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Spectrophotometric Determination Of Palladium Using Some Halogen Derivatives Of Phenylazo-Chromotropic Acid

by

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Spectrophotometric Determination Of Palladium Using Some Halogen Derivatives Of Phenylazo-Chromotropic Acid

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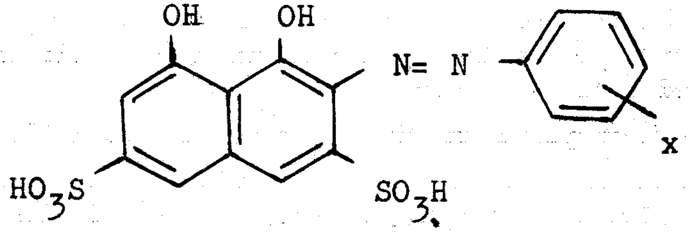
SUMMARY

A comparative study on the reaction of o-chloro-, m-chloro-, p-chloro-, o, p-dichloro-, p-bromo-, and p-iodo- phenylazochromotropic acid with Pd (II) ions have shown that two 1:2 (metal: ligand) violet water soluble complexes are formed at two different pH values. The p-derivatives were found to be very suitable reagents for the spectrophotometric determination of Pd (II) up to 6.3-8.3 ppm. The application of these dyes as indicators in the spectrophotometric titration of Pd (II) with EDTA and the effect of various cations and anions on the determination were reported.

INTRODUCTION

Khalifa determined the acid dissociation constants for the halogen derivatives of phenylazo-chromotropic acid using potentiometric and spectrophotometric methods.(1) The only use of these azo dyes as spectrophotometric reagents was reported by Khater et. al. They were used for the determination of thorium and zirconium.(2–4)

The possibility of using the halogen derivatives of phenylazo-chromotropic acid as spectrophotometric reagents for Pd (II) is the subject of the present article. The dyes used are:



where x = o-Cl (a), m-Cl (b), p-Cl (c), o, p-di-Cl (d), p-Br (e) and p-I (f).

EXPERIMENTAL

Double distilled water and chemicals of the highest purity available by BDH were used in all experiments.

The substituted phenylazo-chromotropic acids were prepared by coupling the corresponding diazotized amines with chromotropic acid in sodium carbonate medium(5), the resulting crude product was recrystallized(6) and the purity of the dyes was then confirmed by elemental microanalysis and potentiometric titration against standard sodium hydroxide solution to be more than 99.5 %. 0.01 M palladium chloride solution was prepared by dissolving the calculated amount in the least quantity of concentrated HCl (10 ml/l) and diluting with water up to the appropriate volume. The solution was then standardized as previously recommended(7). 0.001 M solution was prepared by accurate dilution. 0.001 M solutions of the azo dyes were prepared by dissolving the calculated weight in water. Britton-Robinson buffer solutions were prepared (pH 2-12) and used to control the pH and ionic strength.(8) Solutions containing 1 mg/ml anion or cation for testing the interfering effect were prepared as usual.

The absorption spectra were obtained using PYE UNICAM SP 1750 spectrophotometer.

Procedures:

1- Spectrophotometric determination of Pd (II).

To a solution containing not more than 60-80 ug Pd (II) in a 25 ml beaker add 2 ml of 0.001 M dye and 5 ml universal buffer solution of the recommended pH value (Table 1), the solution is then heated to about 60°C for 4 mins. and transfered quantitatively to a standard 10 ml measuring flask with water and completed to the mark. The absorbance is then measured at the optimum wavelength (Table 1). The concentration is computed by extrapolation from a calibration curve prepared in the same manner.

2- Spectrophotometric titration of Pd (II) with EDTA.

2 ml 0.001 M indicator (a, b, c, d, e or f), 0.3-0.8 ml 0.001 M Pd(II) solution, 5 ml universal buffer of the recommended pH value were de-

Table (1)
Collective data of palladium complexes with the halogen derivatives of phenylazo-chromotropic acid.

ligand	pH	λ_{max} nm	up to ppm	$\varepsilon \times 10^{-4}$	a	S	log K
a	5.0	600	8.51	0.48	0.045	0.022	7.63
	11.0	620	8.51	1.27	0.119	0.008	8.63
b	4.0	610	6.38	0.93	0.087	0.011	6.60
	11.0	620	8.51	1.67	0.156	0.006	6.72
c	6.0	590	7.45	0.91	0.085	0.011	6.51
	12.0	600	7.45	1.47	0.138	0.007	6.65
d	4.0	615	8.51	0.68	0.064	0.015	6.35
	10.0	600	6.38	1.02	0.096	0.010	6.50
e	4.0	590	7.45	1.30	0.122	0.008	6.12
	10.0	600	6.38	1.01	0.094	0.010	6.45
f	5.0	580	8.51	0.60	0.056	0.017	6.40
	12.0	610	8.51	1.47	0.138	0.007	6.75

ε: l. mole^{-1}. cm^{-1}, a: ml. g^{-1}. cm^{-1}, S: ug. cm^{-2}.

livered into each 10 ml beaker and successive volumes (0.05, 0.1, 0.15 ... ml) of 0.001 M EDTA were then added. The solutions were heated up to 60°C for 4 minutes and then transfered quantitatively with water into 10 ml measuring flasks and completed to the mark. The absorbances were measured at the recommended wavelength and plotted against volume of EDTA added.

RESULTS AND DISCUSSION

The absorption spectra of all the Pd (II) complexes with the azo dyes under investigation were studied at different pH values, and the optimum pH values for developing the violet complexes were found to be 5.0 and 11.0 for Pd-a, 4.0 and 11.0 for Pd- b, 6.0 and 12 for Pd- c, 4.0 and 10.0 for Pd- d, 4.0 and 10.0 for Pd- e and 5.0 and 12.0 for Pd- f complexes; Fig. (1) represents the effect of pH on the absorption spectra of Pd- b complex. The absorption spectra of the ligand and Pd complex against water and against ligand at the recommended pH values are recorded, representative curves are shown in Fig. (2). The results indicate that the complexes absorb maximally at 600 and 620 nm, 610 and 620 nm, 590 and 600, 615 and 600 nm, 590 and 600 nm and 580 and 610 nm for the six Pd complexes respectively using the dye as blank. The effect of time and temperature on the formation and stability of the studied palladium complexes revealed that they are formed after

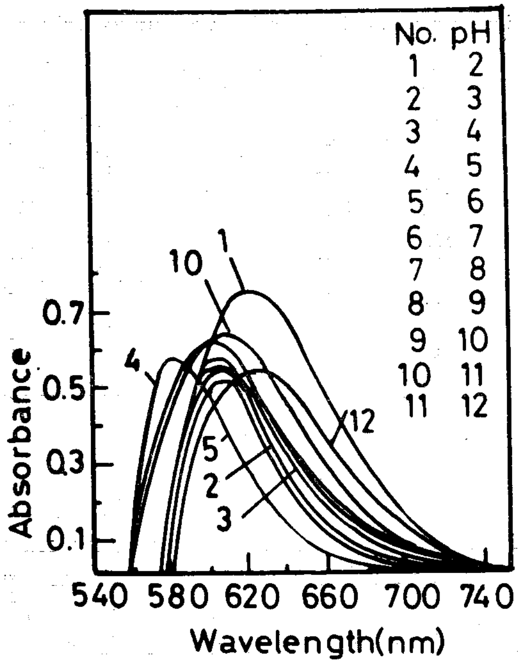


Fig. (1). Effect of pH on (5×10^{-5}M) Pd-b complex.

heating to 60°C for 4 minutes or after standing for 1 hour and remain stable for several days, while boiling destroys the formed complexes. The addition of organic solvents such as ethanol, propanol, isopropanol, acetone and dioxane up to 30 % have no appreciable effect on the complexes.

Beer's law was verified and found to be satisfactorily obeyed when the concentration of Pd was up to 6.3-8.5 ppm according to the ligand used. The results are summarized in table (1) and representative results are shown in Fig. (3). The molar absorpitivities (ε) of the resulting complexes were found to be in the order of 10^4 (table 1). These values are high suggesting the sensitivity of the method adopted. The sensitivity of the method is confirmed by calculating the values of the specific absorptivity (a)(9) (ml. g^{-1}. cm^{-1}) and the Sandell sensitivity (S)(10) (ug. cm^{-2}), the values are listed in table (1) indicating the sensitivity

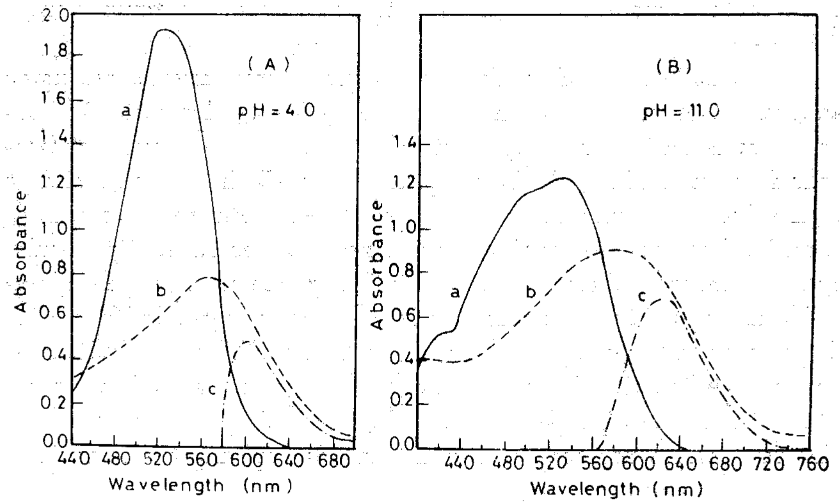


Fig. (2). Absorption spectra of Pd-b complex.
a– Ligand 8 x 10^{-5}M (A), 1 x 10^{-5}M (B), water as blank.
b– Complex 4 x 10^{-5}M (A), 5 x 10^{-5}M (B), water as blank.
c– b against a as blank.

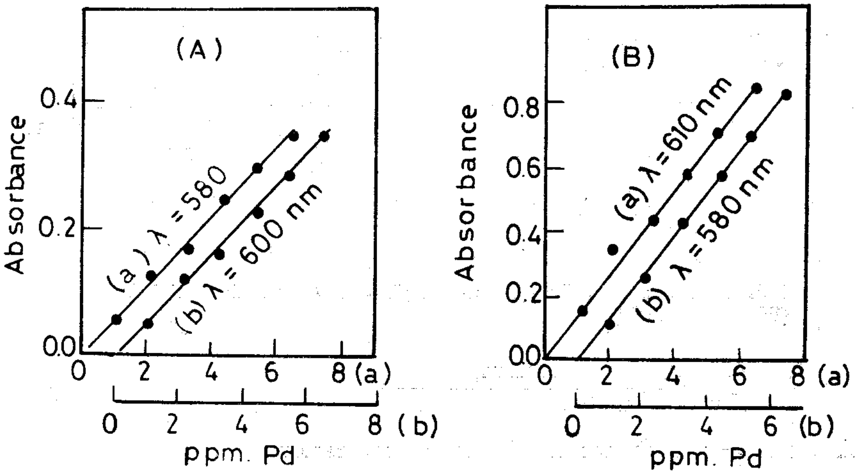


Fig. (3). Beer's law for Pd-f complex at pH=5.0 (A) and pH = 12.0 (B).

for the method suggested for the spectrophotometric determination of palladium..

The stoichiometry of the formed complexes was investigated using standard spectrophotometric methods such as the molar ratio(11), continuous variation(12) and slope ratio (13) methods. The results indicate the formation of 1:2 (M:L) complexes with all the reagents and at all pH values mentioned before; representative results are given in Figs. (4 and 5). The presence of these complexes was confirmed by calculating the number of absorbing species applying Coleman's graphical method(14), as applied to the results of the molar ratio method. The results indicate that only two species were present in all the cases studied namely the free ligand and the complex in equilibrium The stability constants of the formed complexes were calculated using the results of the molar ratio and continuous variation methods applying the relation:

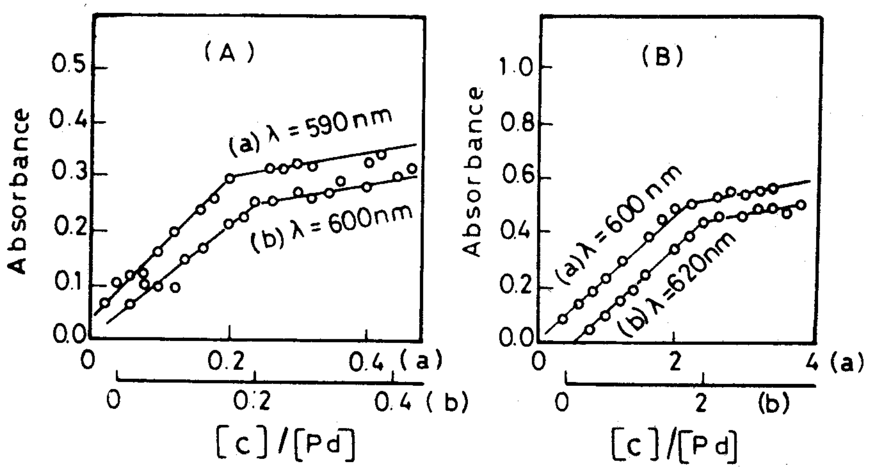


Fig. (4). Molar ratio method for Pd-e complex at pH=6.0 (A) and pH = 12.0 (B), (Pd) = 5 x 10^{-5}M.

$$K_n = \frac{(A/Am)}{(1-A/Am)^{n+1}\, C^n{}_L\, n^2}$$

where: A = absorbance at ligand concentration C_L

Am = maximum absorbance at full colour development

n = stoichiometric ratio of the complex.

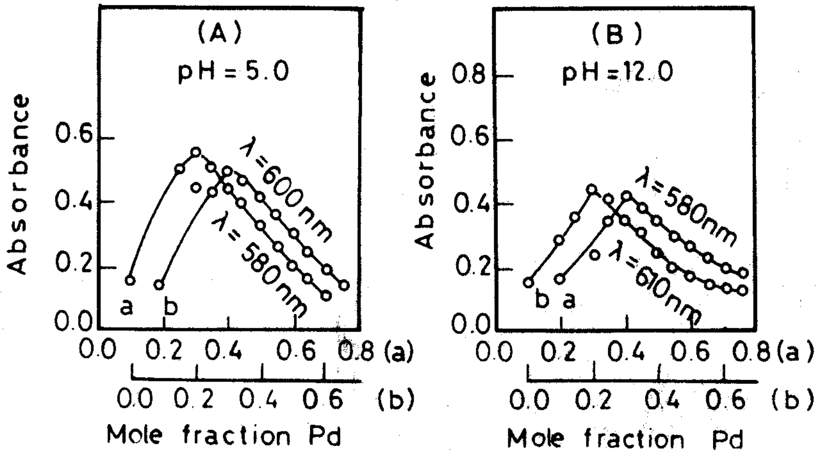


Fig. (5). Continuous variation method for Pd-f complex at pH = 5.0 (A) and pH = 12.0 (B).

The results are listed in table (1).

Effect of foreign ions

Foreign ions such as Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Be, Mn (II), Fe (II), Co, Ni, Zn, Hg (II), Bi, UO_2, Au (III), Ru, Pt (IV), Cl, Br, I, SO_4, phosphate, borate and acetate do not interfere up to 20 folds during the spectrophotometric determination of 1 ppm of pd. On the other hand, Al, Ga, In, Sc, Cu (II), Cr (III), Y, Fe (III), Zr, Th, F, CN, citrate, vanadate, tartrate, EDTA and CDTA ions interfere and should not be present during the determination.

Spectrophotometric titration of Pd

The application of the halogen derivatives of phenylazochromotropic acid as indicators in the spectrophotometric titration of palladium using EDTA has been ascertained. The present method is accurate and highyl reproducible as indicated by the low standard deviation values calculated for the determination of 50 ug Pd /10 ml (10 determinations) amounting to 0.003 This method is useful for the determination of Pd over the concentration range 5.0-8.0 ppm. A representative curve is shown in Fig. (6).

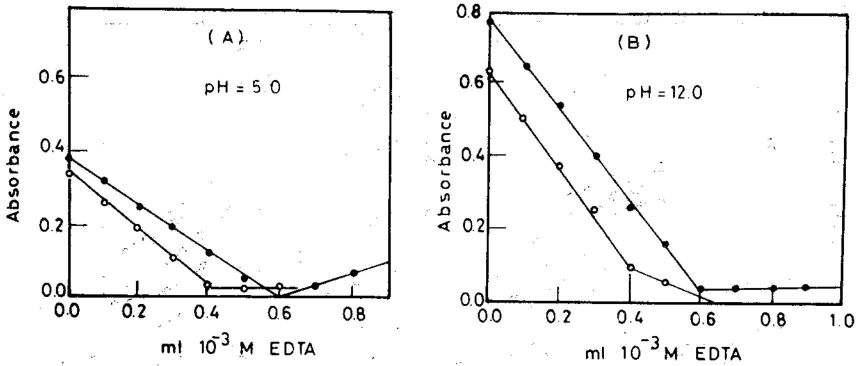


Fig. (6). Spectrophotometric titration of Pd using f as indicator.

CONCLUSIONS

The azo dyes under investigation are considered to be excellent chromophoric reagents for palladium. This may be regarded by the difference in the maximum absorbance between the orange red free dyes (λ max-520 nm) and the violet metal complexes (λ max 580-620 nm) amounting to 80 nm in the average. The dyes are water soluble and stable for a long time and no changes in the dye solution were observed on keeping the solution for several months. The complexes also are water soluble and do not need any extraction process. The values of the molar absorption coefficient are high especially in the alkaline pH range. The values of the specific absorptivity (a) and Sandell sensitivity (S) were calculated, the results indicate the sensitivity on the adopted method. The results of the stability constant indicate that such complexes are fairly stable However, these values are lower than the corresponding Pd-EDTA complex(7), which permit the use of these indicators in the chelatimetric titration of palladium with the end point being detected spectrophotometrically.

Generaly, the p-iodophenylazo-chromotropic acid (f) is the most suitable indicator for the spectrophotometric determination of palladium as shown by the high ε values amounting to 1.47 x 10^5 and the obeyence to Beer's law up to 8.51 ppm.

REFERENCES

1- **Khalifa, H., Khater, M.M., Issa, Y.M.** and **Badawy, S.S.,** Microchem. J., 22, 288 (1977).

2- **Khater, M. M., Issa, Y. M.** and **Badawy, S. S.,** Microchem. J., 22, 299 (1977).

3- **Khater, M. M., Issa, Y. M.** and **Badawy, S. S.,** Z. Anal. Chem., 284, 45 (1977).

4- **Khater, M. M., Issa, Y.M.** and **Badwy, S. S.,** Egypt. J. Chem., 23, 173 (1980).

5- **Ishibashi, M. I.** and **Higashi, S.,** Japan Analyst, 4, 14 (1955).

6- **Mehata, H. U.** and **Shan, K. H.,** Ins. J. Appl. Chem., 29, 122 (1966).

7- **Welcher, F. J.,** "The Analytical Uses of Ethylenepiaminetetraacetic acid" D. Von Nostrand Co. Inc., Princeton (1958).

8- **Britton, H. T. S.,** "Hydrogen Ions" 4 th. Ed. Chapman and Hall London (1952).

9- **Ayers, H. G.** and **Narang, B. D.,** Anal. Chim. Acta, 24, 241 (1961).

10- **Sandell, E. B.,** "Colorimetric Determination of Traces of Metals" 3 rd Ed., Interscience, New York (1959).

11- **Yoe, J. H.** and **Jones, A.L.,** Indst. Eng. Chem. Anal. Ed., 16, 111 (1944).

12- **Vosburgh, W. C.** and **Cooper, G. R.,** J. Am. Chem. Soc., 63, 437 (1941).

13- **Harvey, A. E.** and **Manning, D.L.,** J. Am. Chem. Soc., 72, 4488 (1950).

14- **Coleman, J. S., Varge, L. P.** and **Mastin, S. H.,** Inorg. Chem., 2, 1015 (1970).