CHAPTER - VI

2-MERCAPTOBENZOIC ACID AS AN ANALYTICAL REAGENT

Literature reveals a number of complexing agents for spectrophotometric determination of palladium. In our laboratory 2-mercaptobenzoic acid is under investigation to study its analytical potentiality. A method has been reported to determine palladium spectrophotometrically in microgram levels with the reagent.

Spectrophotometric Determination of Palladium

EXPERIMENTAL

Apparatus and Reagents :

Absorbance measurements were carried out with a Shimadzu PR-1 model spectrophotometer fitted with a pair of matched quartz cells of 10 mm optical path length.

Palladium chloride (Johnson and Matthey) (1 g) was dissolved in conc. HCl (1 ml) and diluted to 250 ml with distilled water. This was standardised with dimethyl glyoxime[1]. A working solution of palladium(II) was prepared by approximate dilution of the stock solution.

A 0.1% ethanolic solution of 2-mercapto benzoic acid (E. Merck) was used for the purpose. Adjustment of pH in the aqueous phase was done by using 0.2 N acetic acid and 0.2 M sodium acetate solution.

Standard solutions of diverse ions were prepared from chlorides nitrates as sulphates of metals (in case of cations); and from sodium, potassium or ammonium salts of the species concerned (in case of anions) to study this interfering effects.

All other chemicals used were of analytical grade.

Determination of palladium :

An appropriate amount of palladium solution (20-100μg) was taken in a 10 ml volumetric flask. To this was added 0.1% ethanolic solution (1 ml) of 2-mercaptobenzoic acid followed by the acetate buffer (5 ml) (pH 3.5). The volume was made up with distilled water and left for 1 min to ensure complete complexation and maximum colour development. Absorbance of the solution was measured at 420 nm against a reagent blank. Amount of palladium present was computed from a calibration curve. To study the interference, the respective foreign ions were added prior to the addition of reagent and volume make up.

RESULTS AND DISCUSSION

Absorption and Spectra :

The absorption spectrum of the Pd(II)-2-mercaptobenzoic acid complex in aqueous solution against the reagent blank taken as reference is shown in Fig. 1. Maximum absorbance as seen from the spectrum, occurs at 420 nm. The reagent blank prepared under conditions of the experiment absorbs considerably below 380 nm but the absorbance became insignificant from 400 nm onwards. Hence the wave length of 420 nm was selected for all analytical measurements.

Effect of pH :

The effect of pH on colour development was examined by measuring at 420 nm the absorbance of the palladium complex over the pH range 0-12. Various buffers were employed for the purpose. The complex exhibits constant and maximum absorbance when the acidity of the aqueous phase was maintained at pH 3-4, showing a gradual decrease in value with increase or decrease in pH. The variation of absorbance with change in pH of the aqueous phase is shown in Table 1 and 4 in Fig. 2.

Effect of reagent concentration :

The effect of 2-mercapto benzoic acid on the colour development of the Pd(II) complex in the aqueous phase was studied by adding different amounts of the reagents. Use of 0.4 ml of 0.1% ethanolic solution of the reagent was sufficient for maximum colour development of the aqueous phase (10 ml) containing 43 μg of palladium. Use of less than 0.25 ml of the reagent probably render the complexation incomplete and low absorbance values of the aqueous solution are obtained. Increased concentrations, on the other hand, do not bring about any significant change in the maximum value of absorbance. However, use of 1 ml of 0.1% ethanolic solution of the reagent is preferred in the proposed method as a part of the added reagent may be consumed - if foreign ions are present. Results obtained in respect of reagent concentration are presented in Table 2.

Stability of colour:

The absorbance of the palladium complex in the aqueous phase was measured at elapsed intervals of .25, 0.5, 1, 2, 4, 8, 12 and 24 hours after the colour development at 420 nm against the reagent blank was measured. No change in the colour intensity was recorded upto 24 hours (Table 3). The complex is thus, sufficiently stable.

Calibration curves sensitivity and precision :

Calibration curve was prepared by standard procedure. Different amounts of palladium were allowed to interact with 2-mercapto benzoic acid maintaining all conditions of the given procedure. Absorption of the Pd-complex was measured at 420 nm against a blank. A standard calibration curve was obtained by plotting absorbance values against corresponding palladium concentrations (Table 4, Fig. 3).

The system conforms to Beer's law over concentrations of 10 ppm of palladium (Table 4, Fig 3). Sandell's sensitivity and molar absorptivity of the complex (on the basis of palladium content) are 0.006 $\mu g/cm^2$ and 1.725×10^4 l $mol^{-1} cm^{-1}$ respectively at 420 nm. This classifies the colour reaction as one of the most sensitive for palladium compared with some other existing methods (Table 5).

Precision and accuracy :

The precision and accuracy of the proposed method was tested by analysing solutions containing a known amount of palladium (II). The results in Table 6 indicated the method to be fairly precise and reproducible. The total operation time for each run required 10-15 min.

Interference :

In a separate set of experiments a standard palladium(II) solution containing 43 μg of palladium in each case was mixed with an aqueous solution of one of the foreign species. Determination of palladium was then computed following the recommended procedure. The tolerance limit was set at that amount of the foreign material for which approximately $\pm$ 3 per cent error would be achieved. The upper limit of concentration investigated was, however, restricted to the amount around 100 fold excess (w/w) of the palladium concentration. The results showing tolerance limits of the foreign materials investigated, are given in Table 7.

Tolerance limits of some ions having serious interference were improved by using masking agents, e.g., iron(III) was masked with fluoride, lead(II) with excess acetate. Among the ions tested mercury(II) has very low tolerance limit.

Application to the analysis of synthetic mixtures :

In absence of real samples the proposed method was extended to some synthetic mixtures to estimate microgram amounts of palladium. Five different synthetic mixtures were prepared by mixing solutions of palladium(II) with those of platinum(II), Rhodium (III), iron(III), copper(II), nickel(II), cobalt(II), zinc(II), cadmium(I), molybdenum(VI) and vanadium(V) in the manner as given in Table 8. The amount of palladium present in each sample was then determined by following the recommended procedure. Masking agent was used wherever necessary.

Conclusion :

The present method for the spectrophotometric determination of palladium is simple, rapid and sensitive. The metal in micro quantities can be estimated in presence of most of the common ions. Influence of some interfering ions can be overcome. The method is, therefore, a selective one. Furthermore, the method is precise and reproducible. The proposed method is thus worthy of finding application for determination of palladium whenver high degree of precision and sensitivity is desired.

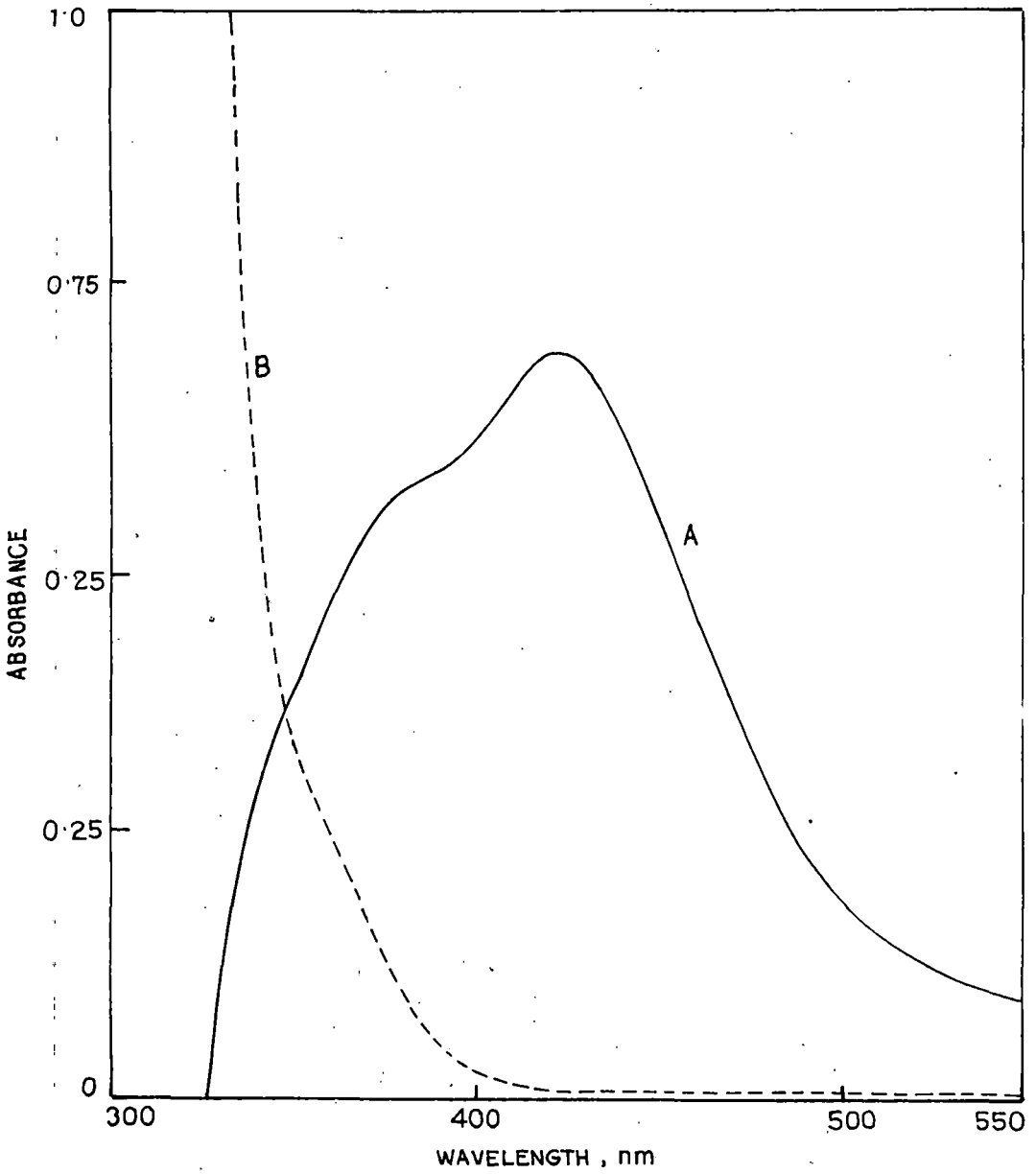

FIG: 1. ABSORPTION SPECTRUM OF Pd(II)-2-MERCAPTOBENZOIC ACID COMPLEX (A) AND REAGENT BLANK (B).(Pd-4·3 ppm)

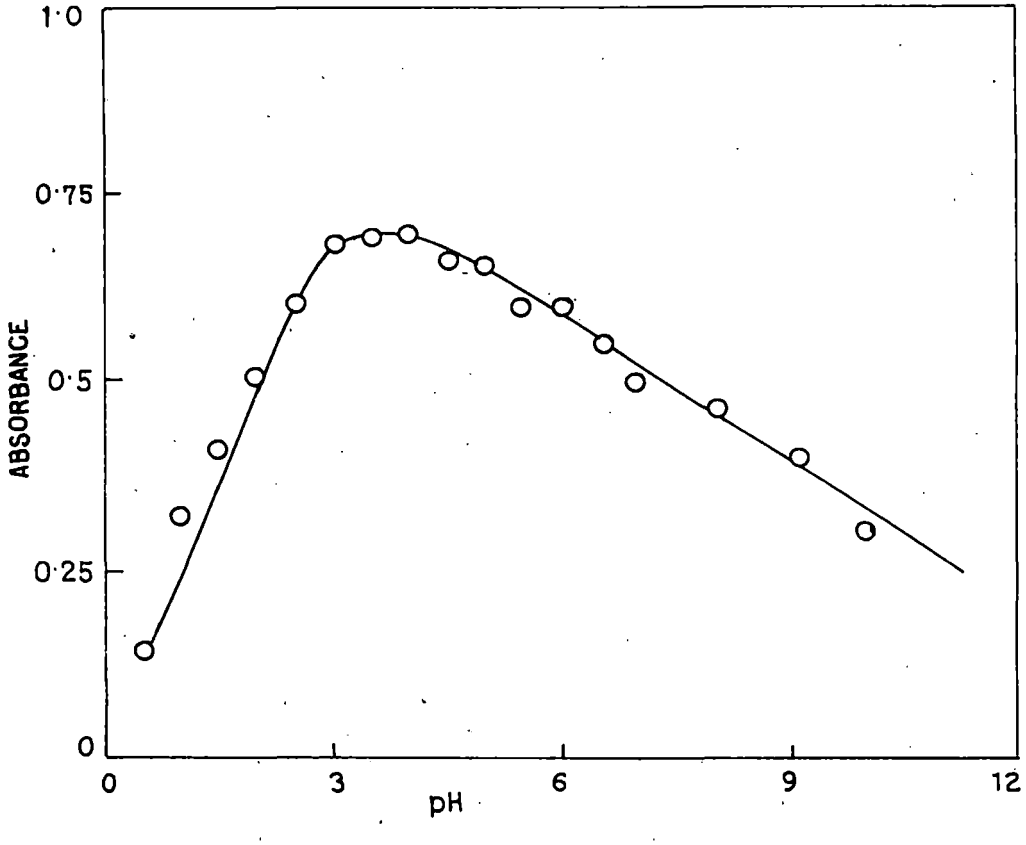

FIG. 2. ABSORBANCE OF PALLADIUM (II) COMPLEX AS A FUNCTION OF pH .

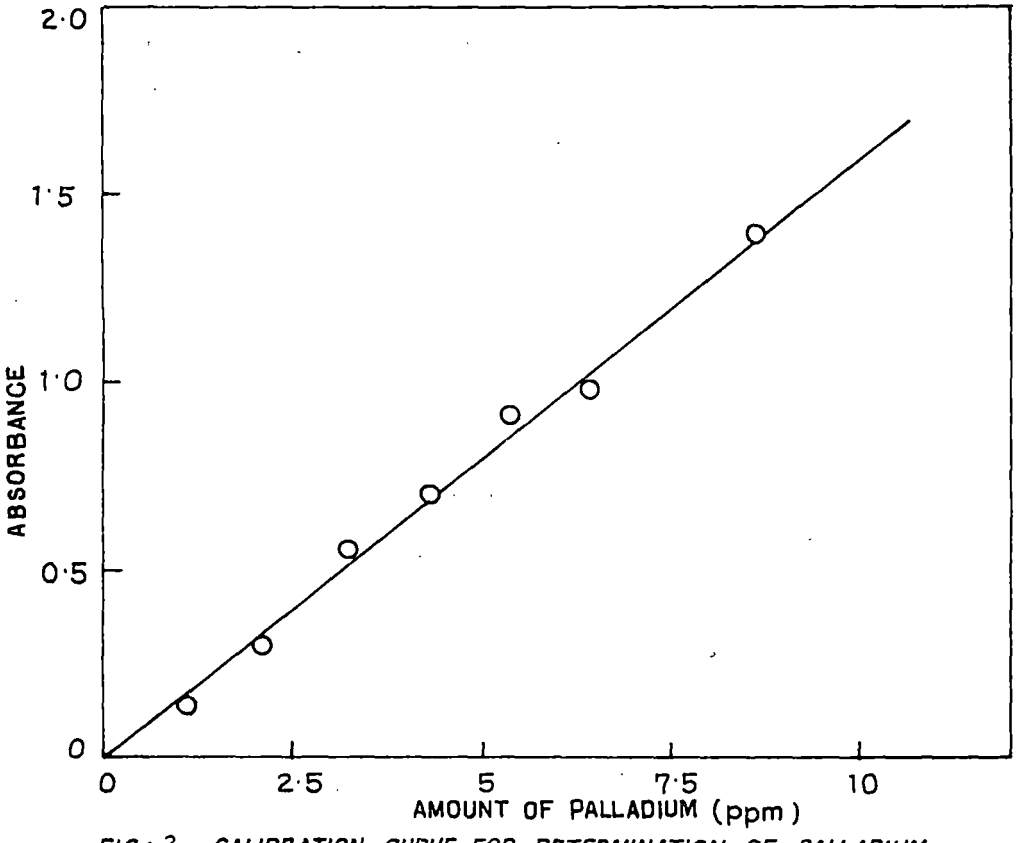

FIG: 3, CALIBRATION CURVE FOR DETERMINATION OF PALLADIUM .

Table 1 : Variation of absorbance with pH of the aqueous phase (The aqueous phase (10 ml) contains 43 μg of Pd(II) and 2 ml of 0.1% ethanolic solution of 2-mercapto-benzoic acid

pH	Absorbance	pH	Absorbance
0.5	0.140	4.5	0.660
1.0	0.322	5.0	0.650
1.5	0.410	5.5	0.600
2.0	0.500	6.0	0.600
2.5	0.610	6.5	0.550
3.0	0.688	7.0	0.510
3.5	0.695	8.0	0.470
4.0	0.695	9.0	0.410
		10.0	0.310

Table 2. Effect of 2-mercaptobenzoic acid. The aqueous phase (10 ml) (pH 3.5) contains 43 μg of Pd. 0.1% ethanolic solution of the reagent was used

Addition of reagent added in ml	Absorbance	Addition of reagent added in ml.	Absorbance
0.05	0.340	0.5	0.695
0.10	0.395	0.6	0.692
0.15	0.430	0.8	0.692
0.2	0.480	1.0	0.695
0.25	0.532	1.5	0.695
0.3	0.430	2.0	0.695
0.35	0.680	4.0	0.695
0.40	0.690	6.0	0.692

Table 3. Variation of absorbance with time

Time in hour	Absorbance
0.25	0.695
0.5	0.695
1	0.692
2	0.695
4	0.695
8	0.695
12	0.695
24	0.695

Table 4. Beer's law data

Concentration of palladium(ppm)	Absorbance at 420 nm
1.07	0.140
2.15	0.322
3.22	0.550
4.30	0.695
5.38	0.890
6.45	0.982
8.60	1.380

Table 5. Comparison of the Method

Ref.	Reagent	pH	λ_{max}	Molar absorptivity	Interference
1.	Isonitroso thiocamphor	5M HCl to pH 2.0	450	3.90×10^3	Cu*, Co*, Pt*, Hg and S_2O_3
3.	Phenothiazine and Promazine	Ethanol medium	551 and 450	3.542×10^3 and 9.213×10^3	Pt(IV), Au(III), Fe(III), Cu(II), Ag(I) and Hg(II)
4.	Sodium Ethyl-trithiocarbonate	1.0-10.0	370	1.277×10^4	Mn*(II), Zn*(II), Cd*(III), Fe*(III), Ni*(II), Co*(II) and Pt.
5.	Xanthates	10M HCl to pH 2.0, pH 1.7 and 2M HCl to pH 7.0	460 and 465	1.9×10^2 1.9×10^2 1.76×10^2 1.82×10^2 1.80×10^2	Fe*, Pb*, Bi(III), Au, Pt(IV), Os(VIII), S_2O_3, vanadate, molybdate, Ni*(II), Co*(II), Cu(II)
6.	2'-Hydroxy-4-methoxy-5'-methylchalkone-oxime	0.5 to 2.5	380	3.38×10^3	Be(III), Ru(III), ZrO(II), citrate, tartrate and EDTA
	Present method	3-4	420	1.725×10^4	Fe*(III), Pb*(II),

* masking agents used

Table 6. Reproducibility of the method

Palladium taken (μg)	Palladium found (μg)			Mean μg	Std. Dev. %
21.5	19.5	21.5	21.0	20.25	0.98
	20.0	20.5	19.0		
43.0	41.5	43.0	42.5	42.25	0.68
	41.5	42.0	43.0		
64.5	64.5	66.0	65.0	65.25	0.52
	65.5	65.0	65.5		
86.0	85.5	84.5	86.5	86.33	1.63
	88.5	88.0	85.0		

Table 7. Effects of diverse ions on the determination of 43 μg of palladium. Average of three determinations was taken in each case

Ion added	Amount tolerated μg	Ion added	Amount tolerated μg
Ascorbate	4000	Fe(III)*	400
Tartrate	4000	Cu(II)	200
Citrate	4000	Cr(III)	4000
Borate	4000	Tu(IV)	1000
Fluoride	4000	Zr(IV)	1000
Oxalate	4000	Mo(VI)	2000
EDTA	2000	Pb(II)*	400
Thiosulfate	200	Hg(II)	100
Thiocyanate	2000	Sn(II)	4000
Iodide	400	V(V)	4000
Phthalate	2000	Au(III)	4000
Arsenate	4000	Mg(II)	4000
Bromide	4000	Ag(I)	1000
Phosphate	4000	Cd(II)	4000
Nitrate	4000	Co(II)	4000
Zn(II)	4000	Sr(II)	4000
Ba(II)	4000	U(VI)	4000
Ni(II)	4000	Bi(III)	4000
		Pt(IV)	4000
		Rh(III)	4000

* in presence of fluoride

*In presence of excess acetate.

Table 8. Analysis of Synthetic Mixtures

No.	Composition with amount (in μg) of each constituent	Palladium found (μg)
1	Pd(43), Pt(200), Rh(200)	43.5, 44.0, 43.5
2	Pd(43), Fe(100)*, Cu(100)	43.5, 44.0, 44.0
3	Pd(43), Ni(200), Co(200)	43.5, 43.5, 43.0
4	Pd(43), Zn(200), Cd(200)	42.5, 44.0, 43.0
5	Pd(43), Mo(200), V(200)	43.0, 43.0, 43.5

* in presence of fluoride.

R E F E R E N C E S

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