CHAPTER - IV

SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II) WITH 5-NITROSALICYLALDEHYDE THIOSEMICARBAZONE

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Introduction :

Copper has known from ancient times. It is one of the elements used to a greater extent in pure form than in alloy forms. The industrially important alloys of copper are brass, bronze, gun metal and nickel-silver alloy. It is important element in electrical industry. Copper alloys like cartridge brass has innumerable uses, including cartridge cases, automotive radiator cores and tanks, lightening fixtures, eyelet, rivets, screws, springs and plumbing products. Nickel silver alloys are used for table flatwear, Zippers, camera parts, costume jewellery, nameplates, radiodials and some electrical switch gear. Cupronickel alloys are well suited for application in industrial and marine installation as condenser and heat exchanger tubing. Copper-tin alloys are widely used for springs and screens in paper making machines. Copper-silicon, tin, iron, or zinc alloys are useful for hardwears. Alloys of copper with sulphur and tellurium increase ease of machining.

Now-a-days there is ever increasing demand for copper and its alloys as a result of rapid industrial advancement and its increasing use as structural alloys in diversified industries. This had led to steady exhaustion of its rich deposits. The availability of copper to present and next

generation is dependent on new methods based on recovery of traces from the effluent of rich solutions and on the extraction of ores with very poor copper content.

Numerous organic reagents have been reported for the spectrophotometric determination of copper. The most extensively used reagents are derivatives of 1,10-phenanthroline[1-3] which are reported to be specific reagents for copper but many metal ions interfere during determination. Also following are the reagents reported for the determination of copper. These include 1,5 diphenyl-3-thiocyarba-hydroazide[4], bis(2-aminoethyl)-dithiocarbamic acid[5], 1-(2-pyridylazo)-2-phenanthrol[6], 1-benzoyl-3-(2-pyridylthiurea)[7], 6-methyl picolinaldehyde[8], 2,4-dinitroresorcinol[9], dithio-oxamide[10], and 1-(2-pyridyl methyleneamino)-2-naphthol[11]. Although these reagents are sensitive they lack selectivity and many metal ions interfere during determination.

Thiosemicarbazones or azines of certain aldehydes and ketones are investigated as possible analytical reagents for spectrophotometric determination of Cu(II). These include picolinaldehyle semicarbazone[12], β-ionone thiosemicarbazone[13], 6-methyl-picolinaldehydeazine[14], picolinaldehyde thiosemicarbazone[15] and thiophene-2-aldehyde thiosemicarbazone[16]. Most of these react with copper in alkaline medium and highly sensitive but suffer from several interferences and required prolonged time of equilibration. Recently some important substituted thioureas reported for the determination of copper include

1-P-tolyl-3-benzoyl-thicarbaamide[17], 1-phenyl 1-3-thiobenzoyl-2-thiourea[18], N-(4-hydroxy-3-methoxy-benzylidine) hydrazine carbothioamide[19], Many metal interfere during determination and in case of some e.g. 1-phenyl-3-thiobenzoyl-2-thiourea 10 min heating on boiling water bath is necessary. Several new hydrazones reported as reagents for copper are benzothiozole-2-carboxyaldehyde-2-quinolyl hydrazone[20], diacetyl monoquinolyl hydrazone[21]. They react with copper in alkaline medium and are highly sensitive but suffer from several interferences and prolonged time of heating required for full complexation e.g. benzothiazole-2-carboxy-aldehyde-2-quinolhydrazone (15 min).

Thiosemicarbazones are reported for the determination of copper as they are selective and sensitive reagents for Cu(II). These include Furion thiosemicarbazone[22], biacetyl bis-(4-phenyl)-3-thiosemicarbazone[23], di(2-pyridyl) gloxal bis (4-phenyl-thiosemicarbazone)[24], only few are used to determine copper in highly acidic medium. Extractive procedures have been developed for determination of copper with numerous oximies. The reaction with copper generally carried out mostly in weakly acidic media are less sensitive. Newly reported oximes are 2-hydroxy acetophenone oxime[25], 5-bromo salicylaloxime[26], 3'-bromo 2'-hydroxyl-5'-methyl acetophenone oxime[27], nioxime[28] Michler'sthioketones[29], furtural oxime[30], phenanthrequinone monoxime[31]. However, the rate of extraction of the copper complex is slow e.g. 5-bromosalicylaldoxime (10 min.). Numerous azodyes have been investigated as sensitive reagents for copper.

These include 2-hydroxy-5-methyl acetophenone ethylene diamineanil (HMAEA) [32], bromopyrogallol red and benzyl dimethyl phenyl ammonium chloride [33], ferron [34], 4-nitrosoresorcinol [35], 4-(2-quinolyl azo) phenol [37], 6-(6-bromo-2 benzothiozolylazo) 2,4 xylenol [38]. Many metal ions interefere in addition to the observed low tolerence limit for platinum metals.

It is possible to determine copper with 1-(2-Quinolylazo-2,4,5-trihydroxybenzene [39], carboxylic acid [40], sodium 1-amidinoazo-2-hydroxy-naphthalene-4-sulphonate [41], 2,6 pyridinediol [42]. These methods suffer from serious interferences due to phosphate, cyanide, Ni, Co, V etc and complex has low stability.

The proposed reagent 5-nitrosalicylaldehyde thiosemicarbazone reacts with copper(II) in acid medium in the range 0.5 M to 2 M HCl to form green complex. The complex is measured at 630 nm. The method is simple, rapid and highly selective as it is possible to determine traces of copper in presence of large number of associated elements. The reagent that is proposed is stable, yellow in colour, readily available. Here the extraction is not necessary.

EXPERIMENTAL

Standard Copper solution :

A standard stock solution (1 mg/ml) of Cu was prepared by dissolving 1.965 gm of copper sulphate penlahydrate (AR) in double distilled water containing few drops of sulphuric

acid. The solution was diluted to 500 ml. The copper content of the solution was determined by volumetric method. It was found that the solution contains 1 mg of Cu(II) per ml. Working solutions of lower concentration were made by diluting stock solution with double distilled water.

Reagent Solution :

A 0.240 gm of the reagent 5-nitrosalicylaldehyde thiosemicarbazone was dissolved in 100 ml freshly purified and distilled dioxane to obtain 0.01M reagent solution. The solution is quite stable towards light and heat. It is easily soluble in dioxane and can be kept over a week period. All solutions used in study of diverse ions were prepared from AR grade chemicals.

Apparatus :

A carl.Zeiss (JENA) spectrophotometer (Spekol) equipped with 1 cm quartz cells was used for all the absorbance measurements.

General Procedure :

To an aliquot of sample solution containing upto 250 µg of copper, 2.5 ml of 1 x 10^{-2} M reagent solution in dioxane were added. The mixture was adjusted to 1M with respect to HCl by rapid addition to HCl. The flask was briskly. Shaken and was made to 25 ml with alcohol. The absorbance of the green complex was measured at 630 nm against reagent blank. The amount of copper was calculated from the calibration curve.

RESULTS AND DISCUSSION

Spectral Characteristics :

The absorbance spectra of Cu(II) 5-nitrosalicylaldehyde thiosemicarbazone complex resulting from different amounts of Cu(II) solution (10, 20, 30, 40 and 50 ppm.) are shown in Fig. 1. The green Cu(II) thiosemicarbazone complex exhibits an absorption maxima at 630 nm. The solution of the reagent in dioxane is light yellow and hence does not absorb significantely at 630 nm. The moar absorptivity of the complex Cu(II) + 5-nitrosalicylaldehyde thiosemicarbazone as determined from Beer's plot is 2859 $mole^{-1}$ cm^{-1} . The sandell sensitivity of the reagent was found to be 22.22 ng/cm^{-2} at 630 nm.

Effect of Acidity :

In order to find out the optimum concentration of hydrochloric acid required for the full colour development of copper (II) complex as a means of acidification, hydrochloric acid was varied in the fig. 2, indicates that the absorbance of the complex at 630 nm, containing 20 ppm. Cu and 1 x 10^{-2} M reagent was found maximum and constant between 1 M HCl. In addition, sulphuric acid, perchloric acid, nitric acid were also tested as a means of acidification. With perchloric acid and nitric acid the absorbance decrease rapidly, hence must not be employed. However, with sulphuric acid optimum concentration range was found to be same as with HCl. Hence 1M HCl has been

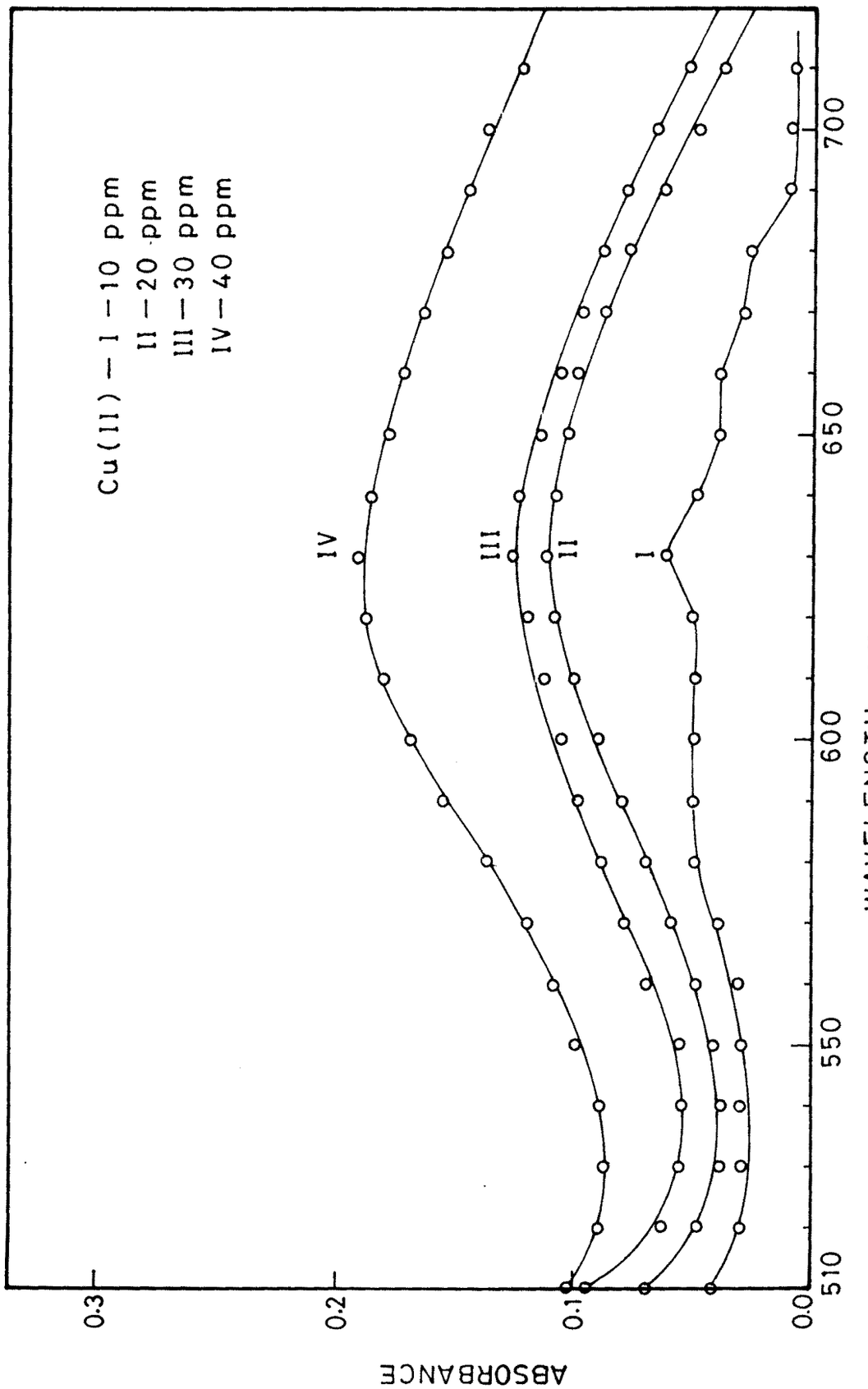


FIG. 1 — ABSORBANCE CURVES OF Cu(II)-5-NO_2 SAT COMPLEX.

recommonded as the means of acidification for further studies.

Effect of Reagnet Concentration :

Solutions containing the same amount of copper (20 ppm) and different amounts of the reagent from 0.5 ml to 5 ml of 1 x 10^{-2} M reagent solution were prepared. The colour was developed as outlined in the general procedure and the abosrbance of the complex was measured at 630 nm. The results of studies as shown in the fig. 3 indicates that 20 ppm of copper required minimum of 1 ml reagent. At this concentration, the metal to reagent ratio in terms of moles is 1:5. However, 2.5 ml of 0.01M (i.e. 10 fold molar excess) reagent was employed for further studies to ensure maximum colour intensity of copper complex. At higher reagent concentration there was insignificant increase in absorbance.

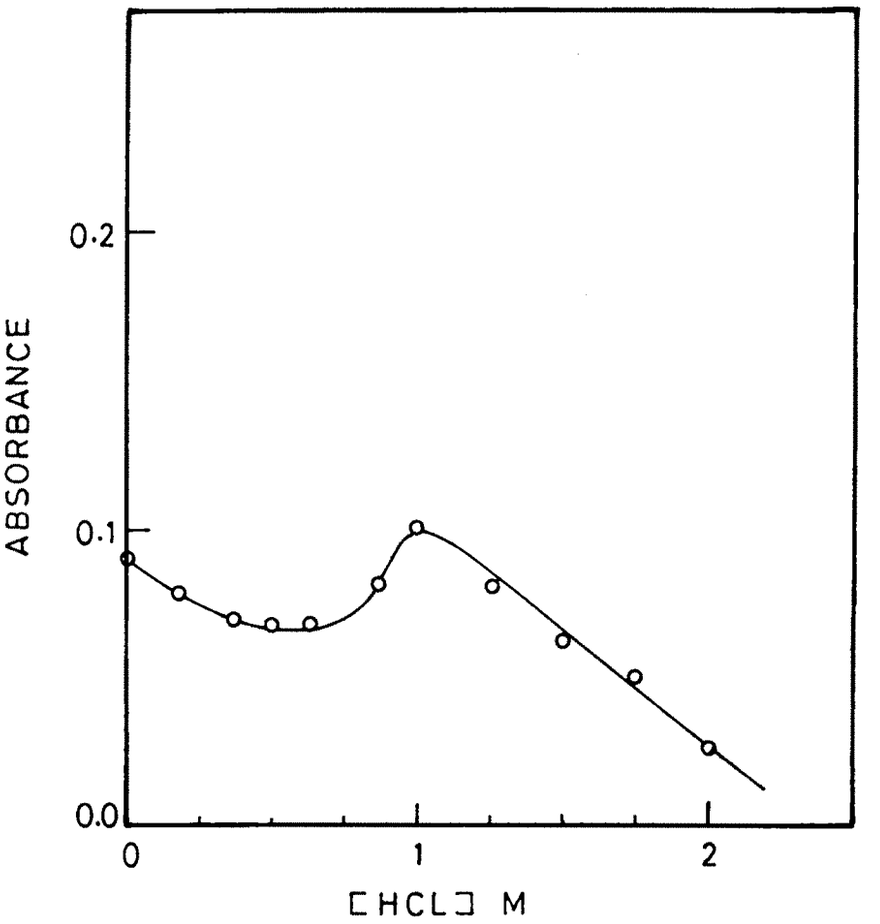
Effect of time and stability of complex :

In order to study the effect of time on the absorbance of the copper complex containing 20 ppm of copper at 1M acidity, the absorption measurements were made at different time intervals at 630 nm. It was observed that the green colour developed instantaneously and the absorbance remained constant over a period of 50 minutes. Hence the absorption measurements of the complex was made within 50 minnuts of the colour development Fig. 4B.

Effect of Alcohol :

In order to find out the amount of alcohol needed

FIG. 2
EFFECT OF
ACIDITY.



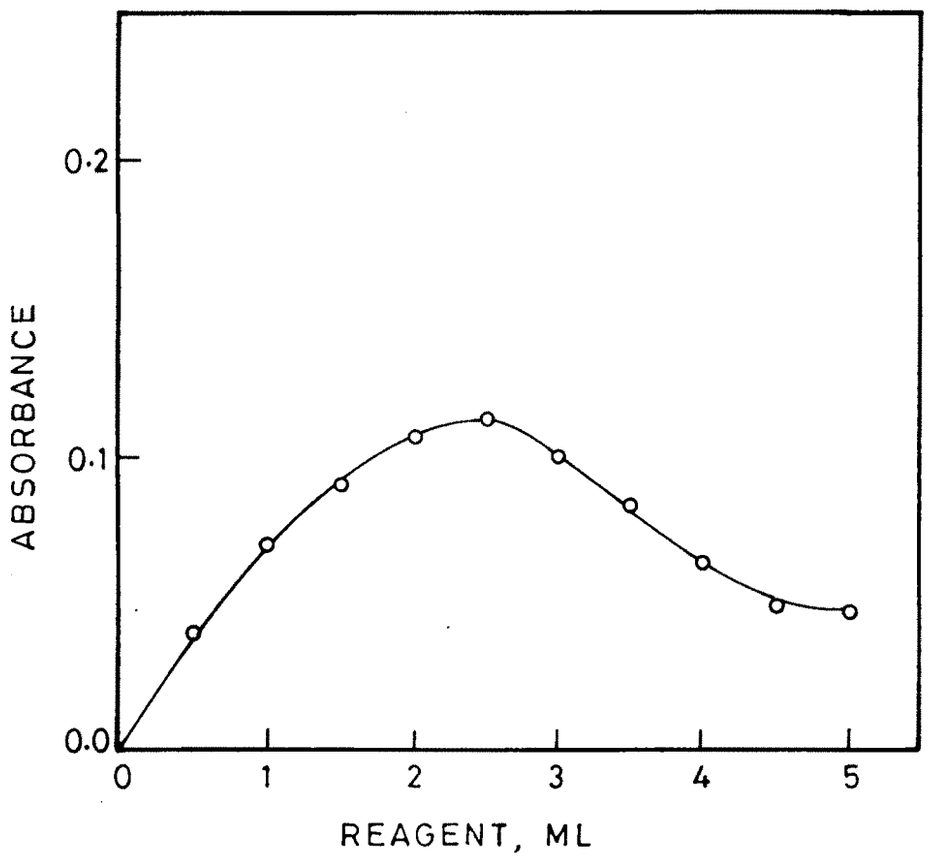


FIG. 3
EFFECT OF
REAGENT
CONCENTRATION.

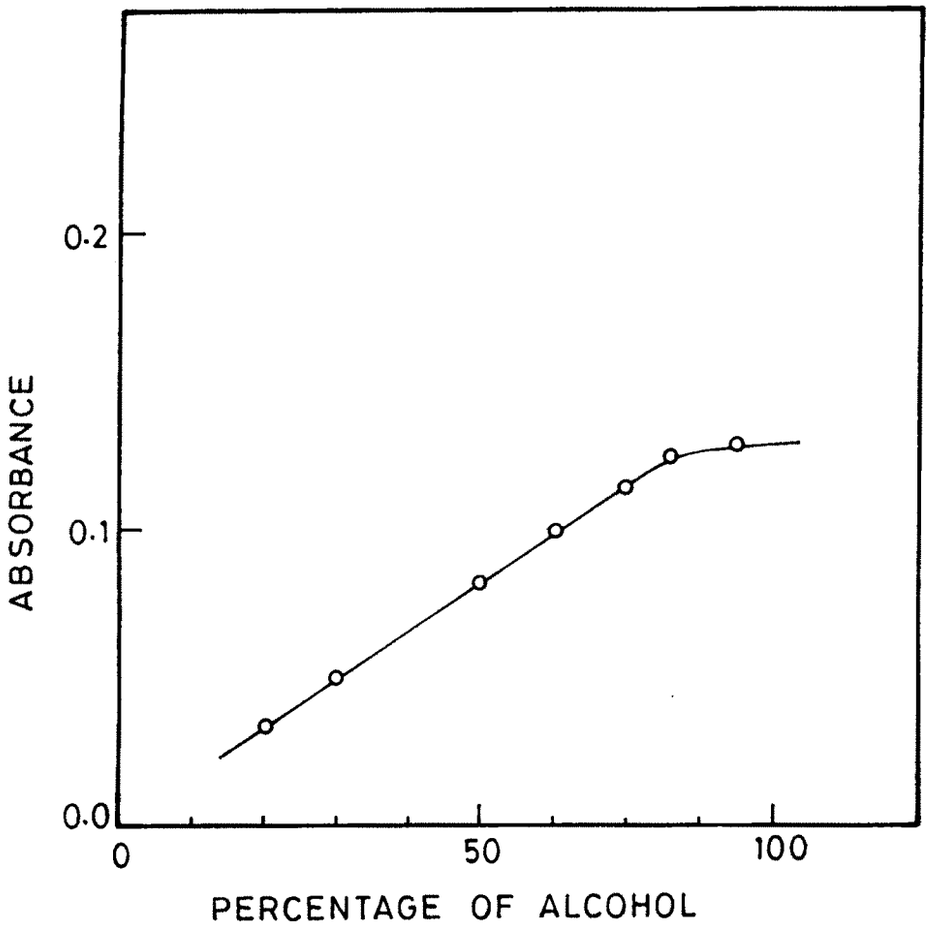


FIG. 4
EFFECT OF
PERCENTAGE
COMPOSITION
OF ALCOHOL.

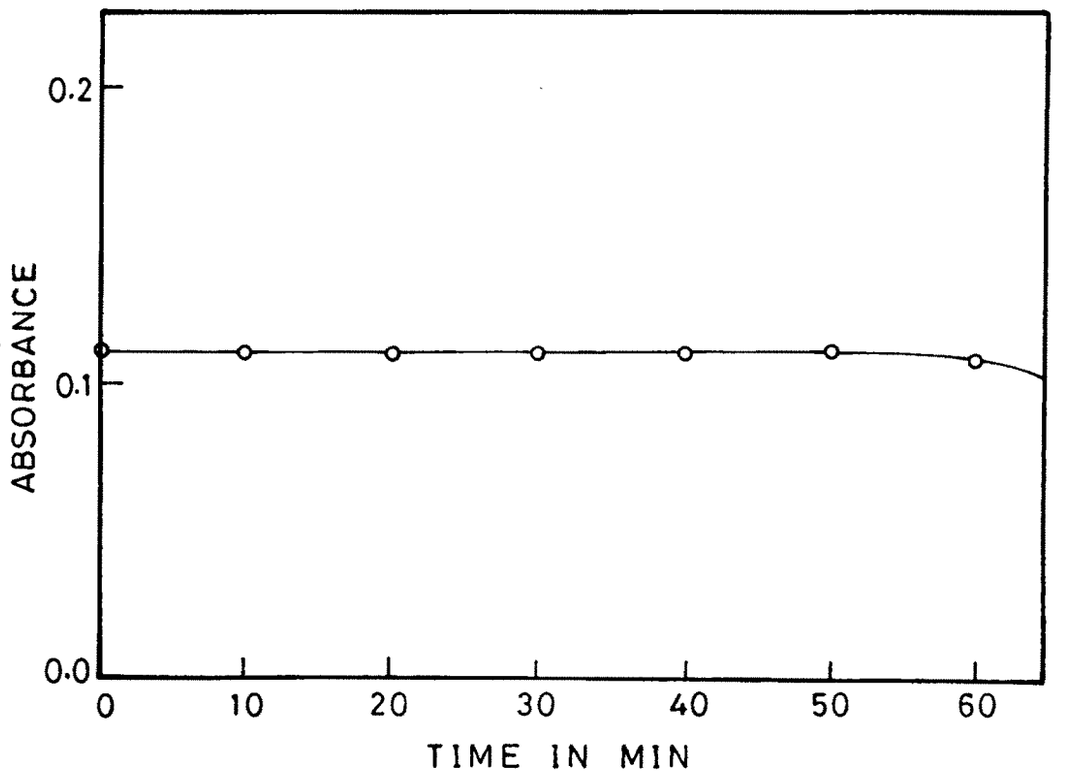


FIG. 4B
EFFECT OF
TIME AND
STABILITY
OF COMPLEX.

during the complexation Cu(II) 5-nitrosalicyaldehyde thiosemicarbazone complex. The percentage amount of alcohol was varied between 30% to 76%. It was found from the curve that the amount of alcohol required for full colour development of Cu(II) complex is in the range 76 to 70% (Fig. 4). At less than 30% alcohol, precipitation occurs whereas decrease in absorbance occured at greater than 76% alcohol. Hence for all the subsequent measurements 70% alcohol was recommended.

Effect of dioxane concentration :

To study the effect of dioxane concentration a series of solutions were prepared containing fixed amount of Cu(II) (20 ppm) and different amounts of dioxane, varying from 0.5 to 5 ml of dioxane. The colour of Cu(II) complex was developed as per general procedure and absorbance was measured at 630 nm against reagent as a blank. The results of studies are showin in Fig. 4C which are indicate that 2.5 ml of dioxane is sufficient for full colour development.

Spectral characteristics :

The absorbance spectra of Cu(II) 5-nitrosalicylaldehyde thiosemicarbazone complex resulting from different amounts of Cu(II) solution (10 to 60 ppm) are shown in Fig. 1. The green Cu(II) 5-nitrosalicylaldehyde thiosemicarbazone complex exhibits an absoption maxima at 630 nm. The solution of the reagent is yellowish in colour and hence does not absorb significantly in the visible region. The molar

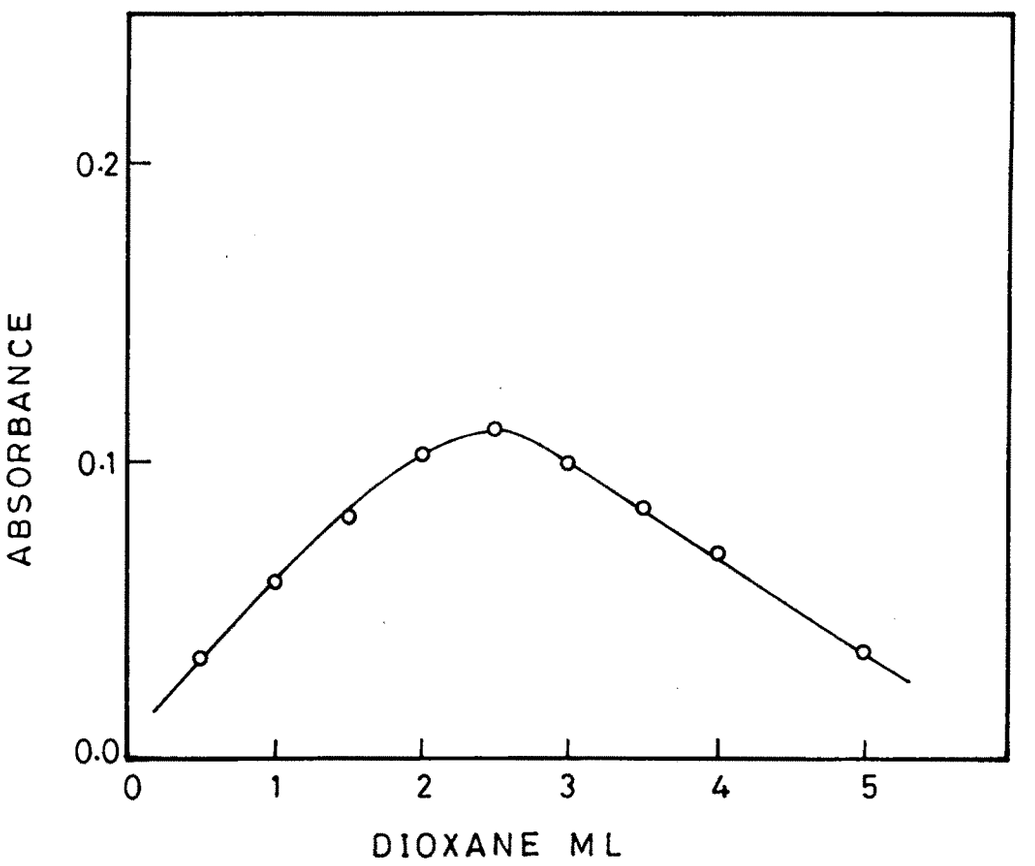


FIG. 4 C – EFFECT OF DIOXANE CONCENTRATION Cu (II) COMPLEX.

absorptivity of the Cu(II) thisemicarbazone complex as determined from Beer's plot is 2859 L $mole^{-1}$ cm^{-1}. The sandell sensitivity of the reagent was found to be 22.22 ng/cm^{-2} 630 nm.

Validity of Beer's Law :

The solution containing different amounts of copper in the range 250 µg to 1750 µg were used for the study of the validity of Beer's law. The colour was developed as per the recommended procedure using 1.0 x 10^{-2} M reagent and the absorbance was measured at 630 nm against the reagent as blank. The curve in fig. 5 shows that Beer's law is valid in the range 10 to 40 ppm of copper.

Composition of the complex :

In order to establish the composition of the complex, the equimolar solutions of metal and ligand (7.86 x 10^{-3} M) were used. The Job's and mole ratio method were used for determining the composition of the complex. A series of solutions were prepared in which mole fraction of reagent varied from 1 ml to 9 ml. Acidity of the solution was adjusted to 1M with HCl and the colour of the complex was developed as per the recommended procedure and the absorbances of the solutions were measured at 630 nm against reagent as a blank. The plot of the abosrbance versus the mole fraction of the ligand indicates that the copper(II) forms 1:1 complex with the ligand 5-nitrosalicylaldehyde thiosemicarbazone. Fig. 6.

The composition of the complex was verified by

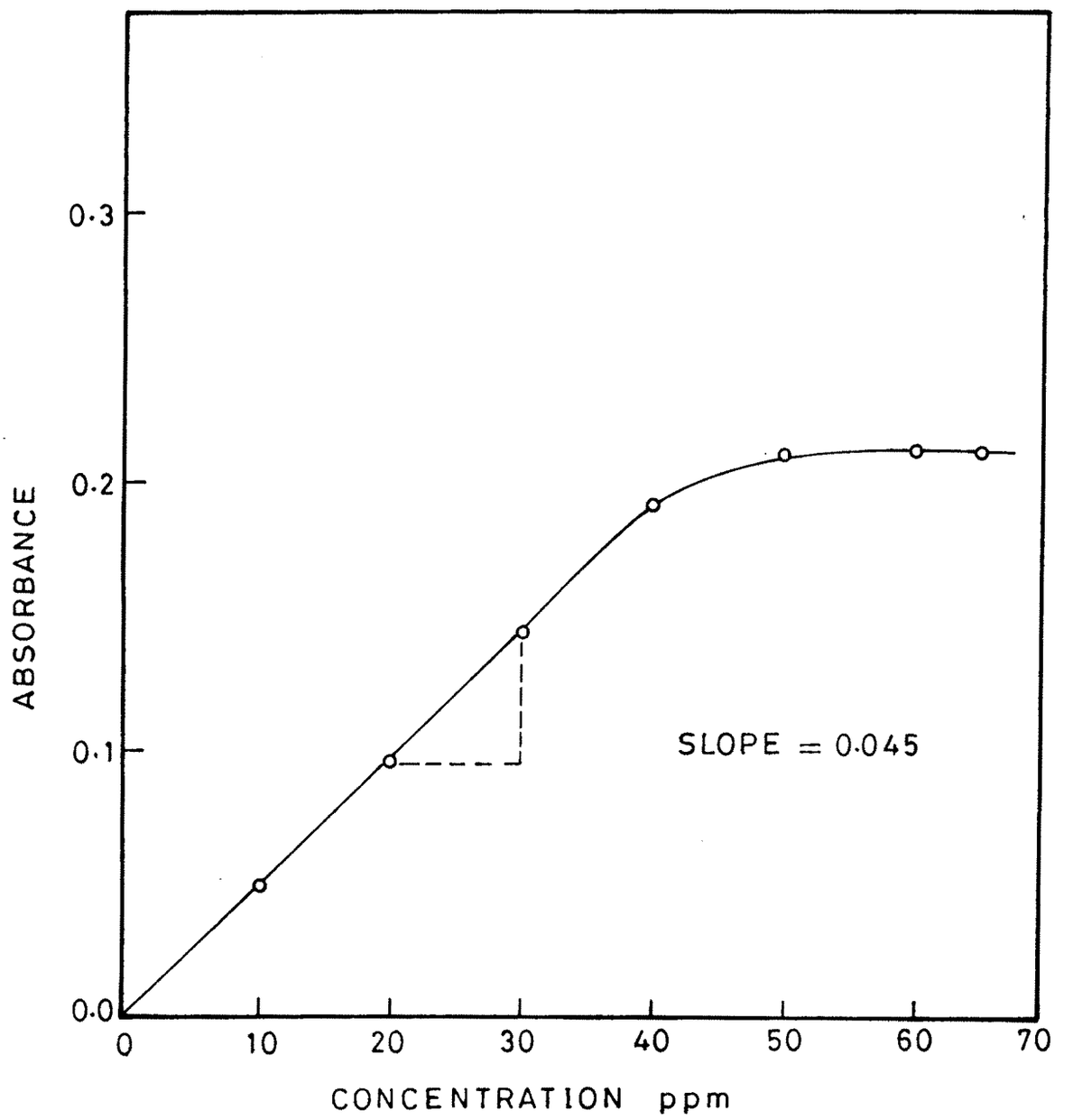


FIG. 5 — VALIDITY OF BEER'S LAW FOR COPPER (II) COMPLEX.

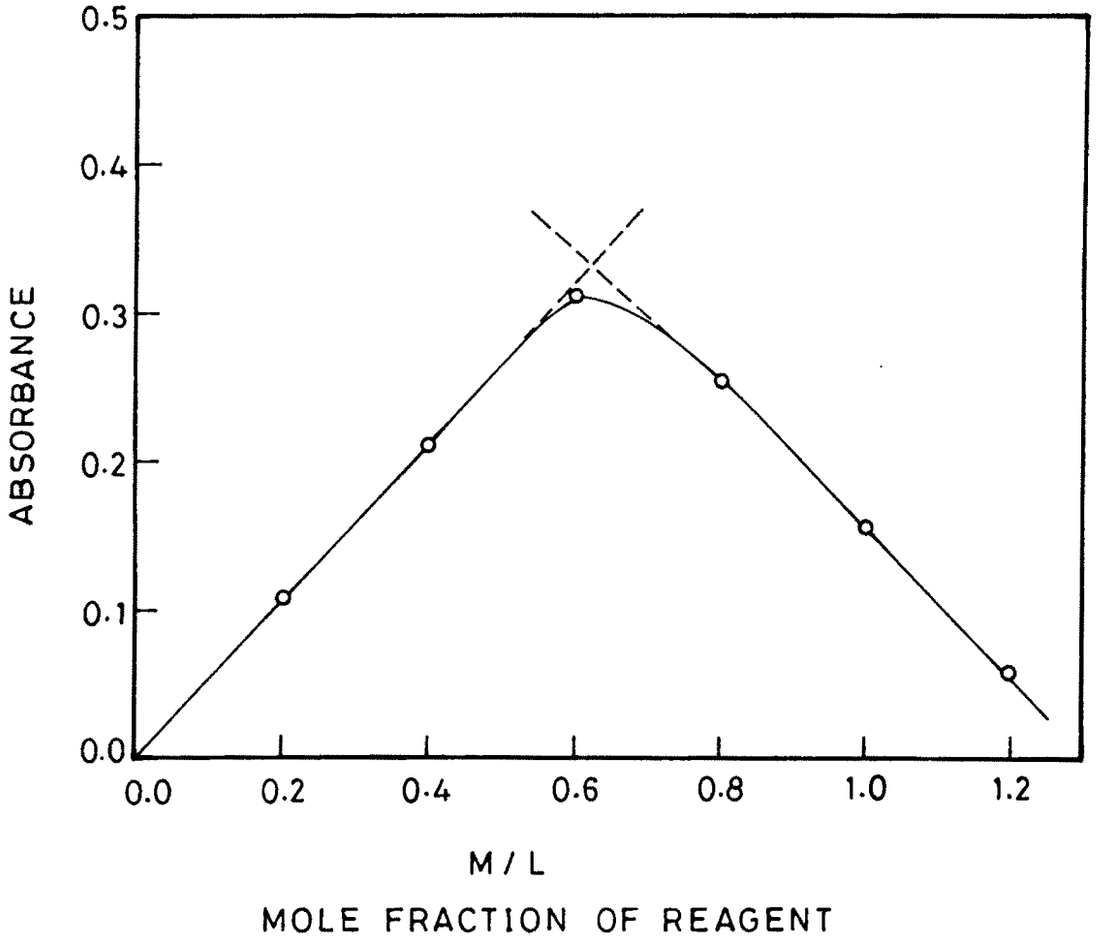


FIG. 6 - JOB'S PLOT.

$[M] = 7{\cdot}86 \times 10^{-3}$

$[L] = 7{\cdot}86 \times 10^{-3}$

mole ratio method. For this method equimolar solutions of metal and ligand were used (7.86×10^{-3} M). A series of solutions containing fixed volume of reagent and different amounts of copper were prepared. The 1M acidity was maintained by adding hydrochloric acid and the colour of the complex was developed as per the recommended procedure. The absorbance of solutions were measured at 630 nm against reagent as a blank. The plot of absorbance versus the reagent to metal ratio (fig. 7) confirms the results obtained by application of Job's method.

Effect of Diverse Ions :

The effect of large number of diverse ions on the determination of 250 µg of Cu(II) with 5-Nitro SAT (2.5 ml of .01M) was investigated following the recommended procedure. An error of less than 2% in abosrbance was considered to be tolerable. The tolerence for the various ions tested has been shown in Table No. 1. The results in the table shows that the cations which do not interfere in 50 fold excess of foregin ion relative to Cu(II) were Mo(VI), U(VI), Mn(II), Cr(III), Pd(II), Ni(II), W(VI), Ti(I) and those which can be tolerated in 10 fold amount were V(V), Au(III), Ag(I), Te(IV), Gq(III). The selenium, Bi(III) are tolerated in 1:5 ratio. In case of mercury and Pb, the ration is 1:2. The ions showing strong interferences are Cd(II), Zn(II), Sn(II), Pt(IV), It(IV), Ru(III), Cu(II), Co(II). Many ions EDTA, phosphate, cyanide, citrate do not interfere in fairly large concentrations.

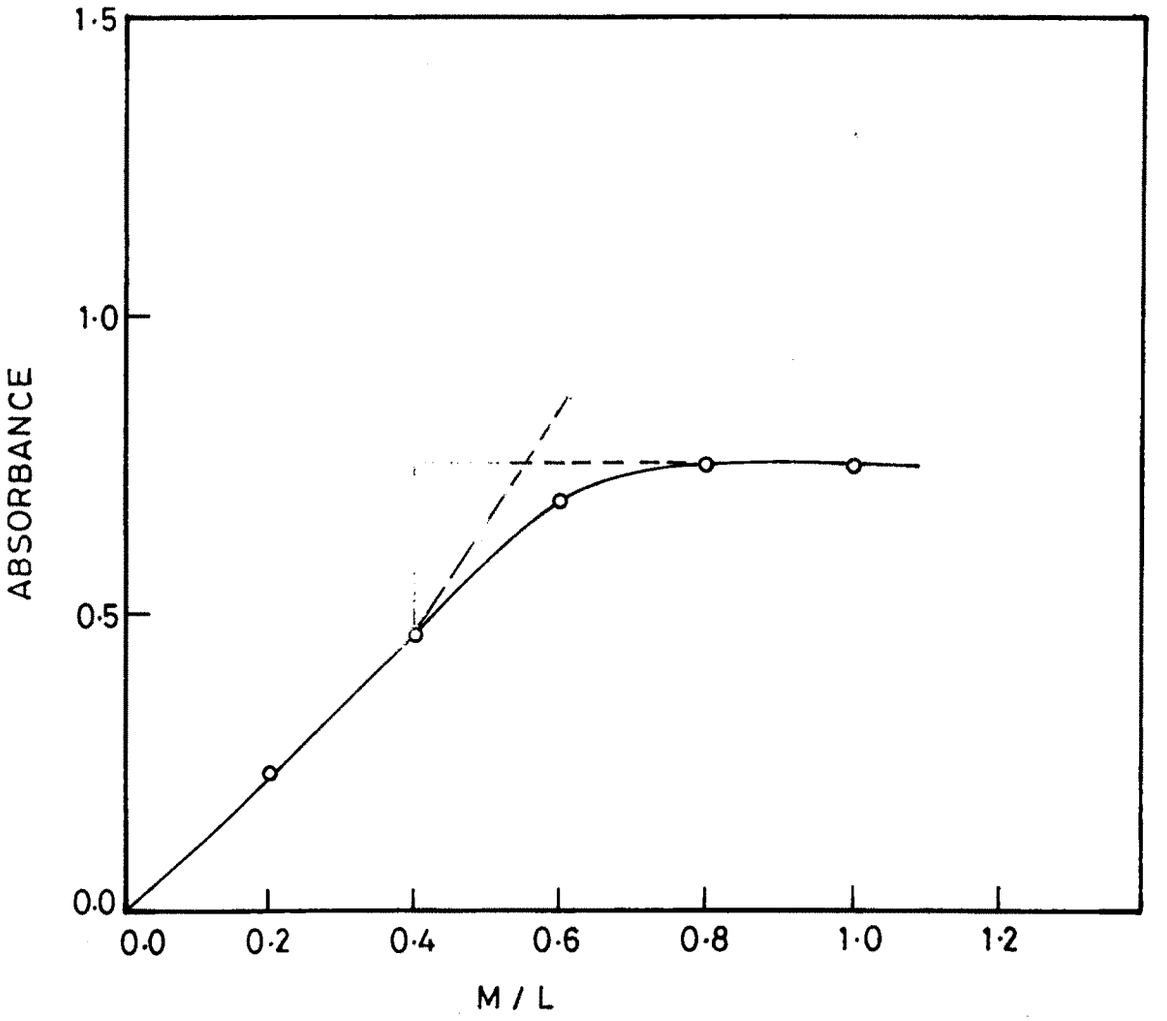


FIG. 7 - MOLE RATIO PLOT FOR COPPER(II) COMPLEX.

(A) $[M] = [L] = 7{\cdot}86 \times 10^{-3}$

Table No.1 : Effect of Diverse Ions

Cu(II) = 250 µg.

5-No_2SAT = 2.5 ml in dioxane

λmax = 630 nm.

Foreign ion	Added as	Tolerance limit, µg
Mo(VI)	Amm molybdate	5000
Cd(II)	$CdSO_4$	none
Ni(II)	$NiCl_2.6H_2O$	500
Bi(III)	$Bi(NO_3)_3$	50
Ga(III)	$GaCl_3.xH_2O$	100
Se(IV)	Na_2SeO_3	50
Te(IV)	Na_2TeO_3	100
V(V)	$NaVO_3$	100
U(VI)	$UO_2(NO_3)_2.6H_2O$	1000
Hg(II)	$HgCl_2$	20
Mn(II)	$MnCl_2.6H_2O$	1000
W(VI)	$Na_2WO_4.2H_2O$	500
Zn(II)	$ZnSO_4$	none
Cr(VI)	Pot. dichromate	50
Tl(I)	TI_2SO_4	500
Sn(II)	$SnCl_2$	none
Cr(III)	$CrCl_3.x\ H_2O$	1000
Pd(II)	$PdCl_2.6H_2O$	1000
Pt(IV)	$H_2PtCl_6.x\ H_2O$	none
Ru(III)	$RuCl_3.x\ H_2O$	none

Ti(IV)	Pot. titanyl oxalate	none
Au(III)	$AuCl_3.x\ H_2O$	200
Cu(III)	$CuSO_4.5H_2O$	1000
Ag(I)	$AgNO_3$	500
Pb(II)	$Pb(NO_3)_2$	20
Tartrate	Sodium Pot. tartrate	2500
PO_4^{3-}	Na_2HPO_4	1000
SCN^-	NH_4SCN	none
Salicylate	Sulphosalicylic acid	2500
EDTA	Na-EDTA	none
$S_2O_3^{2-}$	$Na_2S_2O_3$	2500
Thiourea	Thiourea	5000
F^-	NH_4HF_2	1000
CN^-	KCN	none
Citrate	Citric acid	none

Reproducibility Accuracy and Sensitivity data :

For the study of reproducibility and accuracy of the method, absorbance measurements with ten different identical solutions containing 20 ppm of Cu(II) were performed as outlined in the procedure and concentration determined using calibration curve. The results are shown in table No. 2. It is observed that there is an excellent agreement in the experimental values. The method has high precision and accuracy.

Average of the ten readings are calculated.

Deviation from these average reading was found out in each case and then standard deviation was calculated. From the standard deviation, reproducibility of the results with 95% confidence limit was calculated. The sandell sensitivity of the reaction as calculated from Beer's plot was found out to be 22.22 ng/cm^{-2}.

Table No.2 : Preparation and Accuracy of the Method

Amount of copper(II) taken = 20 ppm

λmax = 630 nm

Concentration of the reagent taken = 1×10^{-2}M

Acidity = 1M HCl.

Sr. No.	Absorbance observed	ppm of Cu(II) found, (X)	$X - \bar{X}$	$(X - \bar{X})^2$
1	0.111	20.00	0.014	0.000196
2	0.115	20.06	0.046	0.002116
3	0.115	20.06	0.046	0.002116
4	0.106	19.95	0.064	0.004096
5	0.111	20.00	0.014	0.000196
6	0.106	19.95	0.064	0.004096
7	0.115	20.06	0.046	0.002116
8	0.111	20.00	0.014	0.000196
9	0.115	20.06	0.046	0.002116
10	0.111	20.00	0.014	0.000196
	Total	200.14		0.01736

$$\text{Average value } (\bar{X}) = \frac{200.14}{10}$$

$$= 20.014$$

Standard deviation (δ)

$$\delta = \sqrt{\frac{(X_1 - \bar{X})^2 + (X_2 - \bar{X})^2 + \text{------} (X_n - \bar{X})^2}{(n - 1)}}$$

$$= \sqrt{\frac{.01736}{10 - 1}}$$

$$= \sqrt{\frac{.01736}{9}}$$

$$= 0.048$$

Error (E)

Error (E) = Observed reading - Actual reading

= 20.014 - 20.00

= 0.014

Relative error

Percent (Accuracy)

$$= \frac{0.014 \times 100}{20}$$

$$= .07$$

Percentage coefficient of variation :

$$\% \text{ C.V.} = \frac{\delta \times 100}{\bar{X}}$$

$$= \frac{0.048 \times 100}{20.014}$$

$$= 0.5895$$

$$= 0.6$$

Reproducibility with 95 percent confidence limit :

$$\delta = \bar{X} \pm 2.26 \times \frac{\delta}{\sqrt{n}}$$

$$= 20.014 \pm 2.26 \times \frac{0.048}{\sqrt{10}}$$

$$= 20.014 \pm 2.26 \times 0.03430$$

$$= 20.014 \pm 0.03430$$

Molar Extinction coefficient :

$$\varepsilon = \frac{\text{Absorbance}}{\text{ppm}} \times 1000 \times \text{Atomic weight}$$

$$= \text{Slope} \times 1000 \times \text{Atomic weight}$$

$$= .045 \times 1000 \times 63.546$$

$$= 2859$$

$$\varepsilon = 2859 \text{ Lmole}^{-1}\text{cm}^{-1}$$

Sandell's Sensitivity (S) :

$$S = 10^3 \times \text{Atomic weight} \times \text{Cmin}$$

$$\text{Where Cmin} = \frac{\text{Dmin}}{\varepsilon \times b}$$

$$= 10^3 \times 63.546 \times \frac{.001}{2.859 \times 10^3 \times 1}$$

$$= 10^3 \times 63.546 \times \frac{.001}{2859 \times 10^3 \times 1}$$

$$S = .02222$$

$$S = 22.22 \text{ ng}|\text{cm}^{-2}$$

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