CHAPTER III

4-Nitrosoresorcinol as an Analytical Reagent

General Discussion

4-Nitrosoresorcinol is a light yellow crystalline solid. Although it is unstable in solid state, its ethanolic solution is stable for weeks.

The colour of the reagent varies markedly with the pH of the solution : below pH 2.5 the colour is pale greenish-yellow, and this increases in intensity and finally becomes orange at about pH 5.6. An increase in the pH above 7.0 results in a slow decrease in intensity of colour.

A programme has been undertaken to develop methods for the spectrophotometric determinations of cobalt, palladium and copper with the reagent.

Section 1 : Extraction and Spectrophotometric Determination of Cobalt

EXPERIMENTAL

Apparatus and reagents :

Spectral curves and absorbance measurements were carried out with a Shimadzu PR1 model recording spectrophotometer, equipped with matched quartz cells of 10 mm optical path length.

pH values were measured with an ECL 5651 digital pH meter. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of cobalt(II) was prepared by dissolving 5.1 gm cobalt nitrate in 250 ml distilled water and was standarised by using a complexometric method with xylenol orange as indicator[8]. Solutions of lower concentrations were prepared by appropriate dilution.

All the chemicals used were of analytical grade. Chloroform (E. Merck), Pyridine (BDH), α-Picoline (Riedel), β-Picoline (BDH), γ-Picoline (Fluka) and 2,4,6 collidine (BDH) were distilled before use.

4-Nitrosoresorcinol was prepared[9] by mixing a solution of 33 gm of resorcinol in 90 ml of absolute alcohol with a solution of 24 gm of potassium hydroxide in a little absolute alcohol and treating in a freezing mixture with 39 gm of freshly prepared isoamyl nitrite. The solution was cooled for 3-4 hrs in ice. The separated potassium salt was washed with alcohol and ether. 50 gm of the salt was shaken with water to form a thin paste and then acidified with careful cooling with 100 gm of 25% sulphuric acid in which pieces of ice were floating. The light yellow crystalline solid, which was formed was filtered off and recrystallized from dilute alcohol. The reagent in solid state is unstable but its alcoholic solution is stable.

1% ethanolic solution of 4-nitrosoresorcinol was used for our routine work.

Buffer solutions of different pH were prepared by standard procedures. Sodium acetate - acetic acid buffer was used for our practical purpose.

Stock solutions of diverse ions were prepared from their nitrates, chlorides or sulphates in dilute acid or water. Sodium or ammonium salts were used in case of anions.

Determination of cobalt :

An aliquot containing upto 200 μg of cobalt(II) was mixed with 0.1 ml of 1% ethanolic solution of 4-nitrosoresorcinol following by the addition of 0.2 ml of Pyridine/α-Picoline/β-Picoline/γ Picoline or 2,4,6 collidine. Buffer solution (pH-6) was then added and volume of the aqueous phase was made up to 10 ml. The solution was then equilibriated with 10 ml of chloroform in a separating funnel for 30 sec. The two layers were allowed to settle. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. Finally the absorbance of the organic extract was measured at 395 nm against a cobalt free reagent blank. Amount of cobalt was determined from a previously prepared calibration curve. To test the effect of diverse ions, the respective foreign ion was added to the system before addition of the reagents.

RESULTS AND DISCUSSION

Absorption spectra :

The spectral curves of cobalt(II) complexes in chloroform are shown in fig.1. The complexes absorbs maximum at 395 nm. The reagent blank absorbs insignificantly in this region. Wave length of 395 nm was chosen for analytical measurements.

Calibration curve :

Different amount of cobalt were extracted following the general procedure. The absorbance measured showed a linear response over a concentration of 30 ppm of cobalt in all cases. The aqueous phases after each extraction were clear and colourless. The results are shown in table 1 and Fig.2.

Molar absorptivities of the complexes (on the basis of cobalt content) and Sandell's sensitivities were evaluated as shown in table 2.

Effect of 4-nitrosoresorcinol concentration :

The extraction behaviour of cobalt(II) complex have been examined by varying the 4-nitrosoresorcinol concentration maintaining the other variables constant. It has been found that 0.1 ml of 1% ethanolic solution of 4-nitrosoresorcinol along with 0.2 ml of Pyridine/substituted pyridines is sufficient to extract 177μg of cobalt in a single operation. Addition of excess reagent caused a high blank absorbance and was avoided.

Effect of pyridine bases concentration :

The extraction behaviour of cobalt(II) complexes in terms of absorbance have also been studied with different amounts of pyridine/α-picoline/β-picolineγ-picoline or 2,4,6 collidine keeping the 4-nitrosoresorcinol concentration fixed. To extract 177μg of cobalt(II) 0.2 ml of the respective pyridine bases has been found to be adequate.

Effect of pH :

Extractibility of cobalt(II) into chloroform was investigated in terms of absorbance of the mixed ligand complexes in the pH range 1-12. Maximum absorbance was obtained in the pH region 4-7 in all cases. In a second consequitive operation, the organic extract virtually showed no absorbance. In this pH range complete and quantitative extraction of the metal was achieved within 30 sec in a single extraction. Absorbance as a function of pH is shown in Fig.3.

Choice of solvent :

Apart from chloroform some other solvents were tested as extracting solvents but those offered no special advantages over chloroform.

Stability of colour :

The reaction between cobalt(II)-4-nitrosoresorcinol and pyridine bases were instantaneous. Time is not a critical factor in the determination of the metal. The absorbance of the chloroform extract were measured at different intervals of time. The colour of the cobalt complex was stable for at least 24 hours. The results are tabulated in table 3.

Interference :

In order to study the effect of diverse ions on the extraction behaviour, a definite amount of cobalt(II),was extracted and determined according to the general procedure in presence of the respective foreign ions. In practice all the bases i.e. pyridine, α-picoline, β -picoline, γ -picoline or 2,4,6 collidine showed similar behaviour in extracting cobalt. In the present investigation -picoline was used as the auxiliary ligand to study interferences. An ion was considered to interfere if the recovery of cobalt (II) differed by more than ± 3% from the actual amount taken. Average of three determination was taken.

177μg of cobalt could be determined without interference of the following ions : Cu(II), Cd(II), Hg(II), Zn(II), Ni(II), Pt(IV), Rh(IV), La(III), Mn(II), Ca(II), Ba(II), Sr(II), Be(II), Zn(IV), Al(III), Th(IV), Pb(II), Cr(II), U(VI), Mo(VI) and V(V). Interference due to iron (III) was avoided using ammonium bifluoride as the masking agent.

Among the anions tested the following did not interfere in the cobalt determination : thiocyanate, thiosulphate, EDTA, borate, phosphate, tartarate, citrate, fluoride, bromide, iodide, as corbate and phthalate. The results are shown in table 4.

Precision and accuracy :

Using β -picoline the precision and accuracy of the method were tested by analysing solutions containing a known amount of cobalt(II) following the recommended procedure. The results are shown in table 5. The proposed method is fairly precise and reproducible. The proposed method has also been compared with some other existing methods (Table 6).

Application:Analysis of synthetic mixtures :

In absence of real samples the proposed method (using β-picoline) was applied to the analysis of various synthetic mixtures containing 177 μg of cobalt. The results are shown in table 7.

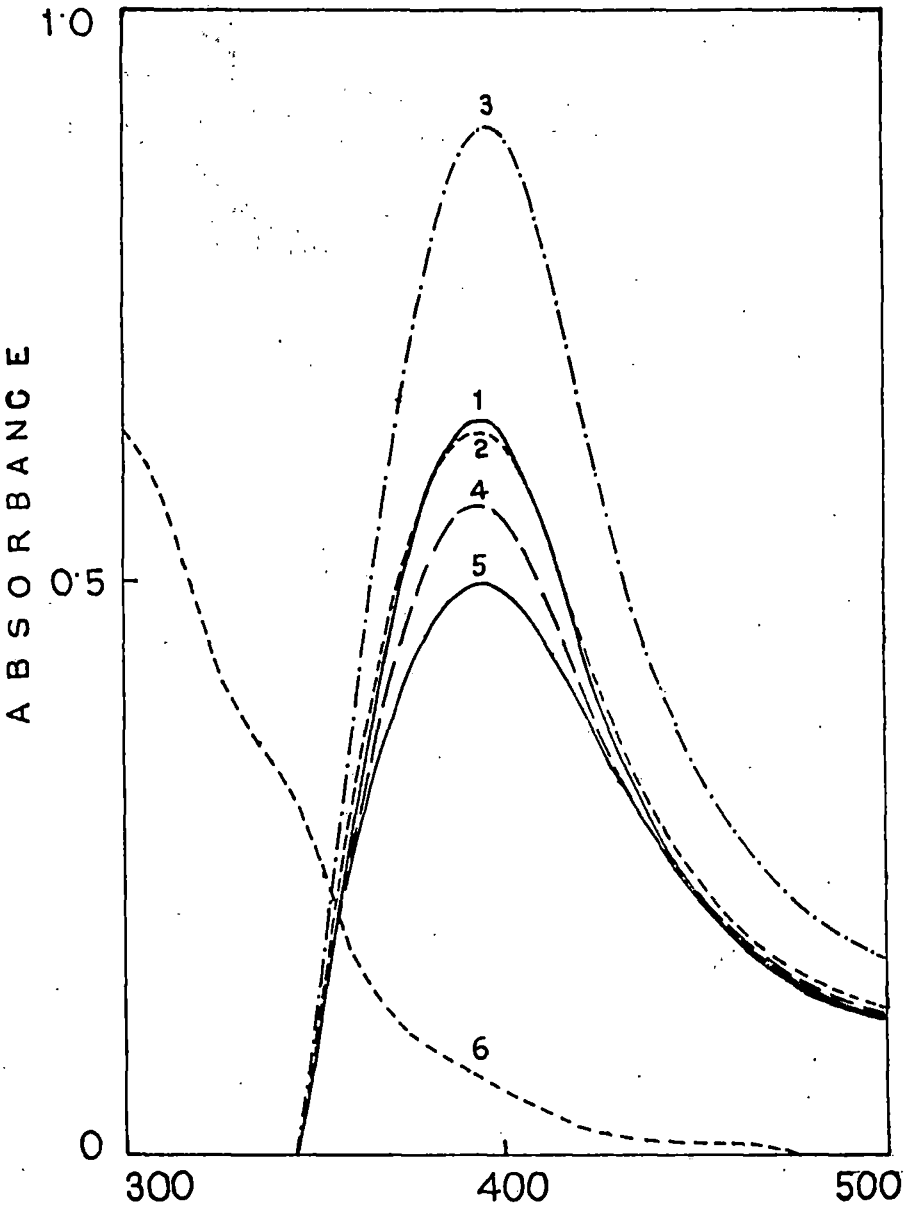

Fig-1. ABSORPTION SPECTRA OF COBALT COMPLEXES (17·7 ppm Co) AND REAGENT BLANK

(1) 4-NITROSORESORCINOL-PYRIDINE
(2) 4-NITROSORESORCINOL-α-PICOLINE
(3) 4-NITROSORESORCINOL-β-PICOLINE
(4) 4-NITROSORESORCINOL-γ-PICOLINE
(5) 4-NITROSORESORCINOL-2,4,6-COLLIDINE
(6) 4-NITROSORESORCINOL-PYRIDINE BLANK

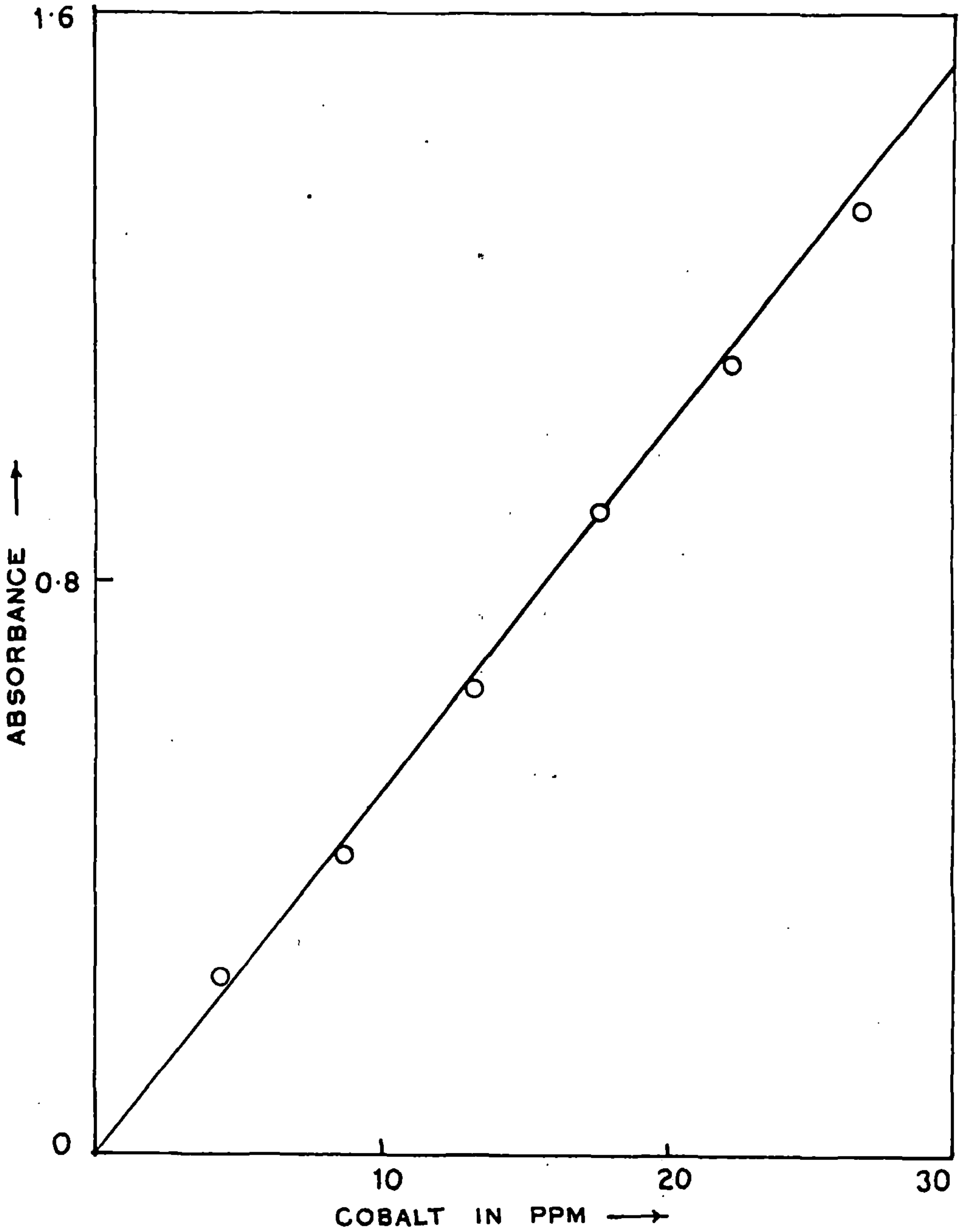

Fig-2 : BEER'S LAW (with β- picoline)

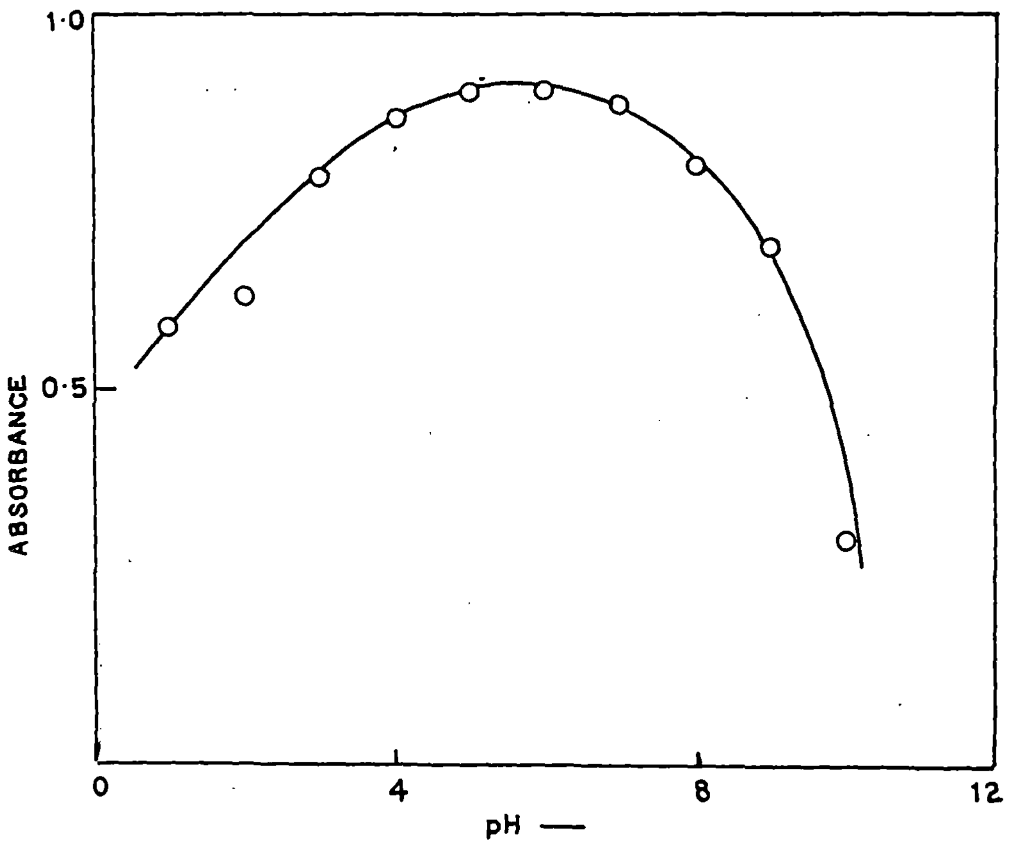

Fig-3- Absorbance as a function of pH. Co taken 177 μg.

Table 1 : Beer's law data
(with β-picoline)

Cobalt in ppm	Absorbance at 395 nm
4.42	0.250
8.45	0.422
13.27	0.650
17.70	0.898
22.12	1.110
26.55	1.330

Table 2 : Details of Extractive Methods

Parameter	Base employed				
	Pyridine	α-Picoline	β-Picoline	γ-picoline	2,4,6-collidine
pH	4-7	4-7	4-7	4-7	4-7
λ_{max}	395	395	395	395	395
Molar absorptivities ($l\ mol^{-1} cm^{-1}$)	2.12×10^3	2.09×10^3	2.99×10^3	1.89×10^3	1.65×10^3
Sandell's sensitivity $\mu g/cm^2$	0.027	0.028	0.019	0.031	0.035

Table 3 : Variation of absorbance with time (with β-picoline) Co taken - 177 μg

Time in hours after extraction	Absorbance at 395 nm
0.25	0.898
0.50	0.898
2.0	0.896
6.0	0.896
12.0	0.895
24.0	0.895

Table 4 : Effect of diverse ions (using β -picoline)
(Cobalt taken 177 μg)

Ion added	Amount tolerated (mg)	Cobalt found (μg)	Error %
Cu(II)	5.1	181.0	2.2
Cd(II)	4.9	177.5	0.3
Hg(II)	5.0	175.0	1.1
Zn(II)	6.0	177.0	0.0
Ni(II)	5.3	177.0	0.0
Pd(II)	5.0	180.0	1.7
Pt(IV)	3.9	179.0	1.1
Rh(III)	3.2	177.5	0.3
La(III)	2.0	174.0	1.7
Mn(II)	5.2	176.0	0.5
Ca(II)	6.0	176.6	0.2
Ba(II)	5.9	178.0	0.5
Sr(II)	5.7	177.0	0.0
Be(II)	5.1	175.4	0.9
Zr(IV)	0.1	173.0	2.2
Al(III)	0.2	173.5	2.2
Th(IV)	0.4	173.5	1.9
Pb(II)	0.5	174.0	1.7
Cr(III)	0.3	174.0	1.7
U(VI)	0.2	173.5	1.9

contd ...

Table 4 contd ...

Mo(VI)	20.0	181.0	2.0
Fe(III)*	1.5	180.0	1.7
V(V)	20.0	180.0	1.7
Thiocyanate	15.0	179.0	1.1
Thiosulphate	7.0	176.0	0.5
EDTA	0.1	173.0	2.2
Borate	20.0	179.0	1.1
Phosphate	0.1	173.0	2.2
Tartarate	20.0	177.0	0.0
Citrate	0.5	176.6	0.2
Fluoride	20.0	177.6	0.0
Bromide	20.0	177.5	0.3
Iodide	11.0	178.5	0.8
Ascorbate	20.0	178.0	0.5
Phthalate	20.0	177.5	0.3

*In presence of NH_4HF_2

Table 5 : Reproducibility of cobalt recovery (using β-Picoline)

Cobalt taken μg	Cobalt found (μg)			Mean μg	Std. deviation
	87.5,	87.0,	89.2		
88.5				88.45	1.13
	90.0,	88.0,	89.0		
	175.5,	176.0,	179.4		
177.0				177.06	1.49
	177.5,	178.0,	176.0		
	263.5,	264.0,	266.5		
265.5				265.0	1.45
	265.0,	267.0,	264.0		

Table 6 : Comparison

Reagent	λ max (nm)	molar absorptivity l mol^{-1}cm^{-1}	Sensitivity μg/cm^2	Ref.
1,6-Hexanediamine-N,N,N′,N′-tetra acetic acid	550	137	0.4301	1
NaOCN and 2,3,5 triphenyl tetrazolium chloride	631	1.08 x 10^3	-	2
Triphenyl tetrazolium cation and tetrathiocyanate cobaltate	620	3.2 x 10^3	-	3
5-Methoxy-2-nitrosophenol	540	5.5 x 10^5	0.0107	4
Potassium propyl xanthate	480	-	0.09	5
	620	-	0.14	
2-Thio ortic acid and Et_3N	-	1.158 x 10^3	0.051	6
Tetrathiocyanato cobaltate(II) and neotetrazolium chloride	-	-	0.02	7
Present method	395	2.99 x 10^3	0.019	

Table 7 : Determination of cobalt (177 μg) in various mixtures with 500 g of each ion added. (Auxiliary ligand used β-Picoline)

Ion added	Cobalt found μg
1. Cu^{+2}, Ni^{+2}, Fe^{+3}*	175.5
2. Mn^{+2}, Cu^{+2}, Fe^{+3}*	174.5
3. Cr^{+3}, Mn^{+2}, Zn^{+2}	176.5
4. Cu^{+2}, Cd^{+2}, Pb^{+2}	180.5
5. Cu^{+2}, Cd^{+2}, Mg^{+2}	178.5

*Plus NH_4HF_2 (2 mg).

Section 2 : Extraction and Spectrophotometric Determination of Palladium

EXPERIMENTAL

Apparatus and Reagents :

Spectral curves and absorbance measurements were carried out with a Shimadzu PR-1 model recording spectrophotometer, provided with optically matched quartz cells of 10 mm path length. pH values were measured with an ECL 5651 digital pH meter. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of palladium(II) was prepared by dissolving 1 gm palladium chloride (Johnson & Mathey) in 1 ml of HCl and diluted to 250 ml with distilled water followed by standarisation with dimethylglyoxime[21]. Working solution (210.5 μg Pd/ml) was prepared by dilution. Solutions of lower concentrations were prepared by appropriate dilution.

All the chemicals used were of analytical grade. Chloroform (E.Merck), Pyridine (BDH), α-Picoline (Riedel), β-Picoline (BDH), γ-Picoline (Fluka) and 2,4,6 collidine (BDH) were distilled before use.

4-Nitrosoresorcinol was prepared as described earlier. 1% Ethanolic solution of the reagent was used for our investigation.

Buffer solutions of different pH were prepared by standard procedures. Standard solutions of diverse ions were prepared from their corresponding salts to study interferences.

Determination of palladium :

An aliquot containing upto 100 μg of palladium was mixed with 0.2 ml of 1% ethanolic solution of 4-nitrosoresorcinol followed by addition of 0.5 ml of pyridine/α-Picoline/β -Picoline/ γ-Picoline or 2,4,6 collidine. The pH of the solution was adjusted to 2.0 with KCl-HCl buffer. The volume of the aqueous phase was maintained at 10 ml. The solution was then equilibriated with 10 ml of chloroform in a separating funnel for 1 min. The two layers were allowed to settle. The separated organic layer was shaken with anhydrous sodium sulphate to remove any moisture. Finally the absorbance of the organic extract was measured at the corresponding absorption maxima (Table 2) against a palladium free reagent blank. The amount of palladium(II) was determined from a previously prepared calibration curve.

RESULTS AND DISCUSSION

Absorption spectra :

The spectra of the mixed-ligand complexes were scanned in the wave-length region 300-600 nm against the corresponding reagent blanks. The Pd(II)-complexes showed absorption maxima at 395-400 nm. As the reagent blanks showed some absorbances in the aforesaid wave-length region, all the analytical measurements were carried out against the respective blanks. Fig.1 shows the spectra of Pd(II) -4-nitrosoresorcinol-γ-picoline and the corresponding blank. The pattern of the spectra of other Pd-complexes extracted in presence of pyridine and other substituted pyridine bases remains the same.

Calibration curve :

Different amounts of palladium have been extracted following the general procedure at pH-2 and the absorbance were measured. The system conforms to Beer's law in each case. In each case the aqueous phase after extraction was clear and colourless. Furthermore the aqueous phase as tested by an independent method was void of palladium. The results are shown in table 1 and Fig.2.

The molar absorptivities of the complexes and Sandell's sensitivities (on the basis of palladium content) are calculated as seen from table 2.

Effect of 4-nitrosoresorcinol concentration :

The extent of absorbance has been examined with different amount of 4-nitrosoresorcinol, keeping all other variables constant. It has been found that 0.2 ml of 1% ethanolic solution of 4-nitrosoresorcinol along with 0.5 ml of pyridine/α-picoline/β-picoline/γ-picoline or 2,4,6 -collidine is sufficient to extract upto 100 μg of Pd(II) in a single operation. The higher concentration of reagent had no adverse effects on the absorbance but was avoided.

Effect of Pyridine bases concentration :

The extraction behaviour of palladium(II) in terms of absorbance has also been studied with different amounts of pyridine, α -picoline, β -picoline, γ-picoline, and 2,4,6-collidine maintaining rest of the variables fixed. It was observed that 0.5 ml of pyridine, α-picoline, β -picoline, γ-picoline or 2,4,6-collidine along with 0.2 ml (1%) of ethanolic solution of 4-nitrosoresorcinol is sufficient to extract upto 100 μg of Palladium(II).

Effect of acidity :

The extraction of palladium complexes was investigated in terms of absorbance in the pH range 0-11. A steady and maximum absorbance was obtained when the extractions were carried out in the pH range 1-8. When the extraction was repeated with the same aqueous phase, the organic extract virtually showed no absorbance. The aqueous phase, after extraction, was also tested for palladium by an independent method. This indicated a complete and quantitative extraction of palladium in this pH range. Extraction of palladium as a function of acidity has been shown in Fig.3.

Apart from chloroform some other solvents were tested as extracting solvents but those offered no special advantages over chloroform.

Stability of colour :

The reaction between palladium(II) 4-nitrosoresorcinol and pyridine bases were instaneous. The absorbance of the chloroform extracts were stable for at least 6 hours as seen from Table 3.

Interference :

In order to study the effect of diverse ions on the extraction behaviour, palladium was determined according to the recommended procedure (using γ-Picoline) in presence of the respective foreign ion. Extraction pH was set at 2 with KCL-HCl buffer. Deviation of not more than ± 3% from the recovery of palladium was taken as the standard tolerence limit. In practice all the pyridine bases i.e., pyridine/α-picoline/β-picoline/γ-picoline or 2,4,6 -collidine showed similar behaviour. Palladium(II) (84.2 μg).could be determined without interference in presence of the followings : Ni(II), Cd(II), Hg(II), Zn(II), V(V), Pt(IV), Rh(IV), Mn(II), Be(II), Mo(VI), Zr(IV), U(VI), La(III), Al(III), Tl(I), Pb(II) and Cr(III). Fe(III) and Cu(II) could be tolerated in presence of ammoniumbifluoride and citrate respectively. High results were obtained in presence of cobalt(II).

Among the anions tested, the system tolerated the followings : borate, phosphate, bromide, iodide, phthalate, acetate, tartarate, citrate, fluoride, ascorbate, oxalate, EDTA, chloride, nitrate and sulphate. Thiocyanate and thiosulphate interfere seriously. The results are presented in table 4.

Precision and accuracy :

With γ-Picoline the precision and accuracy of the proposed method were tested by analysing solutions containing a known amount of palladium(II) following the recommended procedure (Table 5). The proposed method is fairly precise reproducible. The total operation for each run requires hardly 10-15 min. The method has been compared to some other existing methods (Table 6).

Application:Analysis of synthetic mixtures :

In absence of real samples the method has been applied to a number of synthetic mixture to estimate palladium (Table 7).

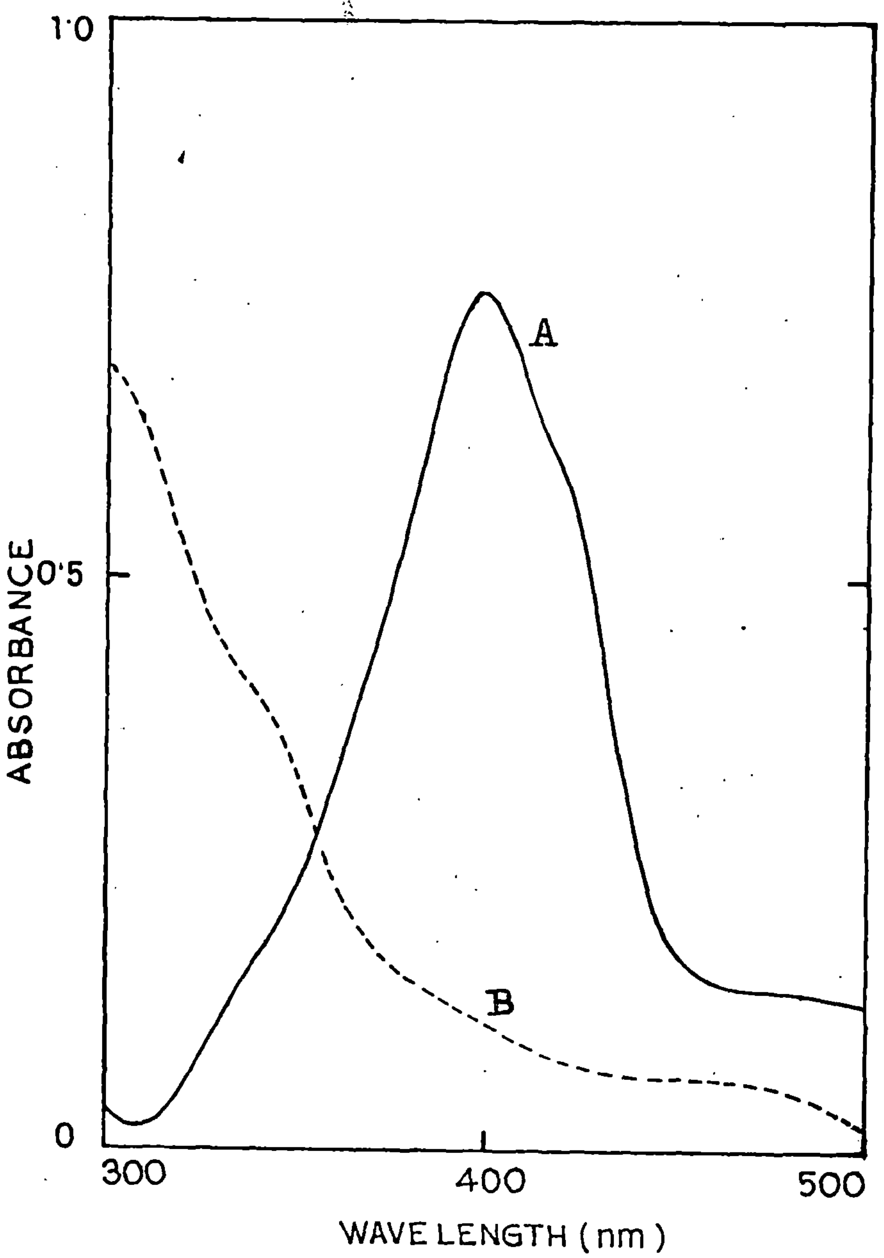

Fig. 1. Absorbanc spectra of (A) Pd(II)-4-nitrosoresorcinol-γ-picoline complex (4·2 ppm Pd) and (B) Reagent blank.

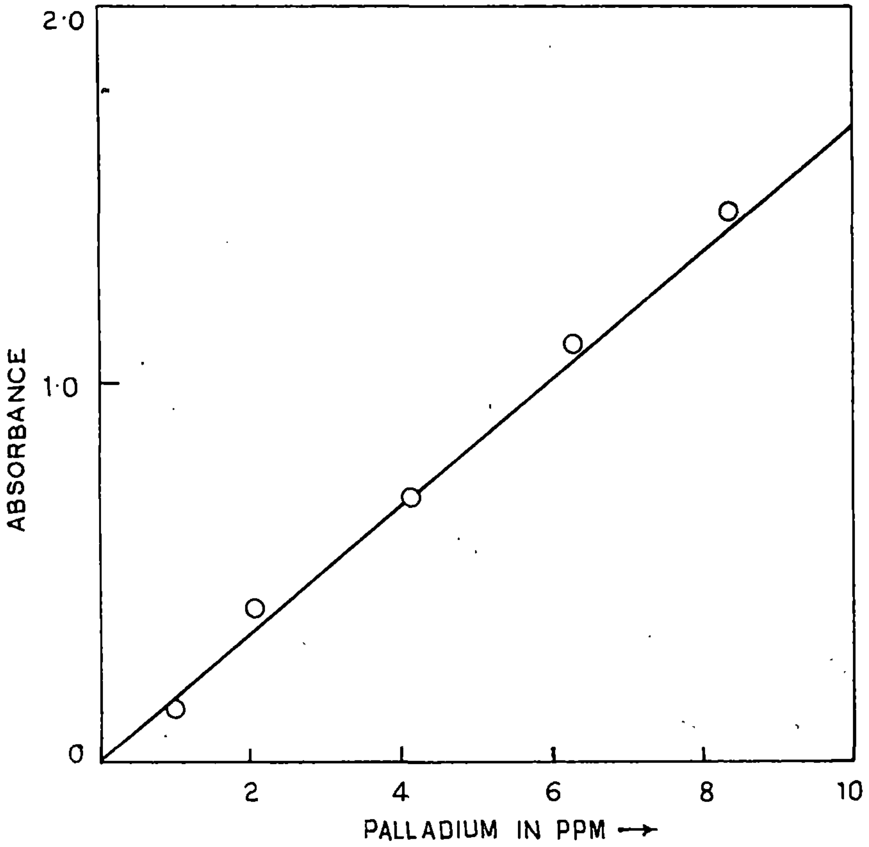

Fig- 2. BEER'S LAW (with γ- picoline)

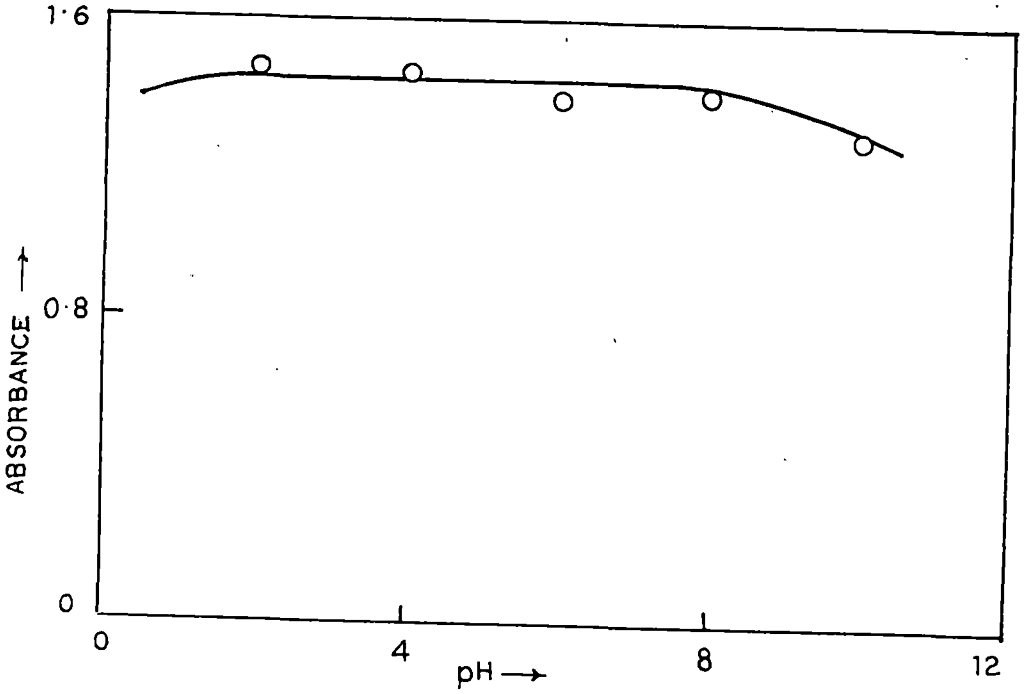

Fig-3: ABSORBANCE AS A FUNCTION OF pH. Pd taken 84·2 μg (with γ- picoline).

Table 1 : Beer's law data
(with γ-picoline)

Palladium in ppm	Absorbance at 395 nm
1.05	0.148
2.1	0.400
4.2	0.690
6.3	1.110
8.4	1.486

Table 2 : Details of Extractive Methods

Parameter	Base employed				
	Pyridine	α-Picoline	β-picoline	γ-picoline	2,4,6-collidine
λ max	395	400	395	395	400, 410*
Molar absorp-tivity ($l\ mol^{-1} cm^{-1}$)	3.28×10^4	2.68×10^4	3.44×10^4	3.52×10^4	3.47×10^4
Sandell's sensitivity ($\mu g/cm^2$)	0.0032	0.0039	0.0030	0.0029	0.0031

*shoulder

Table 3 : Variation of absorbance with time
(Palladium taken 84.2 μg, base used - γ-Picoline)

Time in hours after extraction	Absorbance at 395 nm
0.25	1.486
0.5	1.486
2.0	1.480
4.0	1.482
6.0	1.480

Table 4 : Effect of diversions on determination of 84.2 μg of palladium (using γ-Picoline). Extraction pH-2.0

Ion added	Amount tolerated (mg)	Palladium found μg	Error %
Ni(II)	4.5	83.5	0.8
Cd(II)	4.5	83.0	1.4
Hg(II)	4.0	84.0	0.2
Zn(II)	5.0	85.5	1.5
V(V)	5.0	83.6	0.7
Pt(IV)	3.0	86.0	2.1
Rh(II)	2.5	86.0	2.1
Mn(II)	4.5	82.5	2.7
Be(II)	5.0	82.5	2.7
Mo(VI)	3.0	83.0	1.4
Zr(IV)	2.0	85.5	1.5
U(VI)	2.0	86.0	2.1
La(III)	2.5	84.0	0.2
Al(III)	2.5	84.5	0.3
Tl(I)	2.0	85.6	1.6
Pb(II)	2.5	85.0	1.0
Cr(III)	2.5	84.6	0.5
Fe(III)[1]	1.0	86.0	2.1
Cu(II)[2]	1.0	86.0	2.8
Co(II)	nil	-	-

contd ...

Table 4 contd ...

Borate	8.5	84.5	0.5
Phosphate	8.0	85.5	1.5
Bromide	10.0	84.2	0.0
Iodide	10.0	84.0	0.2
Phthalate	10.0	84.6	0.5
Acetate	10.0	84.0	0.2
Tartarate	10.0	85.2	1.2
Citrate	10.0	84.6	0.5
Fluoride	10.0	84.6	0.5
Ascorbate	10.0	83.6	0.70
Oxalate	10.0	84.8	0.70
EDTA	2.0	83.4	1.0
Chloride	10.0	84.6	0.5
Nitrate	10.0	85.6	1.6
Sulphate	10.0	84.2	0.0

1. in presence of NH_4HF_2
2. in presence of citrate

Table 5 : Reproducibility of palladium recovery

Palladium taken µg	Palladium found µg			Mean µg	Std deviation %
	20.5,	20.5,	20.0		
21.05				20.21	0.46
	19.5,	20.0,	20.8		
	43.5,	41.5,	42.0		
42.1				42.21	0.78
	42.8,	42.0,	41.5		
	83.5,	83.0,	83.0		
84.2				83.50	0.63
	84.0,	84.5,	83.0		

Table 6 : Comparison

Reagent	λ_{max} (nm)	molar absorptivity $l\ mol^{-1}cm^{-1}$	Sensitivity $\mu g/cm^2$	Ref.
1. 2-thiobarbutric acid	374 in water	1.0×10^4	0.0106	10
	386 in EtOH	7.5×10^3	0.0141	
2. 3-bromo-2-hydroxy-5-methyl acetophenone hydrazone	400	4.5×10^3	0.0235	11
3. 2,2 dipyridyl -2-quinolyl hydrazone	570	14.00×10^3	0.0076	12
4. Xanthates	-	$(1.76\text{-}1.9) \times 10^2$	0.5-0.65	13
5. N-Napthyl-N′ -pyridyl thiourea	390	3.4×10^4	0.0096	14
6. Phenanthraquinone monothiosemicarbazone	590	-	0.025	15
	540	-	0.0083	
7. n-Butylxanthate	385	1.32×10^4	0.008	16
8. N-Marcapto acetamide	320	1.85×10^4	0.016	17

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Table 6 contd ...

9.	2-Hydroxy 3,5-dimethyl acetophenone oxime	400	1.08×10^3	0.10	18
10.	Potassium iodide and substituted pyridines	354-360	$(1.6-1.9) \times 10^4$	0.1-0.018	19
11.	Present method	395-400	$(2.6-3.5) \times 10^4$	0.003-0.004	20

Table 7 : Estimation of palladium (84.2 µg) in various synthetic mixtures with 200 µg of each ion added (average of three determinations)

Ions added		Palladium found (µg)
1.	Pd, Pt, Rh, Ni	84.0
2.	Pd, Pt, Ni, Mn	83.5
3.	Pd, Rh, Ni, Mn	84.6
4.	Pd, Fe, V, Mo[1]	86.0
5.	Pd, Cu, V, Mo[2]	86.6

[1] in presence of NH_4HF_2

[2] in presence of citrate.

Section 3 : Extraction and Spectrophotometric Determination of Copper

INTRODUCTION

Numerous methods have been suggested for the separation and determination of copper by liquid-liquid extraction. The principal method used for such extraction procedures involved the utilization of various organic reagents like β-diketone, monoxime, dioxime, nitrosophenol, dithizone, dithiocarbamate and other miscellaneous reagents as the chelating agents, followed by photometric determination of the metal. The ion-association system involved the utilization of thiocyanate, halide, phenanthroline and other organic reagents.

The extraction of copper by diethyl dithiocarbamate[22] was investigated at pH 8.5. The absorbance of the complex was measured at 560 nm in butyl acetate. Other well known method involves the utilization of neo-cuproin[23] and biscyclohexanone oxalyldihydrazone[24] for the determination of copper.

The reaction of copper with pyridine and thiocyanate has been investigated. The greenish-white precipitate, soluble in chloroform, carbontetrachloride and ether, gives an intense blue colour[25].

Hy, Tse-Te and Kao, Fa-Kuei[26] used 2-[(5-bromo-2 pyridyl) azo]-5-(diethylamino) phenol for the spectrophotometric determination of copper. The 1:1 (metal:ligand) complex was extracted into chloroform and the absorbance was measured at 550 nm. Gonzaley et al[27] determined copper (II) spectrophotometrically at 680 nm as its 1:2 (metal: ligand) complex with mucic acid at pH 10.0.

Reddy T et al[28] determined copper(II) by making use of 2-hydroxy acetophenone oxime. The complex was extractable into iso-Bu CoMe at pH 5.5. The absorbance of the organic layer was measured at 355 nm. Copper(II) was determined spectrophotometrically using mono ethyl ester of n-butyl -amino-o-hydroxy benzyl phosphonic acid[29]. The 1:1 green complex was soluble in methyl alcohol and the absorbance of the complex was measured at 400 nm.

More recently, procedures based on the formation of copper complexes with bis (4-hydroxypent-2-ylidine) diaminoethane[30], 6-(2-quinolylazo)-3,4 dimethylphenol[31], di-2-Pyridylglyoxal-2-quinolylhydrazone[32], 1-phenyl-3 thio benzyoylthio carbamide[33], ammonium (2-amino-3-hydroxy-4-pyridylazo) benzene-4-arsonate[34], citric acid or EDTA[35], biacetylmonoquinolyl hydrazone[36], 2,2′-dipyridyl-2-pyridyl hydrazone[37], m-xylene diamine-N,N,N′,N′-tetracetic acid[38], 3,5-dibromo salicyl aldehyde-4-phenyl-3-thiosemicarbazone[39], 4-methyl tetrahydrobenzofurano (6,7-6) coumarin[40], ethylene diamine tetramethylene phosphonic acid[41], 2-(2-furanyl methylene hydrazine carbothioamide) and 2-(diphenylmethylene) hydrazine carbothioamide[42] N-(o-carboxyphenyl)-N′-(P -sulfophenyl-)-c-phenyl formazin[43], 2-methyl-1,3-cyclohexane-dione bis (4-phenyl-3-thiosemicarbazone)[44], Isonitrosothio-camphor[45] have been investigated for the spectrophotometric determination of copper.

Xia, Daopei and Lin, Qingxiong[46] determined copper(I) spectrophotometrically by using 2-(5 bromo-2-Pyridylazo) -5-(diethylamino) phenol and sodium luryl sulphate. The complex exhibits maximum absorbance at 545 nm in the pH range 4.0-7.0. Copper(II) was determined spectrophotometrically by using 2-(-pyridyl)-thioquinalidinamide[47]. The blue-violet chelate was formed over a wide pH range (0.5-6.5). The metal-ligand ratio was found to be 1:3.

Shrivastava, Madhulika and Pandey G.S[48] determined copper spectrophotometrically by using 2-thioortic acid.

The 1:1 complex shows its absorption maximum at 410 nm over the pH range 11.3-11.8. Copper(II) was extracted at pH 4.5 with 3-methoxy salicyl aldoxime[49] into chloroform and was spectrophotometrically determined. The complex absorbs maximum at 360 nm.

Evtimova, B[50] determined copper(II) with chrome azurols and cutionic surfactants. An ion-association complex of copper(II) with alizarin complexon and aldogen[51] has been studied spectrophotometrically. The complex was extractable into tolerence. Another ion-association system for copper involves the utilization of benzyltrimethylammonium chloride in presence of thiocyanate[52]. The complex was extractable into 1,2 dichloroethane and shows its maximum absorbance at 470 nm.

Thokdar T.K[53] et al determined copper(II) by using mixed ligand complex formulation with pyridine, α-Picoline, β -Picoline, γ-Picoline or 2,4,6-collidine in presence of bromide/iodide.

Copper was determined spectrophotometrically after absorption of its tetrahydrofarfuryl xanthate[54] on microcrystalline napthalene at pH 4.0-10.0. The complex absorbs maximum at 430 nm. Xu, Manyi[55] et al determined copper(II) spectrophotometrically by using α, β, γ, δ tetra (4-Pyridyl) -Porphyrin. The 1:1 complex absorbs maximum at 418 nm.

EXPERIMENTAL

Apparatus and Reagents :

A Shimadzu PR1 model recording spectrophotometer with matched quartz cells of 10 mm optical path length was used for the absorbance measurements. All the pH measurements were carried out with ECL 5651 digital pH meter. Separating funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of Copper(II) was prepared from $CuSO_4.5H_2O$ in distilled water containing few drops of sulphuric acid and was standarised[21]. Test solutions were prepared by appropriate dilution of the stock.

All the chemicals used were of analytical grade. Chloroform (E.Merck), Pyridine (B.D.H), α-Picoline (Riedel) β-Picoline (BDH) γ-Picoline (Fluka) and 2,4,6-collidine (BDH) were distilled before use.

4-Nitrosoresorcinol was prepared in the laboratory as before and its ethanolic solution (1%) was used. Buffer solution of different pH were prepared by standard procedures. Standard solution of diverse ions were prepared from their corresponding salts to study interference.

Determination of copper :

An aliquot containing upto 100 μg of Cu(II) was mixed with 1% ethanolic solution (0.2 ml) of 4-nitroresorcinol followed by addition of pyridine/α-picoline/β-picoline/γ-picoline or 2,4,6-collidine (0.5 ml). Buffer solution (pH-2) was then added and volume of the aqueous phase was made upto 10 ml. The solution was then equilibriated with chloroform (10 ml) in a separating funnel. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. Finally, the absorbance of the organic extract was measured at the corresponding absorption maxima against a copper free reagent blank and the amount of copper was determined from a previously prepared calibration curve.

To test the effect of diverse ions, the respective foreign ions were added to the system before addition of the reagents.

RESULTS AND DISCUSSION

Absorption spectra :

The spectra of the mixed ligand complexes were recorded in the wave length region 300-600 nm against the corresponding blanks. The copper complexes showed absorption maxima at 365-375 nm. The reagent blank absorbs insignificantly in the aforesaid wavelength region. The absorption spectra of Cu(II)-4 nitrosoresorcinol- γ-picoline complex and the reagent blank are cited in Fig.1. The pattern of the spectra of other Cu-complexes are similar in nature.

Beer's law :

Different amounts of Copper(II) were extracted as described in the general procedure. In all the cases Beer's law was found to be valid over the concentration of 10 ppm of Copper. The results are shown in table 1 and Fig.2. The molar absorptivities of the complexes (on the basis of copper content) and Sandell's sensitivities were evaluated as seen from table 2.

Effect of Reagent Concentration :

While studying the extraction behaviour of copper in terms of absorbance by varying the amount of 4-nitroresorcinol and the pyridine bases, the optimum concentration of the reagents have been ascertained. It has been found that 0.2 ml of 1% ethanolic solution of 4-nitroresorcinol along with pyridine/α-Picoline/β-Picoline/γ Picoline or 2,4,6 -collidine (0.5 ml) was sufficient to extract upto 100 μg of copper quantitatively. Use of excess pyridine bases resulted incomplete recovery of copper. In presence of higher concentration of 4-nitrosoresorcinol, the absorbance of the blank goes high.

Effect of acidity :

The optimum pH for extraction of copper was ascertained by extracting the mixed-ligand complexes in the pH range 1-11. In all cases maximum absorbance was attained at pH 1.5-2.5. In a second consecutive operation within this pH range, the organic extract virtually showed no absorbance. This indicated quantitative extraction of copper in this condition. Absorbance as a function of pH has been shown in Fig.3.

Stability of colour :

Absorbance of the chloroform extract obtained after the recommended procedure was measured at different intervals of time. In each case the chloroform extracts showed a steady absorbance for at least 24 hrs. So it was convenient to measure the absorbance of the organic extract within 24 hrs after the extraction. Experimental results are shown in the table 3.

Choice of solvents :

Apart from chloroform some other solvent were tested as extracting solvent but those offered no special advantages over chloroform.

Effect of diverse ions :

In order to study the effect of diverse ions on the extraction behaviour, copper(II) was extracted and determined according to the general procedure in presence of the desired foreign ions. Average of three determinations was taken in each case. Deviation of not more than ± 3% from the recovery of copper was taken as the standard tolerence limit for the respective foreign ion. In practice all pyridine bases i.e. Pyridine/α-Picoline/β-Picoline/γ-Picoline or 2,4,6-collidine showed similar behaviour regarding interferences.

Copper(II) (48μg) could be determined without interference in presence of Ni(II), V(V), Pt(IV), Rh(III), Ca(II), Zn(II), Mo(IV), U(VI), La(III), Al(III), Th(IV), Be(II), Mn(II), Ba(II), and Sr(II). High results are obtained in presence of cobalt and palladium. Mercury interfers seriously. Presence of iron and zirconium showed low recovery of copper.

Among the anions tested the followings did not interfere in the determination of copper : borate, phosphate, bromide, phthalate, iodide and acetate. Thiocyanate, thiosulphate, EDTA, oxalate, tartarate, citrate, fluoride, ascorbate interfered. The results are shown in table 4.

Precision and accuracy :

Using γ-picoline the precision and accuracy of the proposed method were tested by analysing solutions containing a known amount of Copper(II) following the recommended procedure. The results are shown in table 5. The method is fairely precise and reproducible. The total operation for each run requires hardly 10-15 min. The proposed method has also been compared with some other existing method as seen from table 6.

Analysis of synthetic mixtures :

In absence of real samples the method has been applied to a number of synthetic mixtures to estimate copper and the results are shown in table 7.

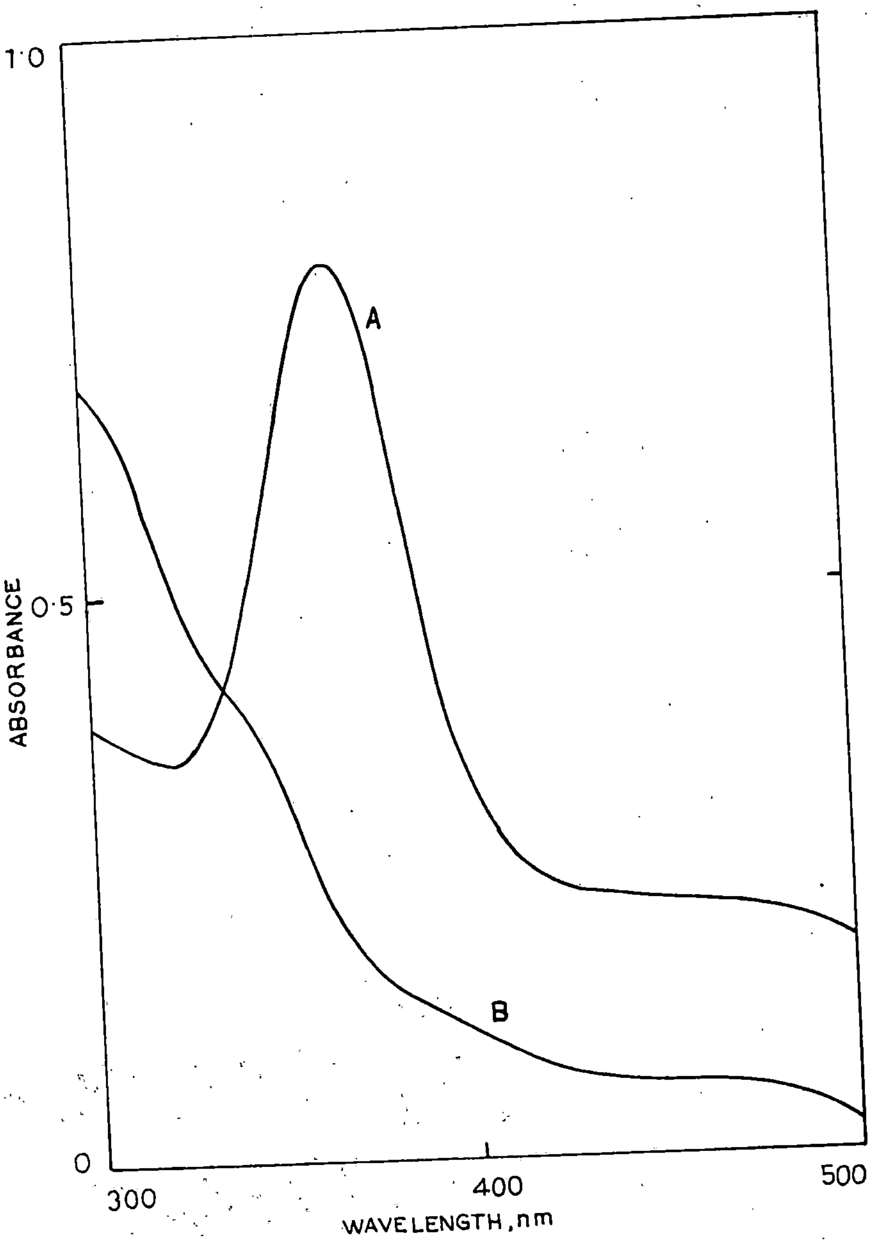

Fig. 1. Absorbance spectra of (A) Cu(II)-4-Nitrosoresorcinol-γ-picoline complex (4·8 ppm Cu) and (B) Reagent blank.

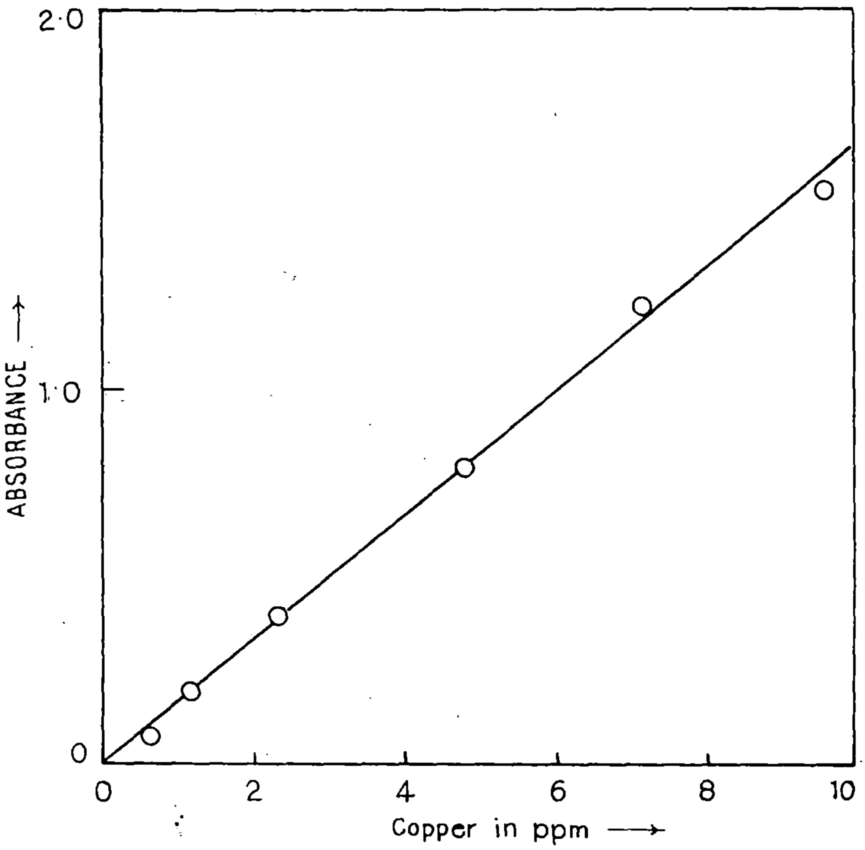

Fig 2: BEER'S LAW (WITH δ - PICOLINE)

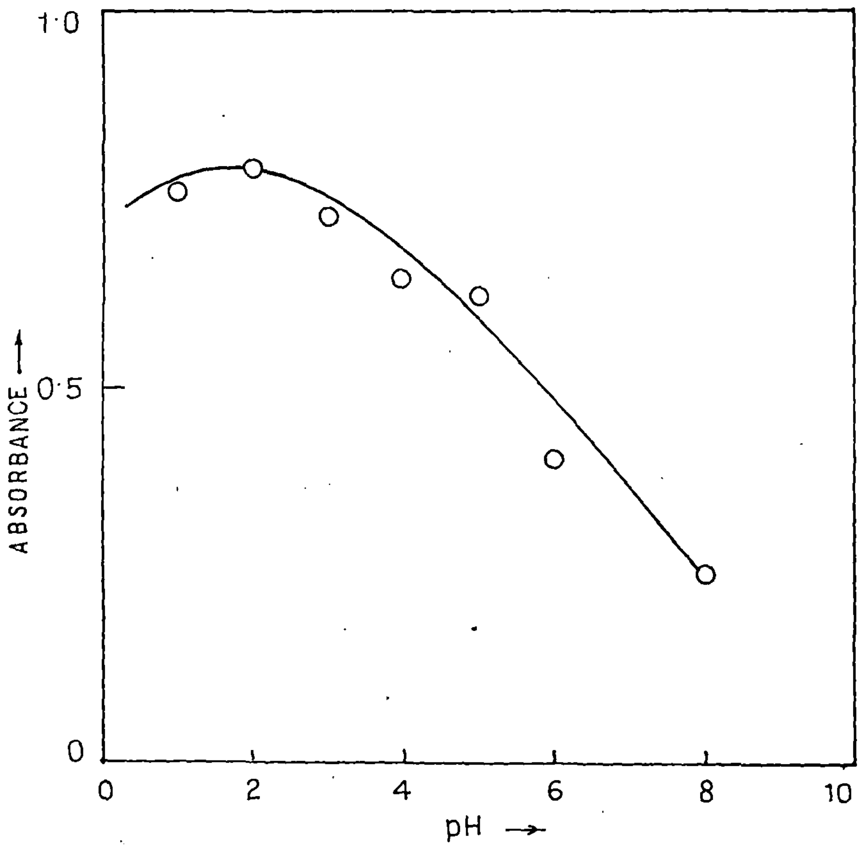

Fig-3: ABSORBANCE AS A FUNCTION OF pH (Cu taken 48 μg)

Table 1 : Beer's law data (with γ-Picoline)

Copper in ppm	Absorbance at 370 nm
0.6	0.080
1.2	0.190
2.4	0.405
4.8	0.800
7.2	1.205
9.6	1.520

Table 2 : Details of extractive methods

Parameters	Base employed				
	Pyridine	α-Picoline	β-Picoline	γ-Picoline	2,4,6-collidine
Extraction pH	1.5 - 2.5	1.5 - 2.5	1.5 - 2.5	1.5 - 2.5	1.5 - 2.5
λ max (nm)	365	375	370	370	365
Molar absorptivity (1 $mol^{-1} cm^{-1}$)	0.71×10^4	0.45×10^4	0.89×10^4	1.06×10^4	0.21×10^4
Sandell's sensitivity $\mu g/cm^2$	0.009	0.014	0.007	0.006	0.030

Table 3 : Variation of absorbance with time (with γ-Picoline)
(Copper(II) taken 48 μg)

Time in hours	Absorbance at 370 nm
0.25	0.800
0.5	0.804
4	0.802
12	0.804
24	0.800

Table 4 : Effect of diverse ions

Copper(II) taken 48 μg. Extraction pH-2. (using γ-picoline)

Ion added	Amount tolerated (mg)	Copper found (μg)	Error %
Ni(II)	3.5	49.0	2.1
V(V)	2.5	48.5	1.0
Pt(IV)	2.0	49.2	2.5
Rh(III)	2.0	46.5	3.1
Cu(II)	4.0	48.0	0

Contd ...

Table 4 contd ...

Ba(II)	4.0	47.5	1.0
Sr(II)	4.0	47.5	1.0
Cd(II)	1.0	49.0	2.1
Zn(II)	1.5	47.2	1.6
Mo(VI)	1.5	49.2	2.5
U(VI)	1.5	49.0	2.1
La(III)	2.0	47.5	1.0
Al(III)	2.0	47.0	2.0
Th(IV)	2.5	47.5	2.0
Be(II)	2.5	48.5	1.0
Mn(II)	2.0	48.0	0
Co(II)	nil	-	-
Pd(II)	nil	-	-
borate	6.0	49.0	2.1
Phosphate	6.0	48.5	1.0
Bromide	6.0	48.8	1.6
Phthalate	6.0	49.0	2.1
Iodide	6.0	47.5	1.0
Acetate	6.0	47.8	0.4

Table 5 : Reproducibility of copper(II) recovery

Copper taken (μg)	Copper found (μg)	Mean (μg)	Std. deviation %
24.0	24.8, 25.6, 23.2 24.0, 25.9, 25.5	24.35	0.93
48.0	48.0, 47.0, 48.5 50.0, 49.5, 46.5	48.25	1.37
72.0	73.5, 72.8, 70.8 71.0, 72.0, 72.8	72.15	1.07

Table 6 : Comparison

Reagent	λ max nm	molar absorptivity l mol^{-1}cm^{-1}	Sensitivity μg/cm^2	Ref.
2-Hydroxy acetophenone oxime	355	3.4×10^3	0.018	28
Bis (4-hydroxy pent-2-ylidene) diamino ethane	540	1.36×10^3	-	30
Tetraphenylarsonium or tetraphenyl phosphonium thiocyanate cuprate	465	2.8×10^3	-	56
1-P-chloroanilino -3-methyl cyclohexane -1-carbolylic acid	445	1.45×10^3	0.0438	57
2-thio ortic acid	410	1.17×10^3	0.0543	58
N-(α-Pyridyl)-2-thioquinaldinamide	520	5.2×10^3	-	59
3-Methoxy salicyl aldoxime	360	7.1×10^3	-	60
3-Hydroxy-3-methyl -1-m-chlorophenyl triazine	415	9.25×10^2	0.0686	61
Present method	370	1.06×10^4	0.006	62

Table 7 : Determination of Copper (48 μg) in various synthetic mixtures with 100 μg of each ion added

	Ion added	Copper found (μg)
1.	Ni(II), V(V), Pt(IV)	48.6
2.	Ni(II), Zn(II), Cd(II)	46.5
3.	Mn(II), Zn(II), V(V)	49.5
4.	V(V), Pt(IV), Zn(II)	48.0
5.	Cd(II), Zn(II), Mo(VI)	48.0

BIBLIOGRAPHY

1. Lorenzo, Ferreira; Rosa A; Lopez, Martinez, M.Angeles; Berjejo, Martinez, F., Acta Quim.Compostelena, 1978, 2(2-3), 65.
2. Mehra, M.C; Leblane, D., Microchem.J., 1979, 24(4), 435.
3. Om.Hari; Wasi Nadira; Singh, H.B; Ktyal, M., J.Inst.Chem (India), 1984, 56(1), 9.
4. Mody, N.F., J.Inst.Chem. (India), 1985, 57(1), 6.
5. Paria, P.K; Majumdar, S.K., Indian J.Chem.Sect A, 1986, 25A(1), 103.
6. Shrivastav Madhulika; Pandey, G.S., J.Inst.Chem. (India), 1986, 58(1), 29.
7. Singh, A.K; Kumar D; Katyal, M., Anal Chim Acta, 1985, 172, 303.
8. Vogel, A.I., A Text Book of Quantitative Inorganic Analysis, ELBS, London, 1978.

9. Welcher, F.J., Organic Analytical Reagents, Vol.3, Van Nostrand, Princeton, 1962.

10. Morelli, Basilio, Analyst, 1984, 109(1), 47.

11. Lal, Keemti; Malhotra Sita Rani.,Ann Chim., 1981, 71 (7-8), 479.

12. Singh, R.B; Jain, P; Garg, B.S; Singh, R.P., Bull Inst Chem Acad, Sin., 1980, 27, 77.

13. Paria, P.K; Majumdar, S.K., Indian J.Chem.Sect A, 1985, 24A(7), 629.

14. Sharma, Saroj; Hawa, S.K; Mathur, S.P; Satake, M; Rev.Roum.Chim, 1986, 31(6), 581.

15. Shravah, Kamini; Sinha, Prem Prakash; Sindhwani Sharwan Kumar, Analyst, 1986, 111(11), 1339.

16. Kumar Atul; Gautam, Mamta; Puri, B.K., Microchem J., 1986, 33(2), 256.

17. Mathur, S.P; Jain, K.K; Bhandari, C.S., Nat.Appl.Sci., Bull., 1977 (Pub 1979), 29(2), 69.

18. Jetley, U.K; Singh,Jai; Rastogi, S.N., Chem Era, 1979, 15(2), 23.

19. Thokdar, T.K; Sarkar, A; Paria, P.K & Majumdar, S.K., Indian J.Chem., 28A, 1989, 181.

20. Sarkar, A; Thokdar, T.K; Paria, P.K & Majumdar, S.K., Indian J.Chem., 1988, 27A, 650.

21. Vogel, A.I., A Text Book of Quantitative Inorganic Analysis, ELBS, London, 1978.

22. Hague, J.L; Brown, E.D and Bright, H.A., J Research Nath.Bur.Standards, 1951, 47 380; Claassen, A and Bastings, L., Z.anal chem, 1956, 153, 30.

23. Gaher, A.R., Anal Chem, 1954, 26, 577.

24. Vogel, I., Text Book of Quantitative Inorganic Analysis, ELBS, London, 1978.

25. Gordieyff, V.A., Analyt.Chem, 1950, 22, 116.

26. Hu, Tse-Te; Kao, Fa-Kuli, Fen Hsi Hua Hsuch, 1978, 6(6), 446.

27. Gonzalez Portal, Aurora; Bermejo Mertinez, F; Baluza Santos C., Act Quim Compostelena, 1978, 2(2-3), 54.

28. Reddy,T,, Sreenivasula; Rao, S, Brahmaji,,Current Science, 1979, 48(10), 439.

29. Zuchi, G., Rev.Roum.Chim, 1979, 24(3), 497.

30. Kafor, O., Emmanuel, Chakwuemeka, Talanta, 1980, 27(11A), 887.

31. Rakhmatallaev, K; Tashmamatov Kh; Rakmatullaeva, M.A., Uzb.Khim.Zh. 1980, 4, 10.

32. Kulshrestha, Hemant; Kumar, Satya; Singh, R.P., J.Indian Inst.Sci., 1980, 62(6), 113.

33. Ilyas, Q.R; Joshi, A.P., Mikrochim Acta, 1980, 2(3-4), 263.

34. Varma, Yashbir Singh, Barua, Sudarshan; Singh, Ishwar; Garg, Bhagwan Singh, Singh, Rajendra Pal., Ann Chim, 1981, 71(5-6), 343.

35. Zaki, M.T.M; Alquasmi, R., Fresenius Z., Anal Chem, 1981, 306, 5, 400.

36. Anipindi, A.R; Jain, P; Singh, R.P., J.Chin,Chen,Soc., 1981, 28(3), 165.

37. Alexaki, T Zivanidon, H; Vasilikiotis, G.S; Microchem J., 1981, 26(1), 1.

38. Lorenzyo Ferreira, Rosa A; Bermejo Martiney, F., Acta Quim. compostelane, 1982, 6(3), 93.

39. Kato, Takeshi, Hasegawa, Akira, Bunseki Kagaku, 1982, 31(10), 579.

40. Tyagi Anil; Tyagi, R.P; Joshi, B.C., Bull.Inst.Chem. Acad.Sin, 1982, 29, 47.

41. Bermejo Barren, Adela; Gomez Doval, Maria Angela; Bermejo Martinez, F., Acta Quim Compostelena, 1983, 7(1), 1.

42. Gowda, H.Sanke; Ahmed, S; Maqbool, Indian J.Chem. 1983, Sect A, 22A(12) 1086.

43. Tang, Fulong; Zhang, Sunwei; Chen, Jianshen; Wu, Xiaohui., Huaxue Shiji, 1983, 5(4), 225-8, 246.

44. Rodringuer, J; De Torres, A.Garcia; Cano-Pavan, J.M., Anal Chim Acta, 1984, 156, 319.

45. Katiyar, G, S; Haldar B.C; J.Indian Chem.Soc., 1984, 61(4), 353.

46. Xia, Daopei, Lin, Qingxiong, Fenxi Huaxue 1985, 13(5), 365.

47. Chakrabarti, Anil K., J.Indian Chem.Soc., 1985, 62(10), 771.

48. Shrivastava, Madhulika; Pandey, G.S., Anal Chim.1986, 76(1-2), 69.

49. Vesugi Katsuya, Nagahiro Tohru Kumagui Tetsu, Yamaguchi Shigeroku, Kenkyu Hokaku Himeje Kogyo Daigaku, 1986, 39A, 16.

50. Evitmova, B., Akad Nauk, 1986, 39(8), 61.

51. Salinas, F; Berzas Nevado, J.J; Espinosa Mansilla, Roman Galan, T., Quim Anal 1987, 6(2), 232.

52. Bayan, K.C., Ph.D Dissertation, Gauhati university, 1987.

53. Thokdar, T.K., Sarkar, A, Paria, P.K., Majumdar, S.K., J.Indian Chem.Soc. Vol.LXV, 1988, 386.

54. Kumar, Asok; Jain, Mamta., Zh.Anal Khim. 1989, 42(12), 2207.

55. Xu, Mianyi; Pan, Zuting; Li, Mu. Fenxi Shiyanshi, 1989, 8(1), 8-10, 4.

56. Tamhina B., Microchem J., 1980, 25(2), 235.

57. Shivpuri, Sushma; Tyagi, M.P; Purohit, D.N., Bol.Soc. Quim.Peru., 1985, 51(1), 32.

58. Shrivastava, Madhulika; Pandey, G.S., Anal.Chim., 1986, 76(1-2), 69.

59. Chakraborty, Anil K., Indian J.Chem.Sect A, 1986, 25A(9), 886.

60. Vesugi Katsuya; Nagahiro Tohru Kumagai Tetsu; Yamaguchi Shigeroku., Kenkyu Hokoku. Himeji Kogyo Daigaku, 1986, 39A, 16.

61. Shivpuri, Sushma; Tyagi, M.P; Purohit, D.N., Cienc Cult (Sao Paulo), 1986, 38(3), 550.

62. Sarkar, A; Thokdar, T.K; Paria, P.K & Majumdar, S.K., J.Indian Chem.Soc., Vol.LXV, Oct. 1988, 742.