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CHAPTER - III

**PHOTOMETRIC DETERMINATION OF MOLYBDENUM(VI)  
WITH 5-NITROSALICYLALDEHYDE THIOSEMICARBAZONE**

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PHOTOMETRIC DETERMINATION OF MOLYBDENUM (VI) WITH  
5-NITROSALICYLALDEHYDE THIOSEMICARBAZONEIntruduction :

Molybdenum is gray, heavy, hard and refractory metal, which is useful principally in the targets of X-ray tubes and structural members in high vacuum tubes for electronic purposes because of the metals ability to form tight seals with glass.

Molybdenum alloys are notable for their hardenability and toughness (which makes them useful for high speed tools, armor plates), for their corrosion resitance and at elevated temperatures (ferrus and non-ferrous alloys). It also finds its way into important catalysts used in the petroleum and chemical industries, pigments, lubricants and fertilizers, compounds of radio tubes and more recentely in jet engines.

Its most stable oxidation states are +3, +5 and +6, the last being the commonest. As a trace element it is essential to the health of plants and probably of animals. Numerous reagents have been reported for the photometric determination of molybdenum in aqueous medium and also number of extractive photometric methods are known, but few are in use. The most extensively used method is the thiocyanate method which is

highly sensitive and selective also. The molybdenum thiocyanate complex is redish-brown and is easily oxidised in air but its stability is enhanced in presence of acetone or on extraction into oxygen containing solvents to allow its application in spectrophotometry.

Molybdenum forms stable and often intensely coloured complexes with poly-phenols and other organic poly-hydroxy compounds.<sup>1</sup> Amongst the aromatic o-dihydroxy compounds used for the photometric determination of Mo, the most important are pyrocatechol,<sup>2</sup> stilbazo,<sup>3</sup> 3,4-toluenedithiol,<sup>4</sup> dihydroxy-3-phenyl coumarin,<sup>5</sup> quercetin,<sup>6</sup> quinalizarin,<sup>7</sup> phenylfluorone.<sup>8-10</sup>

Besides, the methods that have been reported for extractive photometric determination of Mo using chelates are 8-hydroxyquinoline<sup>11-12</sup>, substituted 8-hydroxyquinoline<sup>13</sup>, oximes<sup>14-17</sup>, hydroxamic acids<sup>18-20</sup>, cupferron<sup>21-22</sup>, 8-mercaptoquinoline,<sup>23-24</sup> 1-phenyl-2-methyl-3-hydroxy-4-pyridone<sup>25</sup>, unithiol<sup>26</sup>, 1, 10-phenanthroline<sup>27</sup>, 2, 2'-bipyridyl<sup>28</sup>. Certain chromogenic dyes have also been reported as reagents for photometric determination of Mo in presence of acetyltrimethyl ammonium chloride<sup>29-32</sup>, as a ternary systems. More recently phenylthiosemicarbazone<sup>33</sup>, and thiosemicarbazones of 2,2'-dihydroxybenzophenone<sup>34</sup>, salicylaldehyde<sup>35</sup> are reported as sensitive reagent for determination of molybdenum in aqueous medium. A blue violet colour forms on the reaction of Mo(VI) with stilbazo in acidic medium (pH 2). However, the complex is quite weak and hence needs a large excess of reagent for full

colour development. The method suffers from interferences by large number of common cations. With phenylfluorone the orange-red chelate formed is only slightly soluble in water necessitating the addition of a protective colloid such as gelatin or gum arabic.

The method has narrow range for Beer's validity. Dithiol method is time consuming and requires multiple extraction for quantitative recovery of Mo. Although chromagenic dyes such as bromopyrogallol<sup>28</sup>, Gallein<sup>29-30</sup>, pyrogallol red<sup>31</sup>, are highly sensitive reagents for photometric determination of Mo in aqueous medium, these methods suffer either from interferences of large number of foreign ions or the necessity of heating of the aqueous phase or prolong waiting. 8-Hydroxyquinoline method, however, shows interference due to tungsten, niobium, tantalum, whereas 5, 7-dibromo-8-hydroxyquinoline method is extractive and shows strong interference due to copper, nickel, zirconium, titanium, tartrate, citrate and oxalate.

Extractive separation and photometric determination with benzoin- $\alpha$ -oxime is possible in presence of masking agents. In the extractions with cupferron metals like iron, titanium, vanadium, tin, copper and tungsten are co-extracted, while 8-mercaptoquinoline method needs multiple extraction and the percentage of error in such technique is considerably high. With hydroxamic acids the wavelength of maximum absorption is in the UV region, resulting in the interferences of most common ions. During the extraction of Molybdenum with phenylthiosemicarbazone

the aqueous solution should be heated before extraction. For the removal of interferences due to many foreign ions in the determination of Mo with 2, 2' dihydroxy benzophenone thiosemicarbazone, the aqueous phase needs shaking with 0.1% dithiozone solution in carbontetrachloride. The proposed reagent 5-nitrosalicylaldehyde thiosemicarbazone reacts with molybdenum in acidic medium in the range 0.5-1.2 M HCl to form pink complex in presence of  $\text{SnCl}_2$ . The complex is measured at 520 nm. The method is simple, rapid and highly selective as it is possible to determine traces of Mo in presence of large number of associated elements. The reagents that is proposed is stable, colourless, readily available. Here the extraction is not necessary.

### EXPERIMENTAL

#### Standard Molybdenum Solution :

A standard solution of Molybdenum was prepared by dissolving 0.45 gm of ammonium molybdate in about 100 ml distilled water. The solution was heated gently on hot plate to obtain a clear faint bluish solution. The solution was diluted to 250 ml in volumetric flask with distilled water.

The molybdenum content of the solution was determined gravimetrically by the 8-hydroxyquinoline method. For standardisation of molybdenum, an aliquot of the solution was neutralised to methyl red and then acidified with few drops of sulphuric acid. After addition of 5 ml of 2N sodium acetate

and 60 ml of distilled water, the solution was heated to boiling. Molybdenum was precipitated by the addition of 3% solution of oxine in dilute acetic acid until the supernatant liquid became perceptibly yellow. The precipitate was digested by gentle boiling and simultaneous stirring for 3 minutes. The precipitate was filtered through a sintered glass crucible and washed with hot water until free from the reagent. The precipitate was dried to a constant weight at 130-140 C in oven. It was finally weighed as  $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$ . Suitable concentration containing 100 g per ml was prepared as needed by diluting the stock solution with distilled water.

**Reagent Solution :**

A 0.240 gm of the reagent 5- $\text{NO}_2$ SAT was dissolved in 100 ml freshly distilled and purified 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 period of week. All solutions used in study of diverse ions were prepared from AR grade Chemicals.

**Stannous Chloride Solution :**

4% W/V in 2M hydrochloric acid, 4 gm of colourless  $\text{SnCl}_2$  was dissolved in boiling 20 ml concentrate HCl. A clear solution was then diluted to 100 ml with distilled water. This solution was prepared daily.

**Apparatus :**

Absorption measurements were made with a spectrophotometer Model CL-27 Elico equipped with 1 cm. quartz cells

was used for all the absorbance measurements.

**General Procedure** :

To an aliquot of the solution containing upto 250  $\mu\text{g}$  of molybdenum, 2 ml of  $1 \times 10^{-2}$  reagent solution in dioxane were added. The mixture was adjusted to 0.75M with respect to HCl by rapid addition of HCl followed by 1 ml  $\text{SnCl}_2$  solution. The flask was briskly shaken and was made to 25 ml with distilled water, then cooled in ice bath for five minutes. The absorbance of the pink complex was measured at 520 nm within 30 minutes against reagent blank.

**Results and Discussion**

**Spectral Properties** :

Fig. 1 shows the absorption spectrum of Mo 5- $\text{NO}_2$  SAT complex containing 16 ppm of Molybdenum and  $0.1 \times 10^{-4}$  M reagent at 0.75 M HCl using reagent as blank. Absorption measurements were made in the spectral range 450 to 600 nm. The spectral curve indicates that the complex exhibits absorption maximum at 520 nm, at which wave length the ligand has negligible absorption. The molybdenum complex also has a sharp absorption maximum at 310 nm, which, however, was not found suitable for molybdenum determination, because of the considerable absorption of the reagent at this wavelength. Hence further investigations on Mo-complex were made at 520 nm.

**Effect of Stannous Chloride** :

Fig. 4 shows that the optimum volume of 4%  $\text{SnCl}_2$

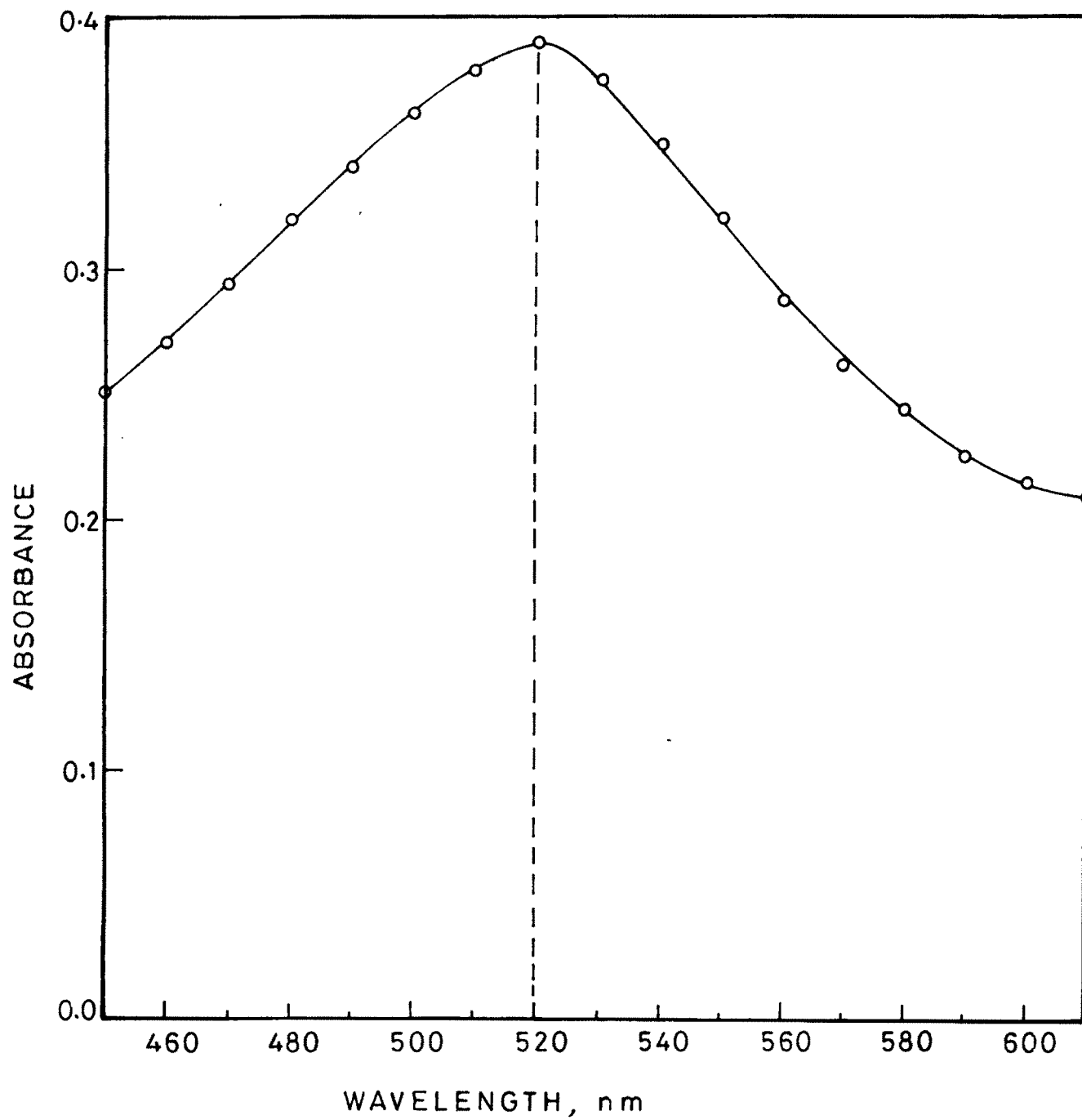


FIG. 1 - ABSORPTION SPECTRUM OF Mo(V) 5-NO<sub>2</sub> SAT.



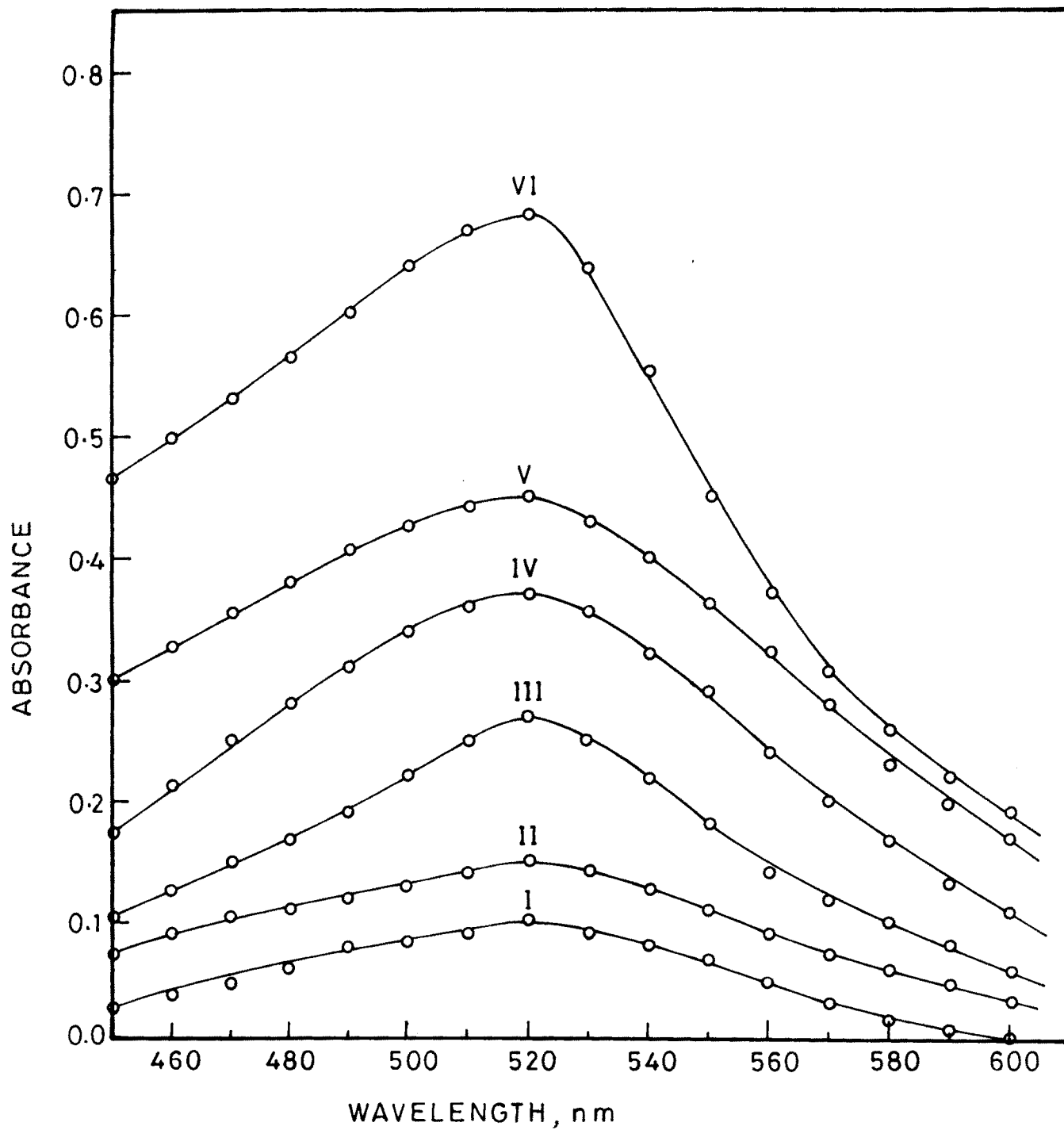


FIG 2 - 6 ABSORBANCE CURVES OF Mo(VI) 5-NO<sub>2</sub> SAT COMPLEX.  
Mo(VI) - I - 10 ppm ; II - 20 ppm ; III - 30 ppm ;  
IV - 40 ppm ; V - 50 ppm ; VI - 60 ppm .

solution required was 0.75-1.5 ml in HCl medium. Hence 1 ml of 4% SnCl<sub>2</sub> was used for investigation of the Mo-complex.

**Effect of Reagent Concentration :**

Solution containing the same amount of molybdenum (16 ppm) different amounts of the reagent varying from 0.5 to 5 ml of  $1 \times 10^{-2}$  M reagent solution were prepared. The colour was developed as outlined in the general procedure and the absorbance of the complex was measured at 520 nm. The results of the studies as shown in the Fig. 2 indicate that 16 ppm of molybdenum required a minimum of 1 ml of 0.01M reagent. At this reagent concentration the metal to reagent ratio in terms of moles is 1:5. However, 2 ml of 0.01M (i.e. 10 fold molar excess) reagent was employed for further studies to ensure maximum colour intensity of molybdenum complex. At higher concentration there was insignificant decrease in absorption.

**Effect of Time and Stability of the Complex :**

In order to study the effect of time on the absorbance of the molybdenum complex containing 16 ppm of molybdenum at 0.75 M acidity, the absorption measurements were made at different time intervals at 520 nm. It was observed that the pink colour developed instantaneously and the absorbance remained constant over a period of 30 minutes, when the solution was chilled in ice bath. Hence the absorption measurements of the complex was made within 30 minutes of the colour development.

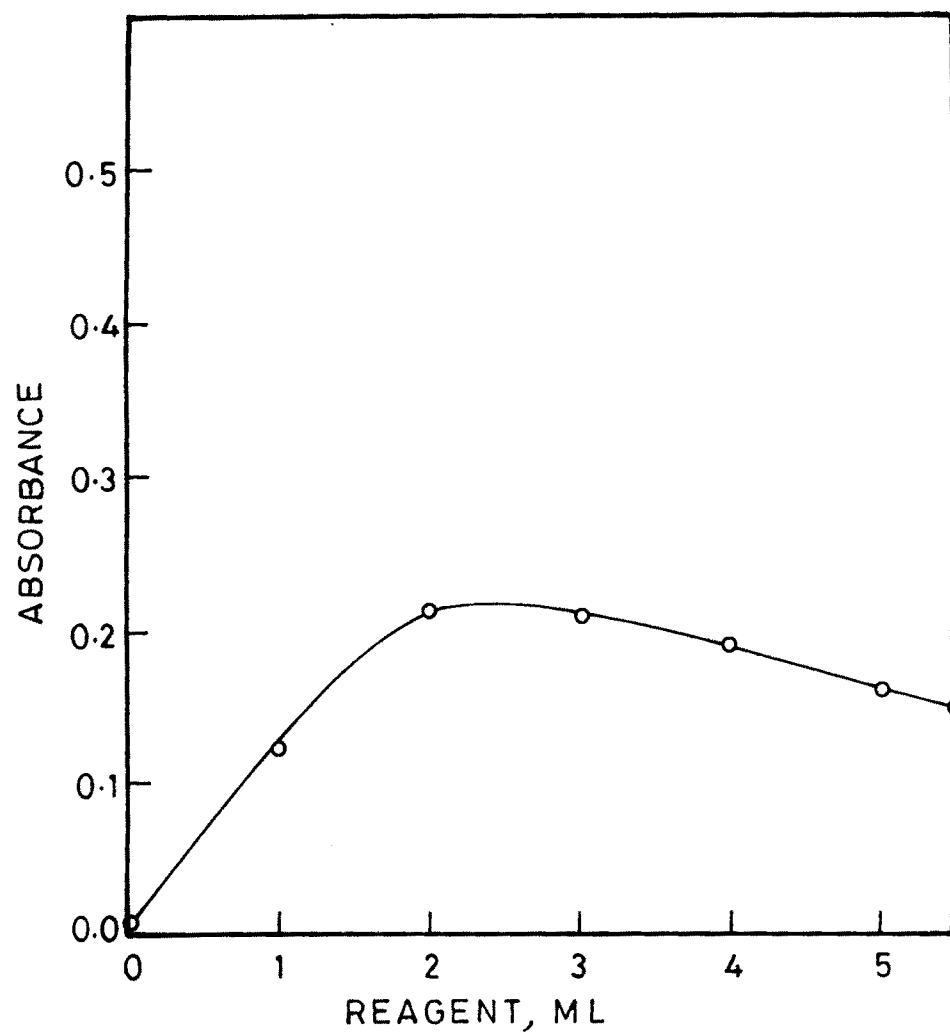


FIG. 2  
EFFECT OF  
REAGENT  
CONCENTRATION.

FIG. 3  
STABILITY OF  
COMPLEX.

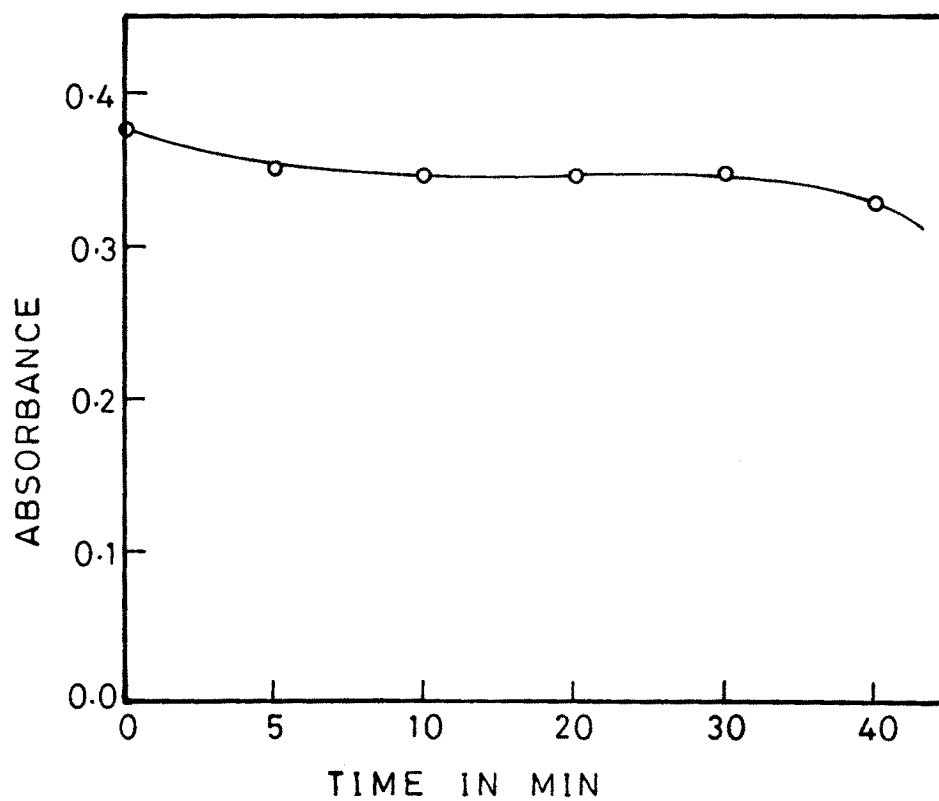


FIG. 4  
EFFECT OF  
ACIDITY

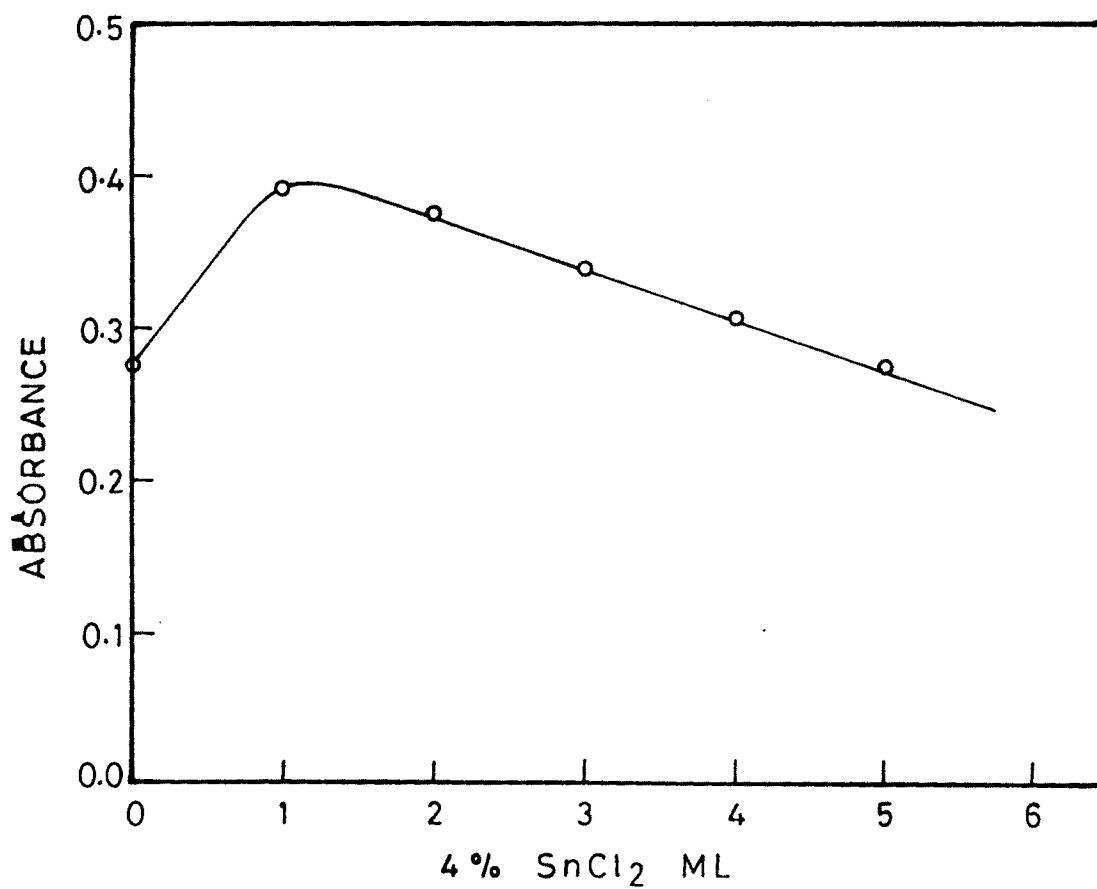
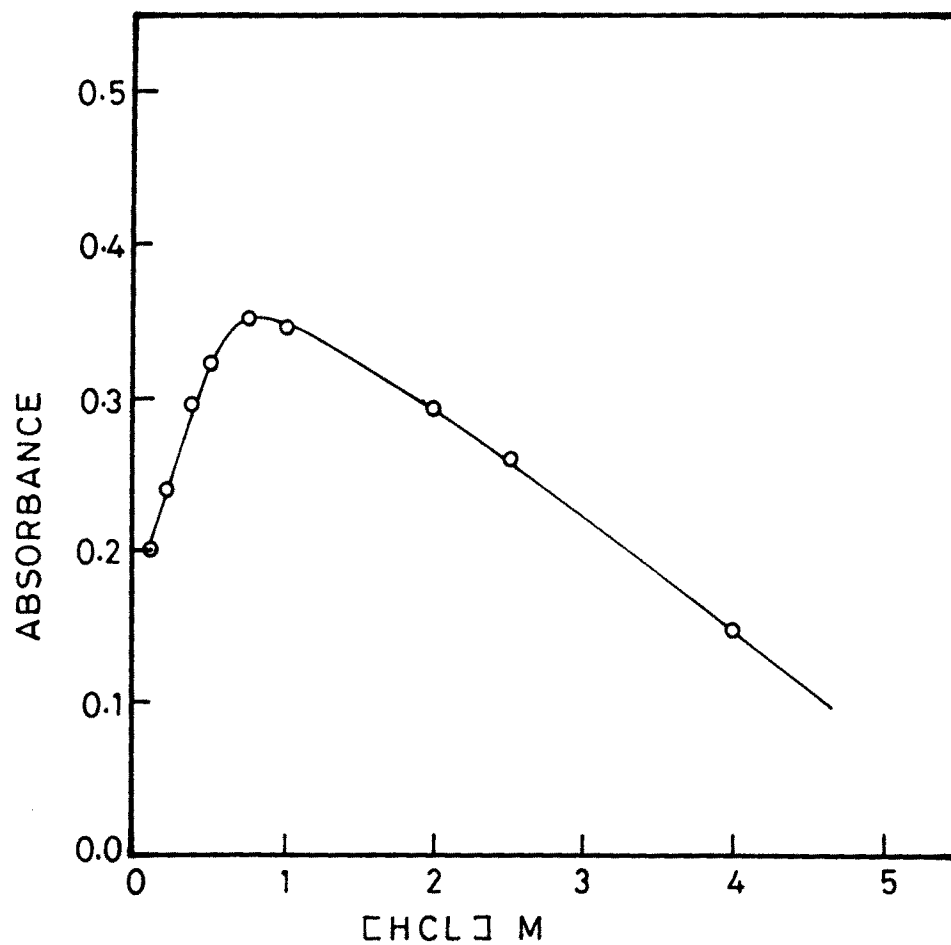


FIG. 5  
EFFECT OF  
SnCl<sub>2</sub>  
CONCENTR-  
ATION.

**Effect of dioxane concentration** :

To study the effect of dioxane concentration a series of solutions were prepared containing fixed amount of Mo (VI) (16 ppm) and different amounts of the dioxane, varying 1 ml to 5 ml of dioxane. The colour of Mo (VI) complex was developed as per the general procedure and absorbance was measured at 520 nm against reagent as a blank. The results of studies are shown in Fig. 3A. Which indicate that 3 ml of dioxane is sufficient for full colour development. For all subsequent measurement 3 ml of dioxane solution was used.

**Validity of Beer's Law** :

The solution containing different amounts of molybdenum in the range 250 to 1750  $\mu\text{g}$  were used for the study of the validity of Beer's Law. The colour was developed as per the recommended procedure using  $1.0 \times 10^{-2}$  M reagent and the absorbance was measured at 520 nm against the reagent as a blank. The curve in fig. 7 shows that Beer's law is valid in the range 10 to 50 PPM of molybdenum.

**Composition of the complex** :

In order to establish the composition of the complex, the equimolar solutions of metal and ligand  $7.521 \times 10^{-3}$  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 was varied from 0.1 - 0.9. Acidity of the solutions was adjusted to 0.75 M with

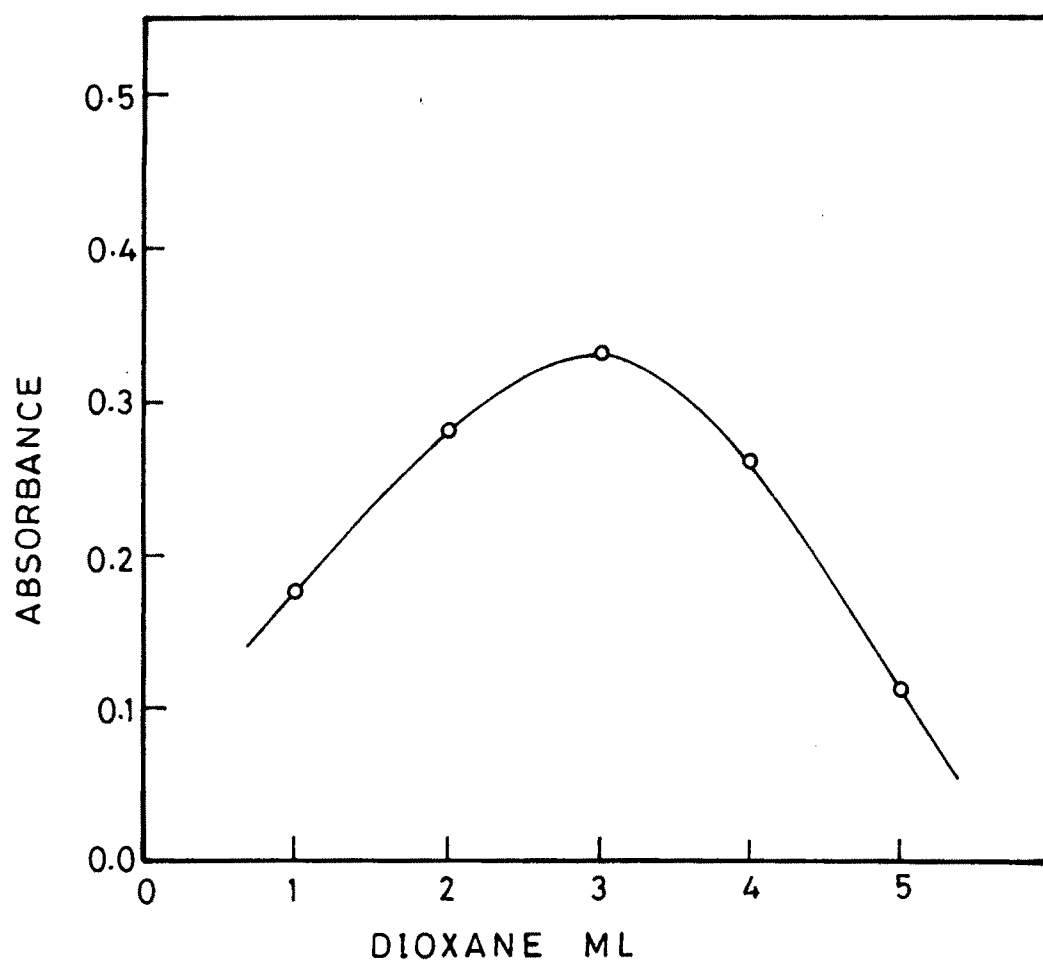


FIG. 3 A - EFFECT OF DIOXANE CONCENTRATION  
Mo(VI) COMPLEX.

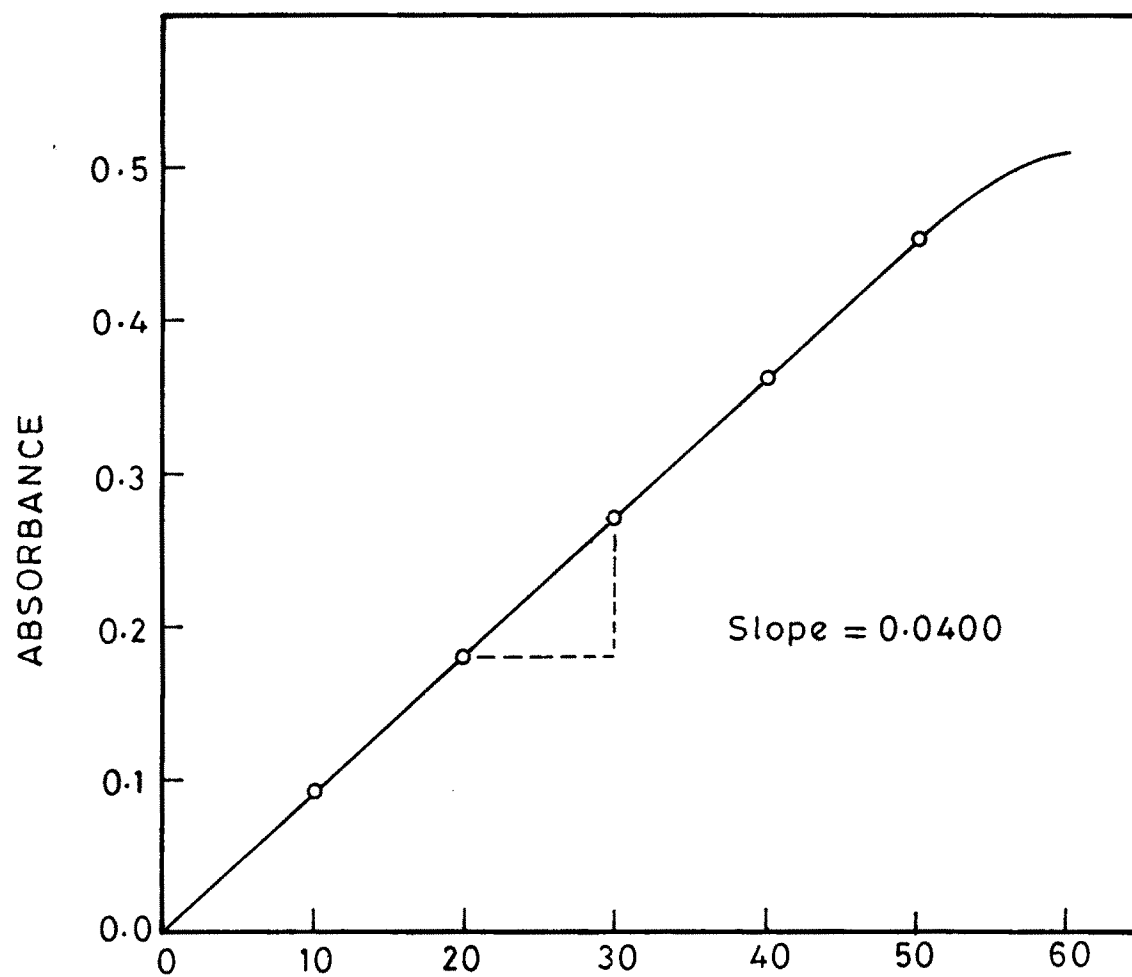


FIG. 7 - VALIDITY OF BEER'S LAW.

HCl and the colour of the complex was developed as per the recommended procedure and the absorbances of the solutions were measured at 520 nm against reagent as a blank. The plot of the absorbance versus the mole fraction of the ligand indicates that the molybdenum (VI) forms 1:1 complex with the ligand 5-nitrosalicylaldehyde thiosemicarbazone (Fig. 8).

The composition of the complex was verified by mole ratio method. For this method equimolar solutions of metal and ligand were used ( $7.521 \times 10^{-3}$  M). A series of solutions containing fixed volume of reagent and different amounts of the molybdenum were prepared. The 0.75 M 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 520 nm. against reagent as a blank. The plot of the absorbance versus the reagent to metal ratio (fig. 8) confirms the results obtained by the application of Job's method.

#### **Effect of Diverse Ions :**

The effects of large number of diverse ions on the determination of 0.25 mg of Mo (VI) using  $1 \times 10^{-2}$  M reagent was studied. The solutions were prepared containing fixed amount of molybdenum and various amounts of foreign ion. The colour of the complex was developed by following the recommended procedure and the absorbance was measured at 520 nm against reagent as blank. An error of less than 2% in absorbance was considered to be tolerable.



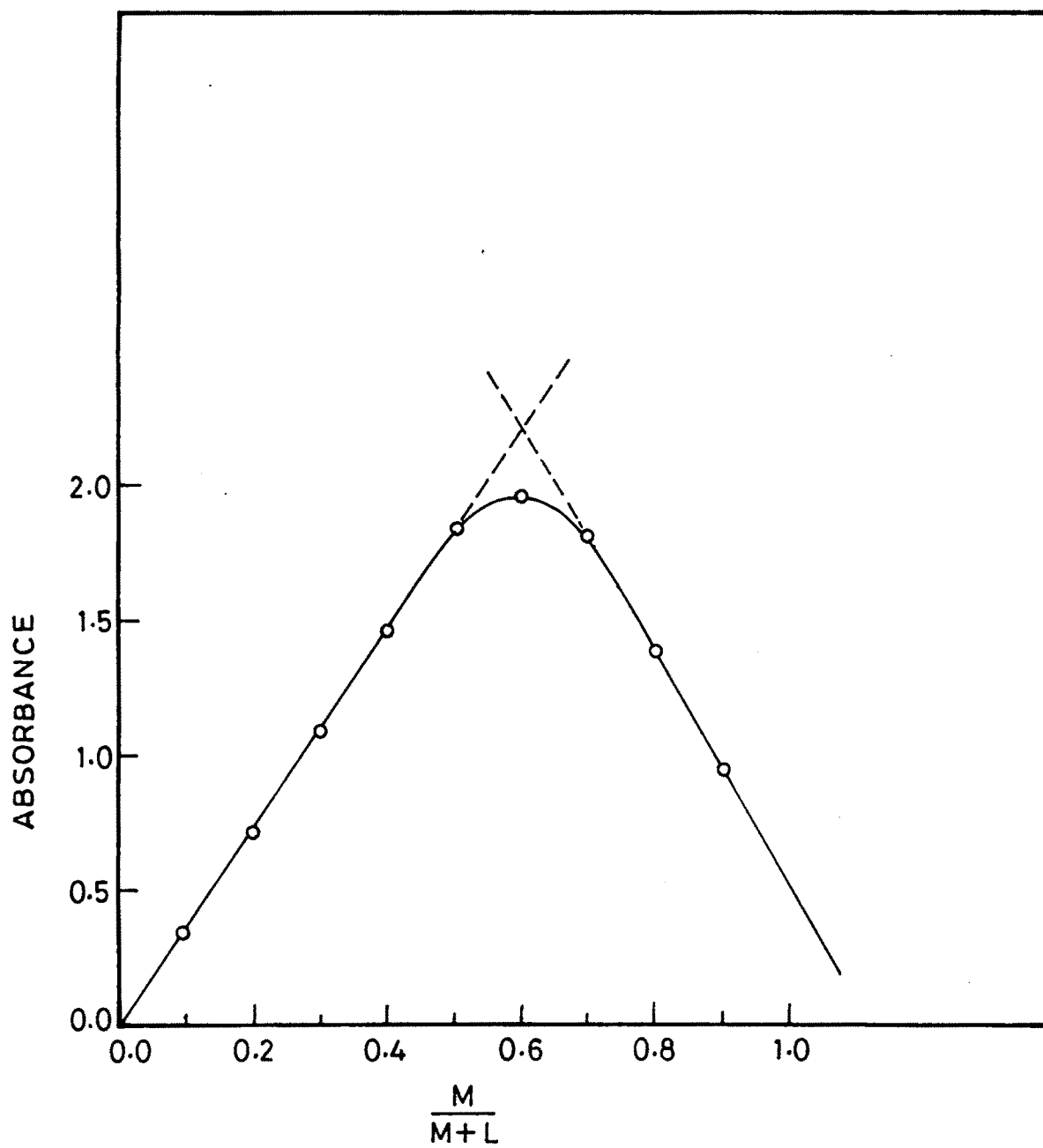


FIG. 8 - JOB'S PLOT .

CONC METAL =  $7.521 \times 10^{-3} M$ CONC REAGENT =  $7.521 \times 10^{-3} M$

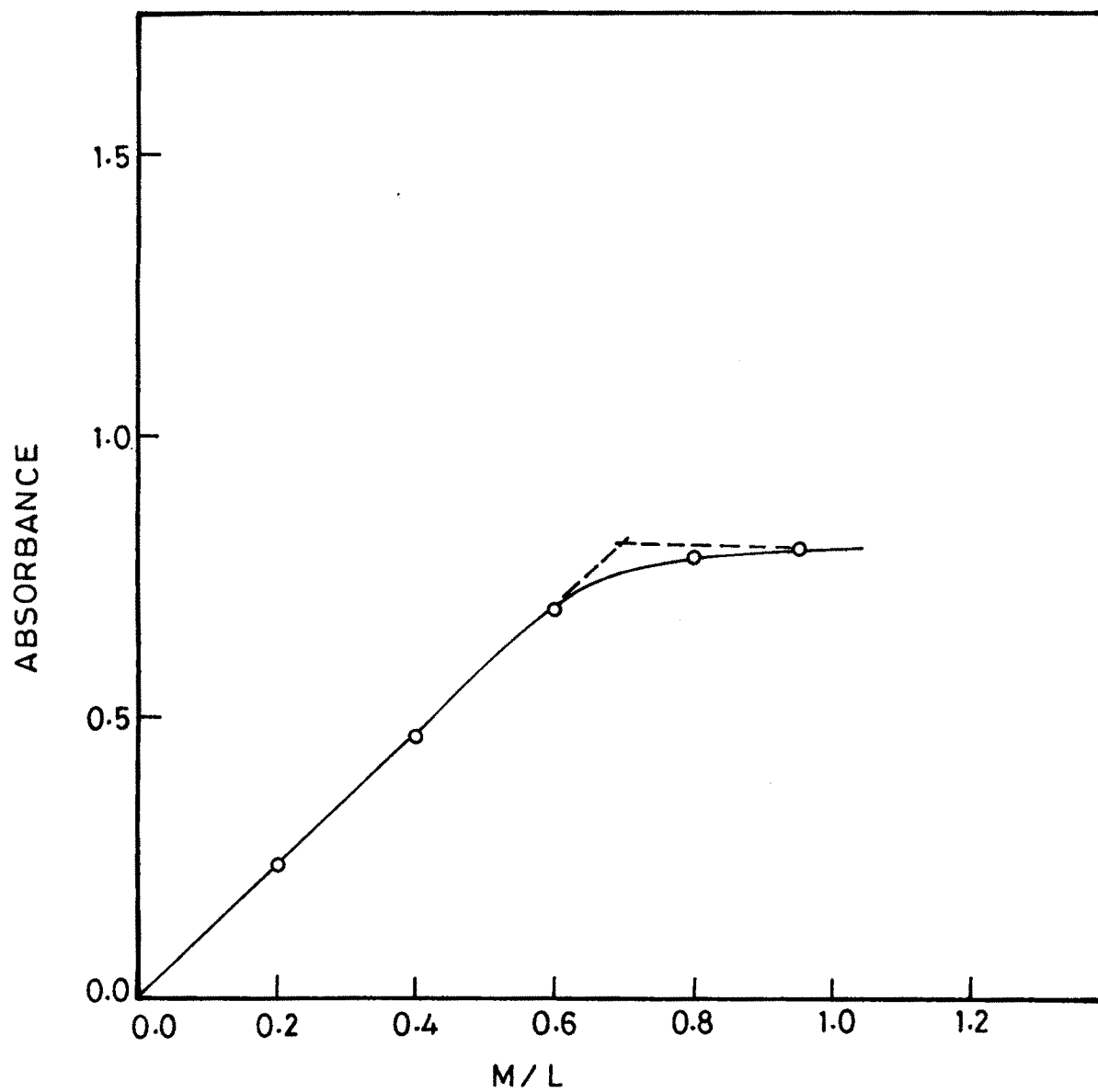


FIG. 9 - MOLE RATIO PLOT.

$$\text{CONC M} = 7.521 \times 10^{-3} \text{ M}$$

$$\text{CONC L} = 7.521 \times 10^{-3} \text{ M}$$

The Table No.1 shows the tolerance limits obtained for various foreign ions. Initially, the large excess of foreign ion was added to the molybdenum solution (20 fold excess for cations). When the interference was intensive, the test were repeated with successively smaller amounts of foreign ion. The results in Table No.1 shows that the cations such as V(V) Ga(III), Sb(III), As(III), Al(III), In(III) and Ru did not interfere when present in 20 fold excess relative to molybdenum. The tolerance limit found for cations like Ti(IV), Mg(II), Mn(II), Fe(III), KI is 5 mg. The ions which interfere in the determination of molybdenum include: Pb(II), Hg(II), TI(III), Zr(IV), Zn(II), Cd(II), Re(VI), Os(VIII), Au(III), Ce(IV), Se(IV), Cr(VI).

Anions showing no interference were thiourea, thiosulphate and sulphosalicylic acid.

**TABLE NO. 1 : Effect of Diverse Ions.**

Mo(VI) = 16 ppm

5-nitrosalicylaldehyde thiosemicarbazone = 0.2% in alcohol.

$\lambda$  max. = 520 nm.

Aqueous phase = 0.75M HCl

FOREIGN ION	TOLERANCE LIMIT in mg
V (V)	5
Ga (III)	5
Sb (III)	5
Mn (II)	4
Bi (III)	4.5
Pb (II)	Interfere

FOREIGN ION	TOLERANCE LIMIT in mg
Hg (II)	Interfere
TI (III)	Interfere
Zr (IV)	Interfere
Zn (II)	Interfere
As (III)	5
Mg (II)	4
Ni (II)	3
Al (III)	5
Cd (II)	Interfere
Re (IV)	Interfere
Os (VIII)	Interfere
Au (III)	Interfere
Ti (IV)	4
U (VI)	3
KI	4
Fe (III)	4
In (III)	5
Ir (VI)	0.5
Ce (IV)	Interfere
Se (IV)	Interfere
Cr (VI)	Interfere
Ru (III)	5
Te (IV)	0.5

**Reproducibility, Accuracy and Sensitivity Data :**

To study the reproducibility and accuracy of the method, ten different identical solutions containing 16 ppm molybdenum were prepared as outlined in the procedure. The absorbance of each solution was measured at 520 nm. against

reagent as a blank. The concentration was determined using the 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 ten readings are calculated. Deviations from these average readings was found out at each case and then standard deviation was calculated. By using standard deviation, the reproducibility of the results with 95% confidence limit was calculated. The sandell sensitivity of the reagent as calculated from Beer's plot was found out to be  $25.08 \text{ ng/cm}^{-2}$ .

**TABLE NO. 2 : PRECISION AND ACCURACY OF THE METHOD**

Amount of Mo = 16 ppm

Sr. No.	Absorbance observed	ppm of Mo found (X)	$X - \bar{X}$	$(X - \bar{X})^2$
1	0.393	16.00	0.062	0.003844
2.	0.390	15.80	0.262	0.06864
3.	0.389	16.00	0.062	0.003844
4.	0.393	16.00	0.062	0.003844
5.	0.394	16.00	0.062	0.003844
6.	0.392	16.16	0.10	0.0100
7.	0.393	16.16	0.10	0.0100
8.	0.392	16.34	0.28	0.0100
9.	0.393	16.16	0.10	0.0784
10.	0.393	16.00	0.062	0.003844
Total		160.62		0.1862

$$\begin{aligned}\text{Average Value } (\bar{X}) &= \frac{160.62}{10} \\ &= 16.062\end{aligned}$$

Standard deviation ( $\delta$ )

$$\begin{aligned}\delta &= \sqrt{\frac{(X_1 - \bar{X})^2 + (X_2 - \bar{X})^2 + \dots + (X_n - \bar{X})^2}{(n - 1)}} \\ &= \sqrt{\frac{0.1862}{9}} \\ &= 0.1438\end{aligned}$$

Reproducibility with 95% confidence limit :

$$\begin{aligned}&= \bar{X} \pm 2.26 \times \frac{\delta}{n} \\ &= 16.062 \pm 2.26 \times \frac{0.1438}{\sqrt{10}} \\ &= 16.062 \pm 2.26 \times \frac{0.1488}{3.162} \\ &= 16.062 \pm 2.26 \times 0.04547 \\ &= 16.062 \pm 0.1027\end{aligned}$$

Error (E) :

$$E = O - A$$

Where O is observed reading

A is Actual reading.

$$\begin{aligned}&= 16.062 - 16 \\ &= 0.062 \text{ } \mu\text{g.}\end{aligned}$$

**Relative Error :**

**Percent (accuracy)**

$$\begin{aligned}&= \frac{0.062 \times 100}{16.00} \\ &= 0.62\end{aligned}$$

**Molar Extinction Coefficient :**

$$\begin{aligned} \epsilon &= \frac{\text{Absorbance}}{\text{ppm}} \times 1000 \times \text{Atomic Weight} \\ &= \text{Slope} \times 1000 \times \text{Atomic Weight} \\ &= 0.0400 \times 100 \times 96 \\ \epsilon &= 3.840 \times 10^3 \text{ LM}^{-1} \text{ cm}^{-1} \end{aligned}$$

**Sandell's Sensivity (S)**

$$S = 10^3 \times \text{Atomic Weight} \times C_{\text{min}}$$

$$S = 10^3 \times 96 \times C_{\text{min}}$$

$$\text{Where } C_{\text{min}} = \frac{D_{\text{min}}}{\epsilon \times b}$$

$$S = 10^3 \times 96 \times \frac{0.001}{3.840 \times 10^3 \times 1}$$

$$= 25.08 \text{ ng/cm}^{-2}$$

$$S = 25.08 \text{ ng/cm}^{-2}$$

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