062	1.22	22
Cu(II)	10	—	—	—	0.086	1.69	69
Cu(II)	100	0.078	1.34	34	0.094	1.84	1.84
Co(II)	100	0.061	1.05	5	0.054	1.06	6

TABLE II. Continued

Ion	Mole ratio to Pd(II)	pH 2			pH 4		
		A_{650}	Pd(II) found 10^5 M	Relative error/%	A_{650}	Pd(II) found 10^5 M	Relative error/%
Ni(II)	100	0.057	0.98	-2	0.052	1.02	2
Pd(II)	1*	0.315	5.43	9	0.309	5.72	14
	200*	0.337	5.81	16	0.318	5.89	18
NaCl	2000*	0.301	5.19	4	0.316	5.85	17
	36000*	-	-	-	0.294	5.44	9

The results presented in Table II also show that Cl^- in the concentration range from 1×10^{-2} M to 1.8 M had no effect on the determination of Pd(II).

CONCLUSIONS

According to the obtained results, it can be concluded that the reaction of Pd(II) with PACA, immobilized onto a solid support, showed attributes appropriate for a application of this system for the detection of low Pd(II) concentrations in aqueous solutions. The advantages of the presented method for the determination of Pd(II) are that the concentration of the metal and the colour development take place simultaneously and that the sensitivity and selectivity are high. As a result, low concentrations can be determined in a conveniently short time.

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ИЗВОД

АПСОРПЦИОНИ МЕТОД ЗА ОДРЕЂИВАЊЕ Pd(II) У ВОДЕНИМ РАСТВОРИМА

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Испитана је реакција Pd(II) и 1,8-дихидрокси-2-(пиразол-5-илазо)-нафтален-3,6-ди-сулфонске киселине, сорбоване на јоноизмењивачкој смоли Dowex 1-X8, у циљу развијања апсорпционо-спектрофотометријске методе за одређивање ниских концентрација Pd(II) у води. Иммобилизовани реагенс са Pd(II) гради комплекс састава 1:1, са апсорпционим максимумом на 650 nm. Одређени су оптимални услови реакције (pH, таласна дужина, време контакта) за дату количину сорбованог реагенса. Добијена је линеарна зависност апсорбанције од концентрације Pd(II) у области од 5×10^{-6} – 5×10^{-5} M, 5×10^{-7} – 5×10^{-6} M и 2.5×10^{-8} – 2.5×10^{-7} M за системе чија је запремина 10, 100 и 200 ml. Нађено је да је детекциони лимит за узорке запремине 200 ml 2.5×10^{-7} M Pd(II). Већина металних јона, осим Cu(II), нема утицај на калибрациони график при концентрацијама 100 пута већим од концентрације Pd(II).

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