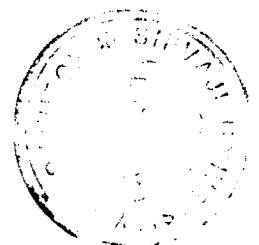


CHAPTER - VI

DETERMINATION OF SILVER



6.1 INTRODUCTION :

Silver is one of the important metals, used especially for jewellery, utensils, and in coinage, but for other purposes also, e.g. for chemical apparatus- crucibles for alkali fusions, for medical instruments and in electrical industry. Silver metal is too soft in a pure condition, therefore is alloyed with other metals such as copper.

Various compounds of silver are used extensively, e.g. in photography, in medicine, in making of marking ink and in laboratory. Silver salts and other silver preparations have wide applications. The most widely used salt, silver nitrate is very important analytical material for the preparation of other silver compounds. Large quantities of silver are employed in electroplating and in the manufacture of mirrors. Silver bromide is extensively used in photography for making the sensitive emulsion for plates and films. Colloidal silver is frequently used in medicine as a germicide, since it has excellent bactericidal properties while being relatively non-toxic towards the bodily organs.

In recent years, numerous reagents for photometric determination of silver have been proposed. But none of them satisfied the requirement of a good photometric reagent for silver. Therefore, suitable reagent and the experimental

conditions for spectrophotometric determination of this element is still a problem to chemists. Several reagents have been suggested for silver, since the introduction of the reagent p-dimethyl aminobenzylidenerhodamine¹, but hardly any one has proved satisfactory.

Silver is determined spectrophotometrically by several reagents such as 4-hydroxybenzylidene rhodamine², 2-(Mercaptoacetamido) pyridine³, ethyl di-(1-sodiotetrazol-5-ylazo) acetate⁴, ammonium 2-cyano-3-iminodithiobutyrate⁵, 1,3-diamino-8-methoxyphenothiazine⁶, thiothenoyl trifluoroacetone⁷, 1,10-phenanthroline⁸, 4-(2-pyridyl-azo) resorcinol⁹, picolinaldehyde thiosemicarbazone¹⁰ and pyridine-2,6-dicarboxylic acid.¹¹ But many of them have one or other drawbacks.

Extractive spectrophotometric determination of complex formation between silver (I) and other reagents such as nitroso derivatives of catechol in presence of bathophenanthroline¹², thiobenzoyl acetone¹³, 2,4-dinitrophenylazocatechol¹⁴ and 1,10-phenanthroline, 1-(2-pyridylazo)-2-naphthol¹⁵, thiodibenzoylmethane¹⁶ and tributyl phosphate¹⁷ have also been studied.

Trace amounts of silver are determined by the formation of dicyanoargentate (I)¹⁸, in some thermoelectric materials¹⁹

and in copper concentrates with eosin.²⁰ The reaction of 18 metallochromic agents²¹ with trace amounts of silver is studied. Pyrogallol red and bromopyrogallol red are both satisfactory reagents at pH 7.0 to 7.5.

Spectrophotometric micro determination of silver is studied with 4-(2-quinolyazo) phenol²² followed by the addition of $\text{Na}_2\text{B}_4\text{O}_7$ and with Michler's thioketone²³, N-benzene sulphonyl-L-cysteine²⁴ is used for semi-micro titrimetric estimation of silver. Gravimetrically silver is determined by the formation of hexaammine cobalt (III) dithiosulphato argentate (I) complexes.²⁵

Silver is also determined in fixing baths²⁶, in nuclearpure uranium²⁷ and in pure selenium and tellurium with 1,5-di-2-naphthylthiocarbazone.²⁸

By spectrophotometric method, silver is estimated as 2-amino-5-methylthiopyrimidine-4-carboxylic acid chelate.²⁹ It is also determined with crystal violet³⁰, with 2,2'-bipyridyl and 2,2' : 6',2''-terpyridyl³¹ and with resorcylic 4-aldehyde thiosemicarbazone.³² But many of them lack either desired sensitivity or selectivity. However several modifications have been made in the experimental conditions to get the best results.

Photometrically silver (I) is determined by means of dithizone³³ without extraction and with 1,10-phenanthroline and halo derivative of fluorescein.³⁴

Absorption, fluorescence and kinetic spectrophotometric methods of silver are reviewed.³⁵

Selective method of separating silver from nitrate-bromide solutions³⁶ is studied. Silver is determined by studying the system silver aromatic amine sulpharsazen³⁷ spectrophotometrically. Selective and sensitive colour reaction for silver is found with a mixture of EDTA, 1,10-phenanthroline, ammonium acetate and bromopyrogallol red.³⁸ The U.V. spectra of yellow complexes of silver with 2,2'-bipyridyl and 1,10-phenanthroline in acid medium³⁹ are investigated.

Silver is studied with other cations also. It is determined spectrophotometrically as impurity⁴⁰ in Cd-Hg-Te thin layers by dithizone method. Ag (I) and Hg(II) are determined with a solid reagent which are formed by the interaction of Brilliant green (C.I. Basic Green I) cation with the tetraphenyl borate anion.⁴¹ Silver and mercury are also determined photometrically with glyoxal dithiosemicarbazone.⁴²

Dipyridylglyoxal thiosemicarbazone⁴³ reagent gives strong colour reactions with numerous cations such as Hg(I), Cu(II), Pd(II), Pt(IV), Fe(II), Co(II), Ni(II), Mn(II) and Ag(I). Tris-(2,2'-bipyridyl) iron (II) tetraphenyl borate⁴⁴ is used as solid analytical reagent in the spectrophotometric determination of Ag(I), Hg(II) and Tl(I). The reactions of picolinaldehyde thiosemicarbazone⁴⁵ with Ag, Hg, Fe(II) and Co are studied in various media and the composition of the complexes are established by spectrophotometric method. Silver, gold, palladium and platinum are determined with thiodibenzoyl methane⁴⁶ by extraction photometric method. Thio-Michler's ketone⁴⁷ [4,4'-bis (dimethylamino) thiobenzophenone] offers a sensitive analytical reagent for spectrophotometric or extraction photometric determination of several metals, such as Ag, Cu, Au, Hg, Pd, Pt, Ir and Se under appropriate conditions of solvent, pH and ratio of reactants.

2-Benzoyl pyridine guanyldrazone is used for photometric determination of traces of silver at pH 11.0 as a yellow complex in ethyl alcohol. The complex is measured at 400 nm. The proposed method is simple, rapid and highly sensitive.

6.2 EXPERIMENTAL :

6.2.1 Standard solutions :

Standard silver (I) solutions

Standard silver solution 0.1 mg/ml was prepared from silver nitrate in doubly distilled water and the solution

was standardized with Volhard's method volumetrically.⁴⁸

Further dilutions for experimental purposes were made by diluting the stock solution with distilled water.

Reagent solution :

A stock solution of reagent (BPG) 0.06% was prepared by dissolving 60 mg of it in 100 ml distilled ethanol. ($2.511 \times 10^{-3} \text{M}$).

All other chemicals were of analytical grade.

Buffer solution :

Buffer solution of pH 11 was prepared by mixing appropriate amounts of caustic soda and sodium tetraborate.

6.2.2 Recommended procedure :

An aliquot of the solution containing 50-100 μg of Ag(I) was taken in 10 ml volumetric flask. To this, 1 ml of reagent (BPG) solution of concentration $2.511 \times 10^{-3} \text{M}$ was added. The pH of the solution was adjusted to 11.0 with buffer solution and was diluted upto the volume with distilled ethanol. The absorbance of the complex Ag-BPG was measured at

400 nm against reagent blank prepared in the same manner excluding metal ion. The concentration of silver in unknown solution was found out from standard calibration curve obtained under identical conditions.

6.3 RESULTS AND DISCUSSION :

6.3.1 Spectral characteristics :

The absorption spectrum of Ag-BPG complex of the solution containing 5.565×10^{-5} M silver and 1.506×10^{-4} M reagent was recorded at pH 11.0 against reagent blank. The complex has an absorption maximum at 400 nm. The molar extinction coefficient of the complex at 400 nm is 1.991×10^4 l mole⁻¹cm⁻¹. Absorption spectra of the complex and reagent are shown in figure 6.1 and the observations are shown in table 6.1.

6.3.2 Effect of pH :

To study the effect of pH, a series of solutions containing 5.565×10^{-5} M Ag(I) and 2.511×10^{-3} M reagent (BPG) in varying pH were prepared as per the recommended procedure. In basic medium, the complex has maximum and constant absorbance over the pH range 10.0 to 13.0. Therefore pH 11.0 was selected as the optimum pH for the study of Ag-BPG complex. The plot of observations is shown in figure 6.2.

Table 6.1 : Molar extinction coefficients of the Ag(I)-BPG complex and the reagent (BPG).

Wavelength, λ , nm	Molar extinction coefficients, ϵ	
	Ag(I)-BPG complex $\epsilon \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$	BPG $\epsilon \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$
360	0.483	0.2948
370	0.721	0.1115
380	1.024	0.0509
385	1.141	0.0422
390	1.347	0.0387
395	1.428	0.0341
400	1.991	0.0298
405	1.383	0.0199
410	1.347	0.0174
420	1.114	0.0049
430	0.826	0.0030
440	0.575	0.0010
450	0.440	0.0000
460	0.336	-
470	0.269	-
480	0.262	-
490	0.251	-
500	0.249	-
510	0.242	-
520	0.203	-
530	0.185	-
540	0.157	-

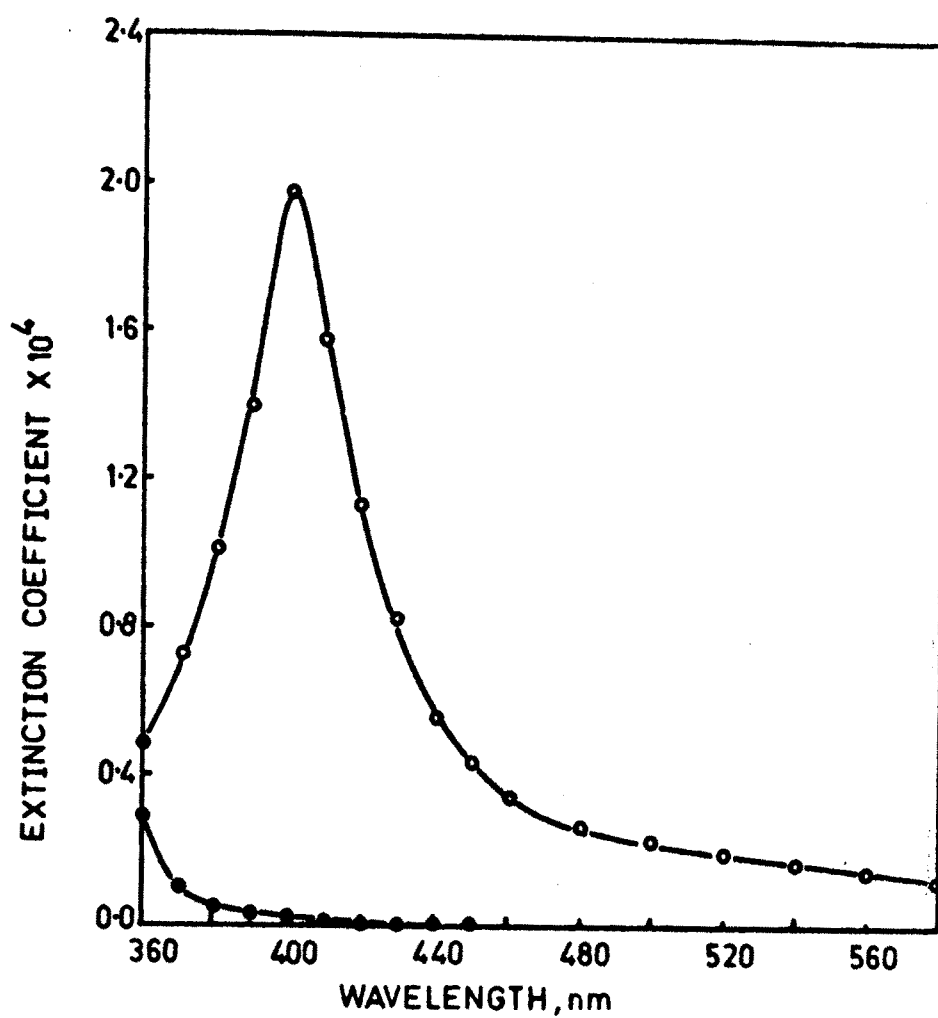


FIG. 6.1 ○—○ ABSORPTION SPECTRUM OF SILVER-BPG COMPLEX
●—● ABSORPTION SPECTRUM OF REAGENT (BPG)

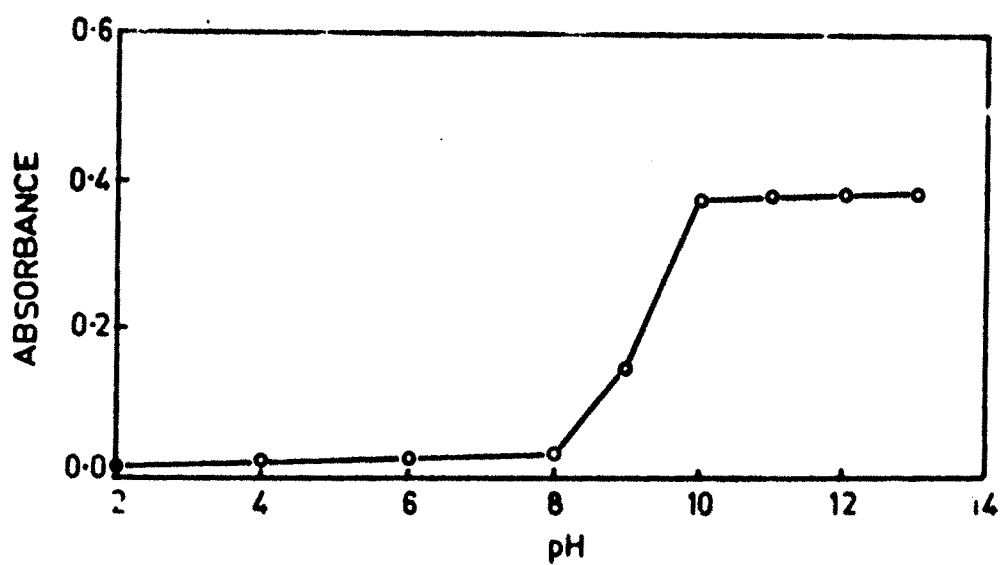


FIG. 6.2 EFFECT OF pH

6.3.3 Effect of reagent concentration :

A series of solutions were prepared in which the concentration of BPG was varied from 5.02×10^{-5} M to 3.514×10^{-4} M, while the concentration of Ag was kept constant at 5.565×10^{-5} M. The pH values of the solutions were adjusted and the solutions were made upto the mark in 10 ml volumetric flask. Absorbances were measured at 400 nm against reagent blank. The results given in table 6.2 show that three-fold molar excess of the reagent is sufficient for full colour development. The observations are given in table 6.2

Table 6.2 : Effect of reagent concentration (BPG)

$$[\text{Ag(I)}] = 6 \text{ ppm}; [\text{BPG}] = 2.511 \times 10^{-3} \text{ M.}$$

ml of reagent	Absorbance at 400 nm
0.2	0.39
0.4	0.42
0.6	0.45
0.8	0.45
1.0	0.45
1.2	0.45
1.4	0.45

6.3.4 Stability and reaction rate :

Ag-BPG complex is stable for several hours and complex formation is instantaneous. Complex formation is independent of temperature.

6.3.5 Validity of Beer's law :

The solutions containing different amounts of silver and same amount of reagent (BPG) 0.6 ml of $2.511 \times 10^{-3} \text{M}$ at pH 11.0 were used to study the validity of Beer's law. It was found that Beer's law is valid upto 10 ppm of silver at 400 nm (Fig. 6.3).

Optimum concentration range for the determination of silver was calculated from Ringbom plot⁴⁹ and was found to be 3.20 to 7.55 ppm at 400 nm (Fig.6.4).

6.3.6 Composition of the complex :

The composition of Ag-BPG complex was determined by Job's continuous variation method⁵⁰, mole ratio method⁵¹ and slope ratio method.⁵² For Job's method, a series of solutions were prepared by keeping the sum of molar concentrations of Ag and BPG constant, while their ratio varied in different solutions. This was achieved by taking equimolar solutions

of Ag (I) and BPG (2.3185×10^{-5} M). A plot of absorbance against mole fraction of reagent indicates that the formation of Ag:BPG complex is 1:1 at pH 11.0 (Fig.6.5). For mole ratio studies, ligand concentration (1.85×10^{-5} M) was maintained constant and different concentrations of metal ranging from 4.637×10^{-6} M to 3.709×10^{-5} M were used. Mole ratio plot indicates and confirms the formation of 1:1 Ag : BPG complex at pH 11.0 (Fig.6.6). This was also confirmed by slope ratio method.

6.3.7 Sensitivity :

The reagent or silver complex do not show any effect due to light.

The photometric sensitivity of the method was calculated by the method of Sandell⁵³ and was found to be $0.01737 \mu\text{g}/\text{cm}^2$.

Molar extinction coefficient of the system at 400 nm is $1.991 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$.

6.3.8 Degree of dissociation and instability constant:

By the method of Harvey and Manning⁵², the degree of dissociation, α , was obtained. The value of α was found to be 0.1160.



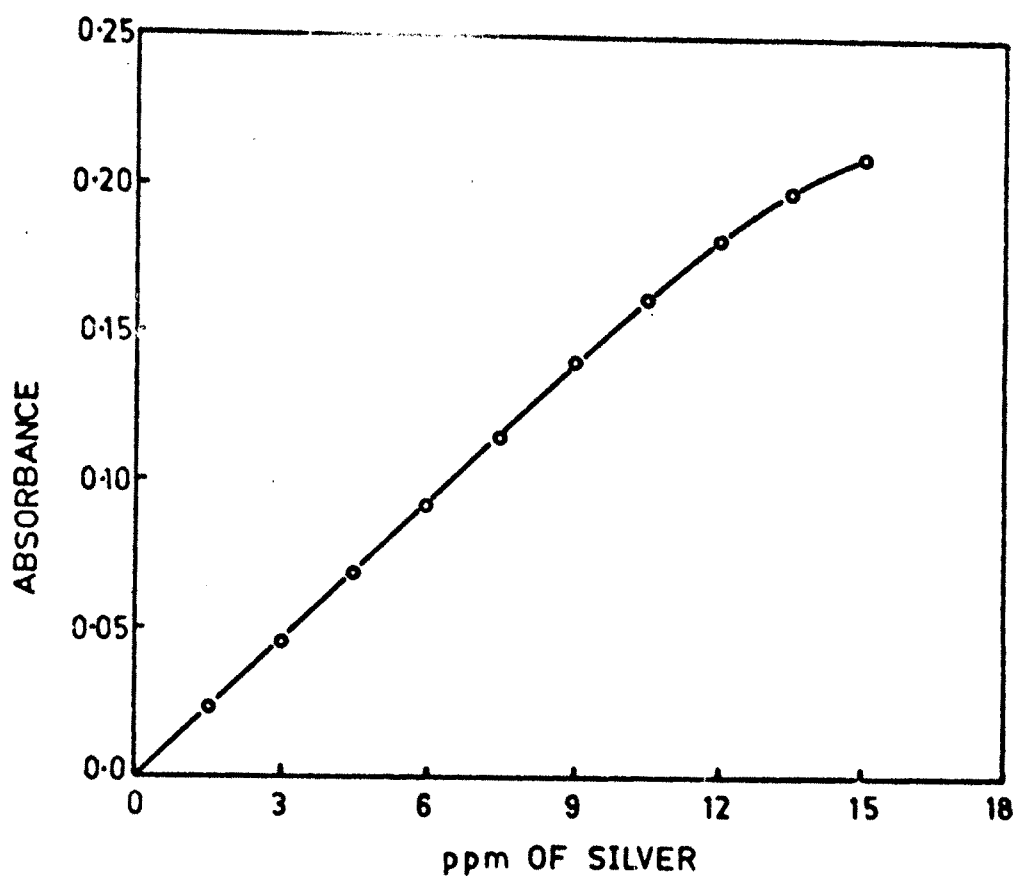


FIG. 6.3 VALIDITY OF BEER'S LAW

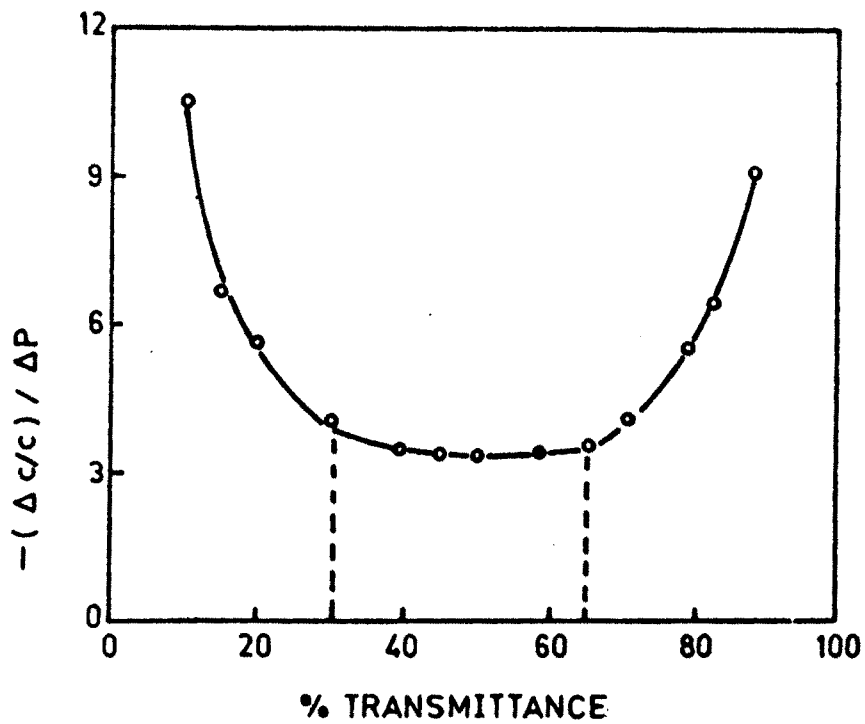


FIG. 6.4 RINGBOM PLOT

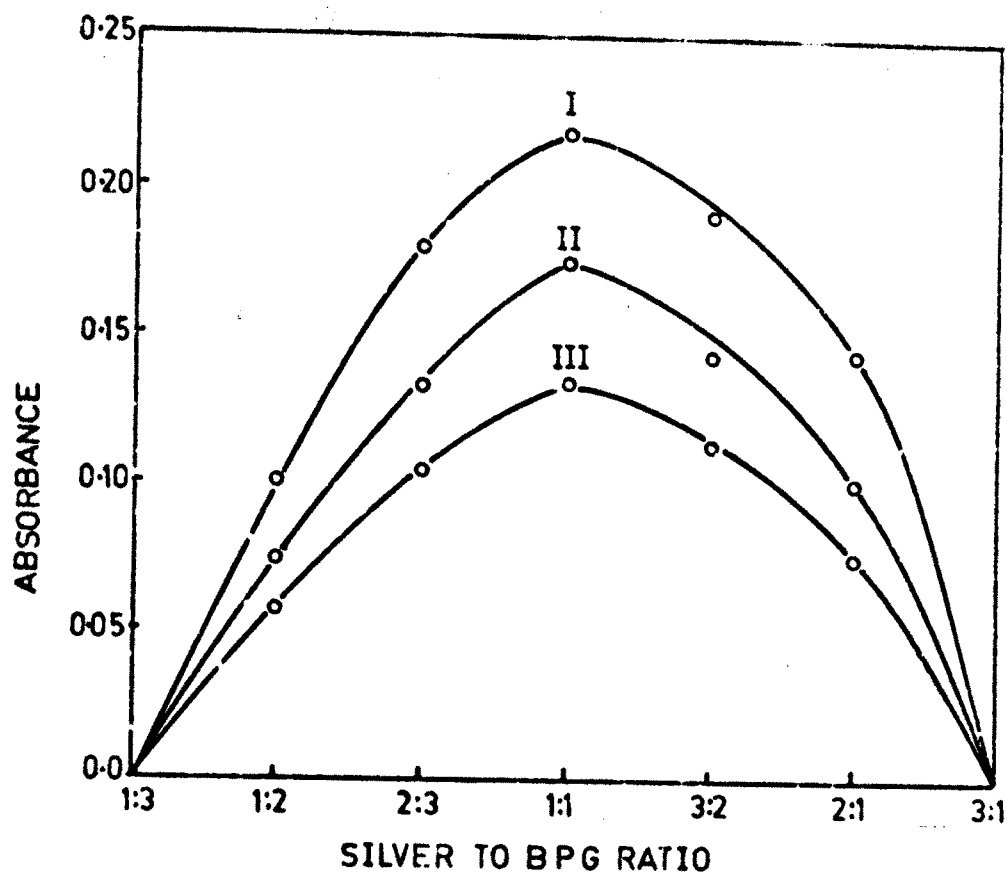


FIG. 6.5 JOBS CONTINUOUS VARIATION METHOD.
I - 400 nm , II - 410 nm , III - 420 nm .

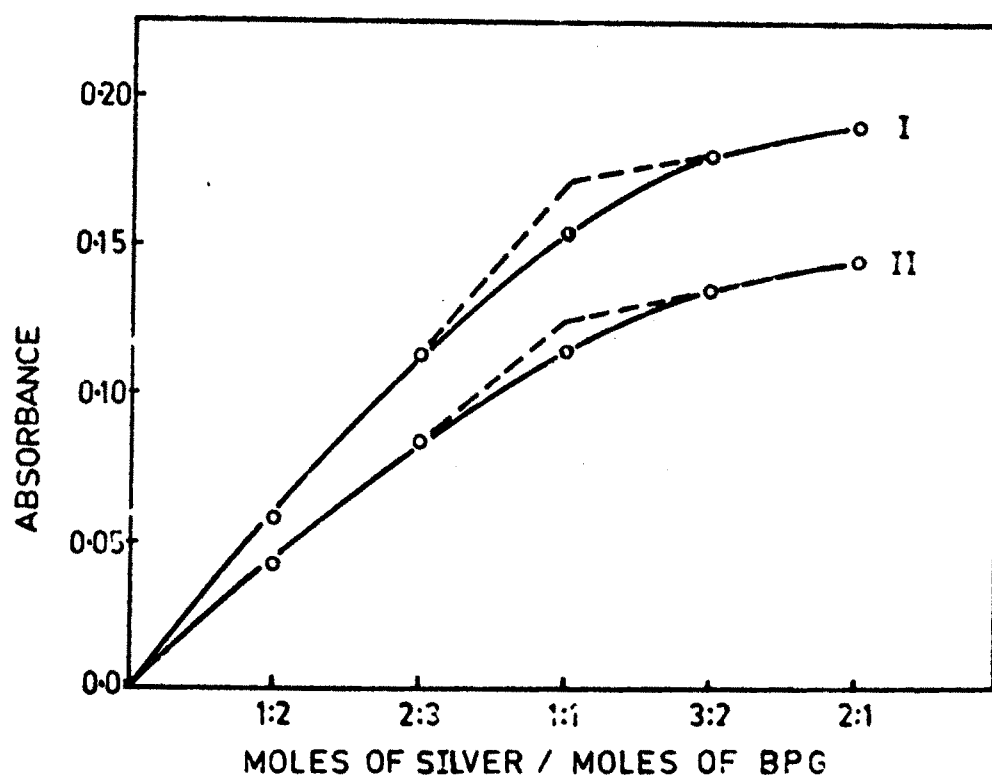


FIG. 6.6 MOLE RATIO METHOD.
I - 405 nm , II - 430 nm .

The apparent instability constant⁵⁴ was found to be 3.529×10^{-7} for Ag-BPG complex. The change in free energy⁵⁵ of the system is -8.859 K cal/mole.

6.3.9 Reproducibility of the method :

The reproducibility of the method was tested by determining different amounts of silver as per recommended procedure. The results are tabulated in table 6.3 which show that the method is reproducible. The standard deviations of the method was calculated for 10 observations and the coefficient of variation are given in table 6.3.

Table 6.3 : Reproducibility of the method:

Silver(I) ppm	Mean of 10 observations	Standard deviation	Coefficient of variation, %
3	0.045	0.001	2.22
6	0.092	0.003	3.24
9	0.137	0.004	2.92

6.3.10 Effect of diverse ions :

The effect of diverse ions was studied using fixed amount of silver (6 ppm) by developing and measuring the

colour intensity as per recommended procedure. Interference was assumed to occur if the observed absorbance of Ag-BPG complex differed from the expected absorbance by 2% in presence of the diverse ion. Cations like Co(II), Ca(II), Ni(II), Ba(II), Al(III), Fe(III), Cu(II), Hg(II) and Mr(II) interfere seriously. The tolerance limit of W (VI) is 140. For various foreign ions, the tolerance limits are listed in table 6.4.

Table 6.4 : Effect of diverse ions

$$[\text{Ag(I)}] = 6 \text{ ppm}$$

$$[\text{BPG}] = 2.008 \times 10^{-4} \text{ M}$$

Foreign ions	Added as	Tolerance limit, ppm
<u>Cations</u>		
Bi(III)	Bi(NO ₃) ₃	2
Co(II)	CoSO ₄ · 7H ₂ O	none
Ca(II)	CaCl ₂	none
Tl(I)	TlCl	2
Ni(II)	NiSO ₄ · 6H ₂ O	none
W(VI)	Na ₂ WO ₄ · 2H ₂ O	140
Ba(II)	BaCl ₂ · 2H ₂ O	none
Al(III)	AlCl ₃ · 6H ₂ O	none
Fe(III)	FeCl ₃	none
Ce(IV)	Ce(SO ₄) ₂	0.5
Cu(II)	CuSO ₄ · 5H ₂ O	none

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Foreign ions	Added as	Tolerance limit, ppm
<u>Cations</u>		
Cr (VI)	K_2CrO_4	1
Zn (II)	$ZnSO_4 \cdot 7H_2O$	6
Hg (II)	$HgCl_2$	none
Mn (II)	$MnCl_2 \cdot 6H_2O$	none
V (V)	V_2O_5	0.5
Pb (II)	$Pb(NO_3)_2$	4
U (VI)	$UO_2(NO_3)_2$	25
<u>Anions:</u>		
Citrate	Sodium citrate	2
Oxalate	Potassium oxalate	3
Thiourea	Thiourea	none
Fluoride	Ammonium fluoride	5
Acetate	Sodium acetate	400
EDTA ⁻⁴	Disodium salt	150
Phosphate	Potassium hydrogen orthophosphate	30
Tartrate	Antimony potassium tartrate	1
Thiocyanate	Potassium thiocyanate	1

6.4 APPLICATIONS :Analysis of copper-silver alloy :

A known weight ≈ 0.05 g of the sample of copper-silver alloy was dissolved in 10 ml 1:1 nitric acid with mild heating. The solution was heated to remove excess nitric acid. The resulting solution was diluted to 100 ml with distilled water. A suitable aliquot of the solution was taken. As the alloy contains large amount of copper, it is removed by extraction with acetyl acetone. Silver from this solution was determined as Ag(I)-BPG complex by recommended procedure. The results are given in table 6.5.

Table 6.5 **L** Analysis of copper-silver alloy :

Alloy	Certified value of Ag, %	Experimental value of Ag, %	Relative standard deviation for 10 observations
Copper- silver	45.00	44.44	0.07

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