

CHAPTER V

Diphenylthiocarbazide as an Analytical Reagent

Extraction and Spectrophotometric Determination of Copper

INTRODUCTION

Diphenylthiocarbazide is obtained as prisms from warm alcohol. It melts at 150°C to form a dark green liquid. It is difficulty soluble in alcohol, benzene, acetone, ether, chloroform and acetic acid. The reagent gives coloured precipitates when added to solutions of salts of a number of the heavy metals¹². Here a method has been proposed for the spectrophotometric determination of copper with diphenylthiocarbazide.

EXPERIMENTAL

Apparatus and reagents :

Spectral curves and absorbance measurements were made with a Shimadzu PR1 model recording spectrophotometer provided with matched quartz cells of 10 mm optical path length. Acidity of the aqueous solutions were measured with a ECL 5651 digital pH meter. Separatory funnels (corning) (50 ml) were used for extraction purpose.

A stock solution of copper(II) was prepared by dissolving 1.9630 gm of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (BDH) in 250 ml distilled water followed by the standardisation as benzoin- α -oximate. Solutions of lower concentrations were prepared by appropriate dilution.

Diphenylthiocarbazide was prepared by mixing one part of carbondisulphide with two parts of phenylhydrazine and washing the white precipitate, so formed, few times with water by decantation and then dried. A 0.4% acetic solution of the reagent was used for the estimation of copper.

KH_2PO_4 - NaOH buffer was employed to adjust pH of the aqueous solution.

All the chemicals and solvents used were of analytical grade. Ethyl acetate, benzene, chloroform 1,2-dichloroethane, carbontetrachloride were distilled before used.

Standard solutions of diverse ions were prepared from their corresponding salts to study interferences.

Determination of copper :

To a suitable volume of sample solution containing 5 - 30 μ g of copper(II) was added 0.4% acetic solution (0.5 ml) of diphenylthiocarbazide followed by phosphate buffer (pH 6; 5 ml). Volume of the aqueous phase was then made upto 10 ml with distilled water and left for 1 min to ensure complete complexation. The solution was then equilibrated with ethylacetate (10 ml) for 1 min. The separated organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the organic extract was read at 540 nm against a copper free reagent blank and the amount of copper deduced from a calibration curve. To study the effects of diverse ions the respective foreign ions along with masking agents, if needed, were added to the aqueous sample solution before addition of the reagent.

RESULTS AND DISCUSSION

Absorption spectrum :

The absorption spectrum of copper(II)-Diphenylthio-carbazide complex in ethylacetate taken against reagent blank as a reference has been shown in Fig.1. The brown copper complex shows absorption maximum at 540 nm. The reagent blank does not absorb in the aforesaid wavelength region. The pattern of the absorption spectrum of the complex remains unchanged when extracted from pH 4-8. This indicates the existence of a single variety of the complex species in the system.

Beer's law and calibration curve :

Different amounts of copper(II) were taken and  extracted as in the general procedure at pH 6.0 and the absorbance was measured against the reagent blank in order to observe the adherence of the colour system to Beer's law (table 1). It has been observed that the Beer's law is obeyed over 0.2 - 4 ppm of copper (Fig.2). In each case the aqueous phase after extraction was clear and colourless. Furthermore, the aqueous phase as tested by an independent method was found to be free from copper.

The molar absorptivity of the complex based on copper content was evaluated to be $(4.87-5.20) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ with Sandell's sensitivity $0.0013 \mu \text{ g/cm}^2$ at 540 nm.

Effect of Diphenylthiocarbazide concentration :

The effect of diphenylthiocarbazide concentration on absorbance has been examined keeping all other variables constant. It has been found that 0.5 ml of 0.4% acetic solution of the reagent is sufficient to extract 20 g of copper in a single operation. Amount of the organic reagent below 0.2 ml results low absorbance value. Higher concentration did not bring about any significant change on the maximum value of absorbance and was avoided. The results are shown in table 2.

Effect of pH :

Effect of pH on the system was examined in terms of absorbance of the copper-diphenylthiocarbazide complex in the organic phase. A steady and maximum absorbance was obtained when extractions were carried out from pH 4-8. In each case, after extraction the aqueous phase was clear and colourless. Complete and quantitative extraction of copper as a function of pH has been shown in fig.3.

Choice of solvents :

Apart from ethylacetate, some other common organic solvents were also tested as extracting solvents. Use of 1,2 dichloroethane offers no special advantages over ethylacetate. Benzene, carbontetrachloride or chloroform does not extract the complex.

Stability of colour :

The reaction between Copper(II) and diphenylthiocarbazide was instantaneous. Time is not a critical factor in the determination of copper(II). The absorbance of the ethylacetate extract containing copper(II)-diphenylthiocarbazide complex were measured at different intervals of time. The colour of the Copper(II) complex in ethylacetate was found to be stable for at least 24 hr as seen from table 3.

Interference :

In order to study the effect of diverse ions on the extraction behaviour, copper was determined according to the recommended procedure in presence of the respective foreign ions. Extraction pH was set at 6.0 with KH_2PO_4 -NaOH

buffer. The tolerance limit was set as the amount of foreign ions required to cause a maximum $\pm 3\%$ error in the estimation of copper. Copper(II) ($20 \mu\text{g}$) could be determined without interference in presence of Ni(II), Mo(VI), Ca(II), Mn(II), Cr(III), La(III), Al(III), Ba(II), Sr(II), Mg(II), Co(II), U(VI), Be(II), Ag(III), Pt(IV), Rh(III), Th(IV), V(V), Cd(II) and Zn(II).

Interference due to Fe(III) and Sn(II) was eliminated using ammonium hydrogen fluoride as the masking agent. To avoid interference due to Pd^{+2} , copper was extracted in presence of ammonium thiocyanate. Potassium iodide masks Hg(II), Pb(II) and Bi(III).

Among the anion tested the system tolerated the followings : tartarate, citrate, oxalate, bromide, iodide, phosphate, acetate, thiocyanate, fluoride, phthalate, thiourea, ascorbate, EDTA and thiosulphate. However in presence of borate and nitrite high results are obtained. The results are presented in table 5.

Precision and accuracy :

The proposed method has been tested by analysing solutions containing a known amount of copper. The results for the determination of copper(II) is presented in

table 4. The method is fairly precise and reproducible. The total operation time for each run requires 10-15 minutes. The method is compared with some other existing methods with respect to molar absorptivity and Sandell's sensitivity as seen from table 6.

Application :

The metal has been estimated in synthetic mixtures and some standard samples following the general procedure.

a) Determination of copper in presence of As, Bi, Pb, Hg :

To a copper solution (20 μ g), were added 2 mg each of As(III), Bi(III), Pb(II), and Hg(II) followed by 10 mg of KI. Acidity of the aqueous solution was adjusted to pH 6 with phosphate buffer. Acetonic solution (0.5 ml, 0.4%) of diphenyl thiocarbazine was added to the system and the mixture was left for 1 min to ensure complete complexation. Copper was then determined according to the recommended procedure and was found to be 19.8 μ g (average of four determination).

Determination of copper in presence of Fe, Co, Ni, Sn :

To a copper solution (20 μ g) were added 2 mg each of Fe(III), Co(II), Ni(II) and Sn(II). Ammoniumhydrogen-fluoride (10 mg) was then added to the system and pH was

adjusted as usual followed by addition of acetic solution (0.5 ml, 0.4%) of diphenylthiocarbazide. Copper was then determined by the recommended procedure and was found to be 19.5 μ g (average of four determination).

Determination of copper in presence of Pd, Pt, Rh :

To a sample solution containing copper (20 μ g) were added 1 mg each of Pd(II), Pt(IV) and Rh(III) followed by addition of 5 mg each of KI and NH_4SCN . pH was adjusted to 6 with phosphate buffer. Copper was then estimated as usual and was found to be 19.5 μ g (average of four determination).

Determination of copper in cupro-nickel alloy in presence of nickel :

The alloy sample (100 mg) was dissolved in a mixture of HCl and HNO_3 (2:1). The solution was evaporated to dryness after addition of a few drops of conc H_2SO_4 . The residue was dissolved in water and the resulting solution was diluted to 250 ml with distilled water in a volumetric flask. The solution was further diluted as needed. A 2 ml aliquot portions were taken in several of the determinations with 0.4% diphenylthiocarbazide (0.5 ml) being added in a separating funnel and pH was adjusted to 6 with phosphate buffer. The mixture was equilibrated with ethylacetate

(10 ml) and the absorbance of the organic extract was read at 540 nm. Copper was deduced from a calibration curve. Copper was found to be 69.2% (average of four determination) (certified 68.12% cu in cupro-nickel).

Determination of copper in white metal in presence of Pb, Sb, Sn, Bi, Ni, As :

The sample (1 gm) was dissolved in 6 M hydrochloric acid (10 ml) and digested on a hot plate. The clear solution was evaporated, cooled and diluted with distilled water. The solution was filtered to remove a major portion of lead, precipitated as lead chloride and washed few times with distilled water. The filtrate and washings were transferred quantitatively into a volumetric flask (100 ml) and the volume made up to the mark. A 2 ml aliquot portions were taken in several of the determinations followed by addition of 10 mg of KI and 5 mg NH_4HF_2 along with acetic solution (0.5 ml, 0.4%) of diphenylthiocarbazide. pH was adjusted to 6 with phosphate buffer, copper was estimated by the recommended procedure and was found to be 0.13% (average four determinations) (certified : 0.12% cu in lead base white metal).

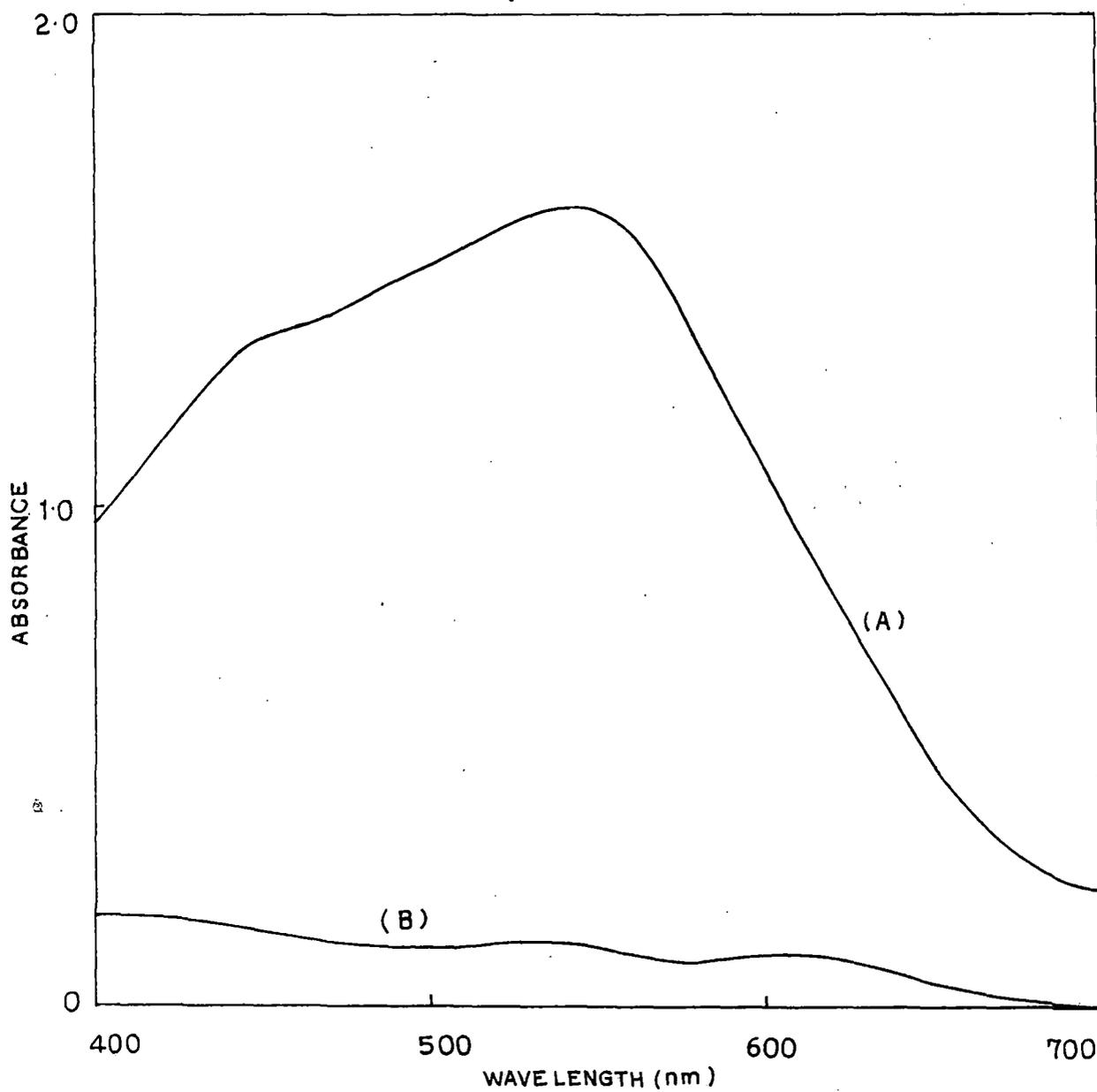


Fig-1: Absorbance spectra of (A) Copper-DPTC complex (2 ppm Cu) and (B) Reagent blank.

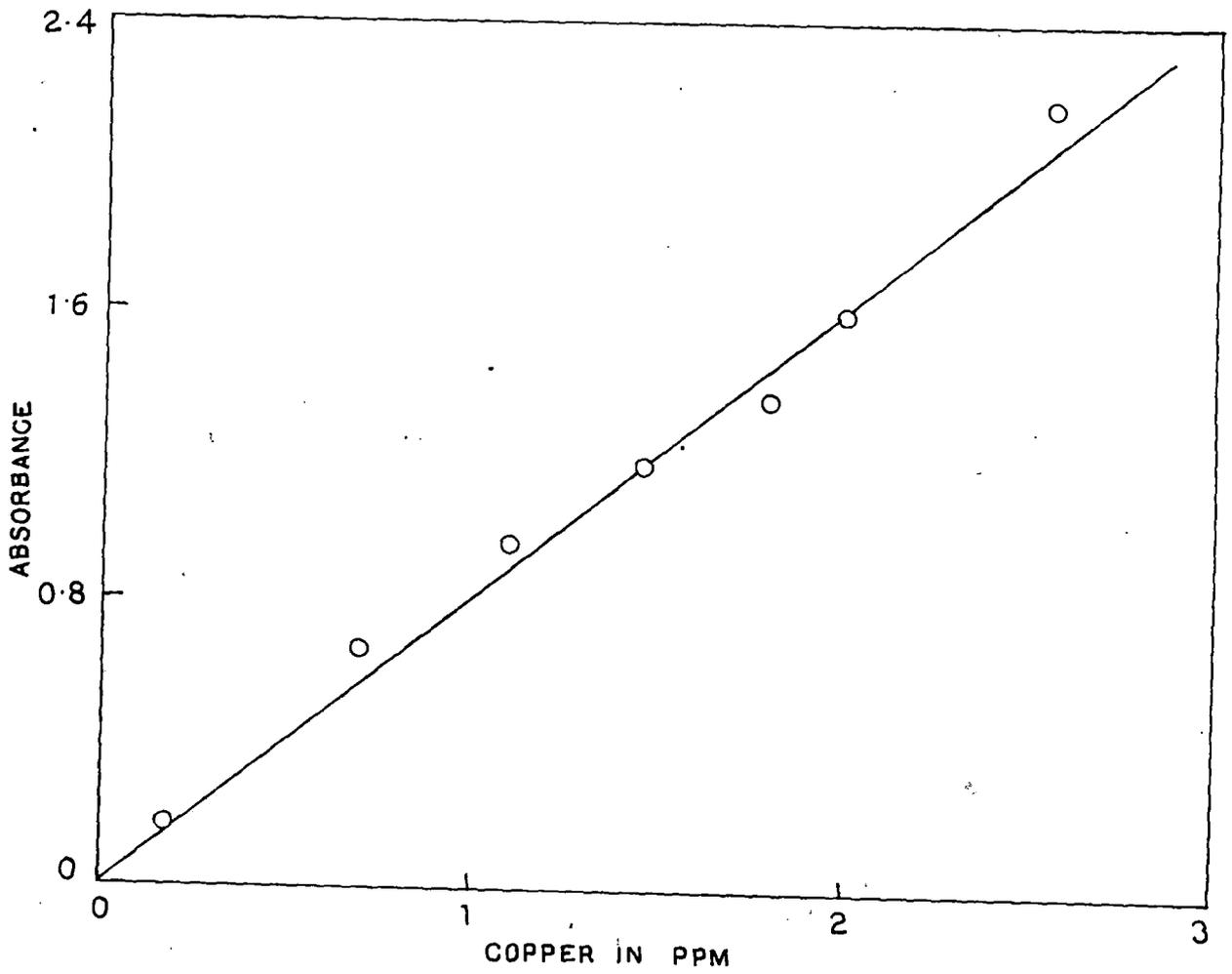


Fig-2: BEER'S LAW (Copper - DPTC system)

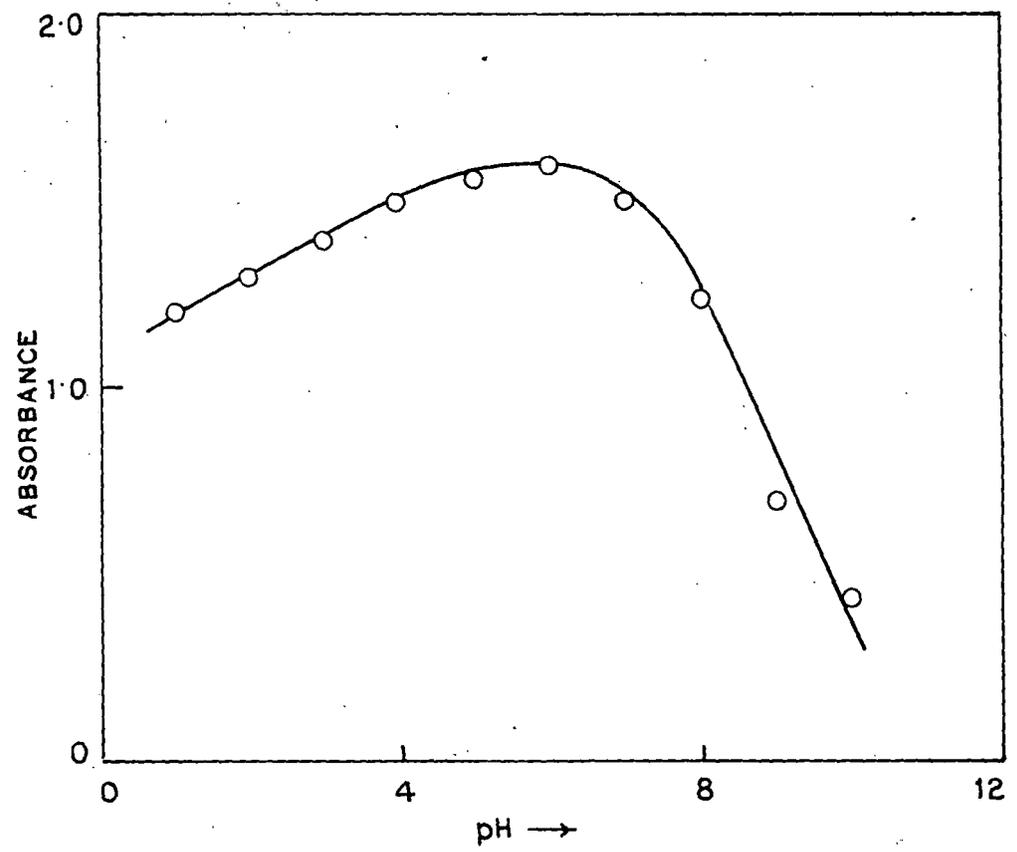


Fig - 3: ABSORBANCE AS A FUNCTION OF pH (Cu taken 20 μg)

Table 1 : Adherence to Beer's law

Copper in μ g	Absorbance at 540 nm
1.81	0.180
7.20	0.670
10.90	0.960
14.45	1.180
18.18	1.360
20.00	1.600
25.45	2.180

Table 2 : Effect of diphenylthiocarbazine concentration

The aqueous phase (10 ml) contains 20 μ g of copper(II)
Extraction pH - 6.0.

Diphenylthio- carbazine concentration in %	Amount added, (ml)	Absorbance at 540 nm
0.4	0.05	-
0.4	0.075	0.680
0.4	0.15	1.020
0.4	0.20	1.200
0.4	0.30	1.320
0.4	0.40	1.580
0.4	0.50	1.600
0.4	0.60	1.608
0.4	0.80	1.600
0.4	1.0	1.605

Table 3 : Variation of absorbance with time. Copper(II) taken 20 μ g

Time in hours after extractions	Absorbance at 540 nm
0.25	1.605
0.50	1.605
1.0	1.600
6.0	1.605
12.0	1.605
24.0	1.600

Table 4 : Reporducibility of copper recovery

Copper taken (μ g)	Copper found (μ g)	Mean (μ g)	Std deviation (%)
14.45	15.5, 14.8, 14.4	14.46	0.72
	15.0, 13.5, 14.0		
20.0	20.5, 18.8, 19.0	20.05	0.97
	21.2, 20.8, 20.0		
25.45	24.55, 24.80, 25.60	25.36	0.80
	26.8, 25.40, 25.0		

Table 5 : Effect of diverse ions on determination 20 μ g of copper. Extraction pH set at 6.0

Ion added	Amount tolerated (mg)	Copper found (μ g)	Error %
Fe (III)	4.0 ^a	20.5	2.5
Co (II)	3.5	20.2	1.0
Ni (II)	4.0	20.2	1.0
Pd (II)	2.5 ^b	20.6	3.0
Zn (II)	0.1	19.5	2.5
Mo (VI)	4.0	20.0	0.0
Pt (IV)	2.5 ^c	20.5	2.5
V (V)	0.1	19.8	1.0
Hg (II)	1.5 ^c	20.6	3.0
Ca (II)	4.0	20.2	1.0
Mn (II)	4.0	20.0	0.0
Cr (III)	4.0	20.2	1.0
La (III)	4.0	20.2	1.0
Al (III)	4.0	19.8	1.0
Be (II)	3.0	20.0	0.0
U (VI)	3.5	20.2	1.0
Ba (II)	4.0	20.0	0.0
Sr (II)	4.0	20.0	0.0
Rh (III)	2.5	20.2	1.0
Th (IV)	2.5	19.5	1.0
Pb (II)	1.5 ^c	20.6	3.0

contd ...

Table 5 contd ...

Cd(II)	0.1	20.5	2.5
Mg(II)	4.0	20.0	0.0
Sn(II)	2.5 ^a	19.4	3.0
As(III)	3.0	20.6	3.0
Bi(III)	1.5 ^c	20.5	2.5
Tartarate	9	20.2	1.0
Citrate	10	20.4	2.0
Oxalate	9	20.2	1.0
Bromide	10	20.4	2.0
Iodide	8	20.4	2.0
Phosphate	10	19.8	1.0
Acetate	12	20.0	0.0
Thiocyanate	8	20.2	1.0
Fluoride	10	19.8	1.0
Phthalate	10	20.0	0.0
Thiourea	10	20.0	0.0
Ascorbate	4	19.8	1.0
EDTA	4	19.8	1.0
Thiosulphate	4	19.5	2.5
Borate	Nil	-	-
Nitrite	Nil	-	-

a : in presence of NH_4HF_2

b : in presence of thiocyanate

c : in presence of iodide

Table 6 : Comparison

Reagent	λ_{\max} nm	Molar absorptivity $l \text{ mol}^{-1} \text{ cm}^{-1}$	Sandell's sensitivity $\mu\text{g}/\text{cm}^2$	Ref.
O-isopropyl-s-methyl dithiophosphate	420	1.1×10^4	-	1
4-methyltetrahydro- benzofurano (6,7-b) cumarin	370	12700	0.0036	2
1-P-chloroanilino-3- methylcyclohexane	445	1.45×10^3	0.0438	3
2-thiogortic acid	410	1.17×10^3	0.0543	4
N-(α -Pyridyl)-2 -thio qualdinamide	520	5.2×10^3	-	5
3-methoxysalicyl aldoxime	360	7.1×10^3	-	6
3-Hydroxy-3-methyl-1 -m-chlorophenyl triazene	415	9.25×10^2	0.0686	7
Bis (4-hydroxypent-2 -zlidene) diamino ethane	540	1.36×10^3	-	8
Tetra phenyl arsonium or tetraphenyl phosphonum thiocyanate	465	2.8×10^3	-	9
Tetrahydrofarfuryl- xanthale	430	1.59×10^3	0.004	10
Present method	540	5.04×10^4	.0013	11

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