CHAPTER - II

DETERMINATION OF GOLD (III)

2.1 INTRODUCTION

On account of its brilliance and stability, gold has attracted attention of the primitive man and it is one of the first metals known to man.

Gold is relatively a rare metal which occurs in nature almost exclusively in the native state associated with other metals like silver, copper, platinum, lead etc. Native gold is found in veins of quartz as reef gold and in alluvial sand as alluvial gold. Traces of gold have been detected in sea-water. From the studies of the solar spectrum, the abundance of gold in the sun is found to be 0.04 ppm, while in the earth crust it is about 0.004 ppm.

Gold is the most beautiful of the chemical elements. Pure gold is a bright lustrous metal with a high specific gravity (19.3). It melts at 1063°C and molten metal appears green. It is most malleable and ductile. A gold leaf of about 0.0001 mm thickness can be obtained. Gold is a noble metal and it is not acted upon by air or oxygen or H_2S. However, it is directly attacked by halogens. It is not attacked by alkali solutions or by any acid not even by hydrofluoric acid. However, it is dissolved in aqua regia.

Gold is mainly used for ornamental purposes and in jewellery since it retains its bright surface untarnished. Pure gold is too soft for this purpose, it is mixed with small quantities of copper to make it harder.

Gold is also used for gold-plating. Gold was formerly used in currency but this use of gold has been appreciably decreased now-a-days.

Its purity or fineness is expressed in carats. Pure gold is 24 carat. Colloidal gold is used in colouring glass and enamels. Gold has high thermal and electrical conductivity, hence it is used in electronics. The infra-red reflectivity of gold leads to its use in aeronautics and space industries. While its low chemical reactivity leads to use in lining specialised chemical plant and alloyed with platinum, in the production of viscous rayon. It is also useful as a catalyst in hydrogenation of alkenes, alkynes and dienes. The use of gold in microelectronic circuit is increasing rapidly. There is an increasing interest in the development of new gold complexes for use in the treatment of arthritis.

In 1965, Beamish published a critical review of the methods for photometric determination of noble metals[1]. He has also written an important reference work on the analytical chemistry of noble metals[2]. Beamish comments on the deficiency of the methods,for the more common of the noble metals, namely gold and platinum. Recently, Bhattacharya et al.[3] have reviewed the reagents and methods used for the determination of gold. The monograph describing the chemistry of gold[4] has appeared recently.

Numerous methods have been proposed for the photometric determination of gold (III). However, very few have analytical value. Several spectrophotometric methods based on the formation of colloidal precipitate of elemental gold using stannous chloride[5], p-dimethyl aminobenzylidene - rhodanine[6], variamine blue[7] etc. have been reported. The colloidal suspensions are unstable thereby rendering the method less reliable. Au(III) is a strong oxidising agent. It oxidises various organic substances to intensely coloured products in mineral acid solutions and several methods for determination of Au(III) based on this principle have been described, e.g. oxidation of leuco-compound of malachite green[8], o-toluidine[9], o-dianisidine[10], luminol[11] etc. But such methods are unspecific.

Several attempts have been made to separate gold from other elements. Numerous reagents are available for trace determination of gold and most of them are used for extractive photometry.

Ascorbic acid[12] forms complex, which is stable for one hour. o-Aminobenzene arsonic acid[13] forms complex after 40 to 90 minutes. Complexes of o-toluidine[14], NNN'N' tetramethyl o-toluidine[15] and azide[16] are stable for very short time and colour of the complex goes on fading. So these methods are less reliable. In case of p-amino hippuric acid[17], solution is kept in dark for colour development. Ammonium pyrrolidine-1-carbodithioate[18] forms complex after heating on boiling water bath, but many cations and anions interfere seriously in this method. Complex of methylene blue[19] is formed in artificial light. 1,2,4-Triazole-3-thione[20] forms complex of gold which is measurable at 250 nm. Extraction of gold-thionaphthenic acid[21] requires shaking for 15 minutes.

Reagents like phenyl pyridyl ketoxime[22], methyl violet[23], brilliant green[24], ferroin[25], 2,2'-bipyridyl ketoxime[26] and 4-(2-pyridylazo) resorcinol[27] can be successfully used for trace determination of gold. Most general methods for the same purpose involve the use of rhodanine[28], rhodamine-B[29], and dithizone[30], o-phenylene diamine[31] and acridine orange[32] are very sensitive reagents for gold.

Sanke Gowda et al. have reported the use of promethazine hydrochloride and fluphenazine hydrochloride[33], triflupromazine, promethazine, mepazine[34], for photometric determination of Au(III) in aqueous medium, but platinum metal interferes.

Au(III) was determined recently spectrophotometrically by the reagents such as 1,2,4,6 tetraphenyl pyridinium perchlorate[35], 4,4'-bisdiethylamino thiobenzophenone dodecyldimethyl ammonium acetate[36], 4,4'-bisdiethylamino diphenyl thioketone[37], thio-michler's ketone[38-42], o-aminobenzoic acid[43], trypan blue dye[44], 4,4'-bis(diethylamino) diphenyl thioketone and zephiramine[45], crystal violet[46], polyurethane foam[47], 5-(4-sodium sulfonate phenylazo) 8-amino quinoline[48], azostyrene schiff bases[49], N-methylaniline carbodithioate[50], pentacyano aminoferrate and 2,2'-bipyridine[51], 7-(2-pyridylazo) 5-chloro-8-hydroxyquinoline[52] and victoria blue B[53].

For the extractive spectrophotometric determination of gold, various reagents are used such as anisaldehyde-4-phenyl-3-thiosemicarbazone[54], astrazon blue 5 GL[55], malachite green[56], naphthyl bismuthiol[57], methyl green[58], N-phenyl-N-octylbenzamidine[59], methylene blue[60], and methyl violet and brilliant green[61].

Spectrophotometric determination of gold was studied with the systems such as Au(III)-thiocyanate-nile blue[62], Au(III)-tin(II) chloride-crystal violet[63], Au(III)-thiocyanate-rhodamine B[64] and Au(III)-$SnCl_2$-malachite green[65].

Catalytic photometry for the determination of gold was studied with the reagents dimethyl formide[66] and phosphomolybdic acid[67].

The proposed reagent 2-benzoyl pyridine guanylhydrazone (BPG) is useful for the determination of gold. The method is rapid, simple and reproducible. In merit it is fairly comparable with the above mentioned reagents for gold.

2.2 EXPERIMENTAL

2.2.1 Standard Solutions :

Standard gold(III) solution :

A stock solution ofAu(III) (1 mg/ml i.e. 5.076×10^{-3}M) was prepared by dissolving 100 mg of pure gold in a few ml of aqua regia (a mixture of three parts of conc. hydrochloric acid + one part of conc. nitric acid) and was evaporated just to dryness on the waterbath. Concentrated hydrochloric acid 1.0 ml was added and it was evaporated almost to dryness to remove oxides of nitrogen. Finally it was dissolved in dilute HCl and made up to the mark in 100 ml volumetric flask with distilled water. The solution was standardised gravimetrically[68]. Working solutions of lower concentrations were prepared by diluting it with distilled water.

Reagent (BPG) solution :

A stock solution of reagent 2-benzoyl pyridine guanylhydrazone (BPG) 0.6 mg/ml (i.e. 2.5×10^{-3}M) was prepared by dissolving 60 mg of the reagent in 100 ml of distilled ethyl alcohol.

Buffer solution :

Buffer solutions were prepared by dissolving appropriate amounts of borax and sodium hydroxide.

All other reagents used were of analytical grade.

2.2.2 Recommended Procedure :

An aliquot of the solution containing 100 μg of gold (III) was taken in a 10 ml volumetric flask. Then 1.0 ml of 2.5 x 10^{-3}M reagent (BPG) solution was added which provides desired excess quantity to complete the complex formation. The pH of the solution was adjusted to 10.5 by adding 1.0 ml of buffer solution and it was diluted up to the mark with distilled water. The absorbance of the complex was measured at 395 nm against reagent blank. The concentration of gold in an unknown solution was found out from standard calibration curve obtained under identical conditions.

2.3 RESULTS AND DISCUSSION

2.3.1 Spectral Characteristics :

The absorption spectrum of Gold(III)-BPG complex of the solution containing 5.076 x 10^{-5}M gold and 2.5 x 10^{-4}M reagent (BPG) was recorded at pH 10.5 against reagent blank. The absorption measurements were made in the spectral range from 365 nm to 560 nm. The complex has an absorption maximum at 395 nm. The molar extinction coefficient of the complex at 395 nm is 0.2859 x 10^{4} l $mole^{-1}$ cm^{-1}. The reagent does not absorb in this region. The observations of absorbances and molar extinction coefficients of the complex and the reagent are given in table 2.1 (Figure 2.1).

Table 2.1 : Absorbances and molar extinction coefficients of Au(III)-BPG complex and reagent (BPG)

Wavelength	Absorbance		Molar extinction coefficient, ϵ	
λ, nm	Au(III)-BPG complex 5.076×10^{-5}M	BPG, reagent 2.5×10^{-4} M	Au(III)-BPG complex $\epsilon \times 10^{4}$ l mole^{-1}cm^{-1}	BPG, reagent $\epsilon \times 10^{4}$ l mole^{-1}cm^{-1}
365	0.110	0.115	0.2169	0.0460
370	0.120	0.115	0.2366	0.0460
375	0.125	0.110	0.2465	0.0440
380	0.130	0.110	0.2564	0.0440
385	0.135	0.105	0.2662	0.0420
390	0.140	0.105	0.2761	0.0420
395	0.145	0.100	0.2859	0.0400
400	0.140	0.095	0.2761	0.0380
405	0.135	0.090	0.2662	0.0360
410	0.130	0.090	0.2564	0.0360
420	0.125	0.075	0.2465	0.0300
430	0.120	0.065	0.2366	0.0260
440	0.115	0.055	0.2268	0.0220
450	0.110	0.045	0.2169	0.0180
460	0.105	0.035	0.2071	0.0140
480	0.085	0.030	0.1676	0.0120
500	0.070	0.020	0.1380	0.0080
520	0.055	0.010	0.1084	0.0040
540	0.045	0.005	0.0887	0.0020
560	0.035	-	0.0690	-

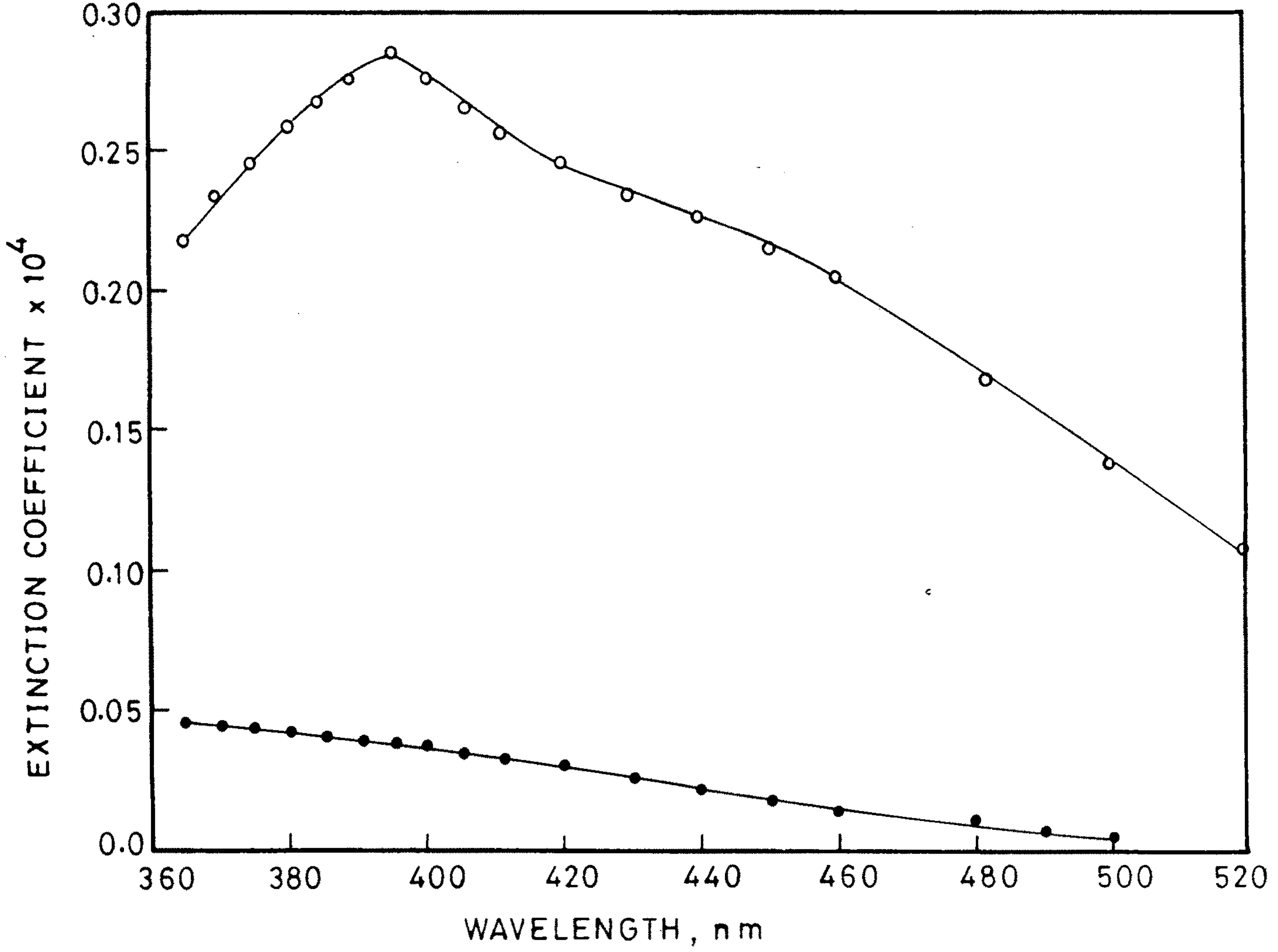


FIG. 2·1 — ○—○ ABSORPTION SPECTRUM OF GOLD (III) - BPG COMPLEX.

●—● ABSORPTION SPECTRUM OF REAGENT (BPG).

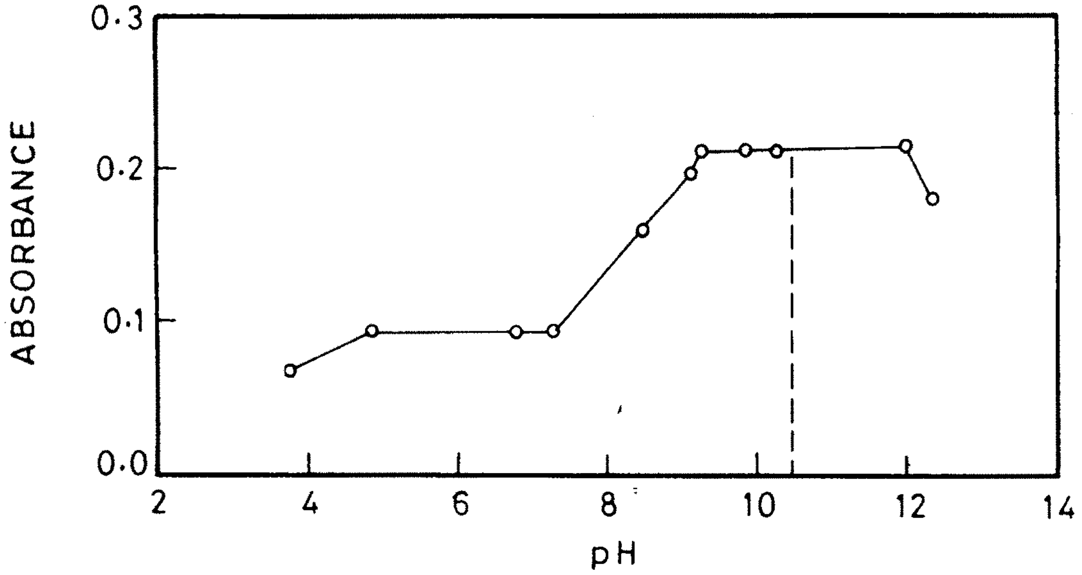


FIG. 2·2 — EFFECT OF pH.

2.3.2 Effect of pH :

To study the effect of pH of the solution on the absorbance of the complex, a series of solutions containing 1.0 ml of 0.1 mg/ml of Au(III) and 1.0 ml of 2.5×10^{-3}M reagent (BPG) were prepared as per recommended procedure from a range of pH 3.80 to 12.30 The absorbances were measured against corresponding reagent blank. It was found that the complex has maximum and constant absorbance over the pH range 9.30 to 12.0. Therefore pH 10.5 was selected as the optimum pH for further studies. The observations are given in table 2.2 (Figure 2.2).

Table 2.2 : Effect of pH

$[\mathrm{Au(III)}] = 5.076 \times 10^{-5}$M; $[\mathrm{BPG}] = 2.5 \times 10^{-4}$M

pH	Absorbance at 395 nm
3.80	0.070
4.90	0.090
6.80	0.090
7.30	0.090
8.50	0.160
9.20	0.200
9.30	0.215
9.80	0.215
10.20	0.215
12.00	0.215
12.30	0.180

2.3.3 Effect of Reagent Concentration :

It was observed that the amount of excess of reagent was the least critical. About five fold excess molar concentration relative to the metal ion concentration was satisfactory. A series of solutions were prepared in which the volume of reagent was varied from 0.2 ml to 1.6 ml of concentration 2.5 x 10^{-3}M, while the concentration of gold was kept constant at 5.076 x 10^{-5}M. The pH value of each solution was adjusted and was made up to the mark in 10 ml volumetric flask. The absorbances were measured at 395 nm wavelength against reagent blank. The results are given in table 2.3 which show that five fold excess of the reagent is sufficient for full colour development of 10.0 ppm gold.

Table 2.3 : Effect of reagent concentration

[Au(III)] = 10.0 ppm; [BPG] = 2.5 x 10^{-4}M

Amount of BPG added, ml	Absorbance at 395 nm
0.2	0.150
0.4	0.170
0.6	0.205
0.8	0.210
1.0	0.215
1.2	0.215
1.4	0.215
1.6	0.215

2.3.4 Stability and Reaction Rate :

Gold (III)-BPG complex is stable for several hours and complex formation is instantaneous. Complex formation is independent of temperature.

2.3.5 Validity of Beer's Law :

The solutions containing different amounts of gold and the same amount of reagent (BPG) i.e. 4.0 ml of 2.0×10^{-4}M at pH 10.5 were used to study the validity of Beer's law. It was found that Beer's law is valid upto 40.0 ppm of gold at 395 nm (Table 2.4, Figure 2.3).

The optimum concentration range for the determination of gold was calculated from Ringbom Plot[69], and was found to be 15.0 to 40.0 ppm at 395 nm (Figure 2.4).

Table 2.4 : Validity of Beer's law

$[\text{BPG}] = 8.0 \times 10^{-4}$M

Amount of Au(III), ppm	Absorbance at 395 nm	Transmittance, %	$-(\Delta c/c)/\Delta P$
5.0	0.075	84.1	7.20
10.0	0.170	67.6	3.57
15.0	0.250	56.2	3.04
20.0	0.340	45.7	2.78
25.0	0.415	38.5	2.73
30.0	0.500	31.6	2.77
35.0	0.580	26.3	2.89
40.0	0.670	21.4	3.11
45.0	0.730	18.6	3.31
50.0	0.760	17.4	3.51

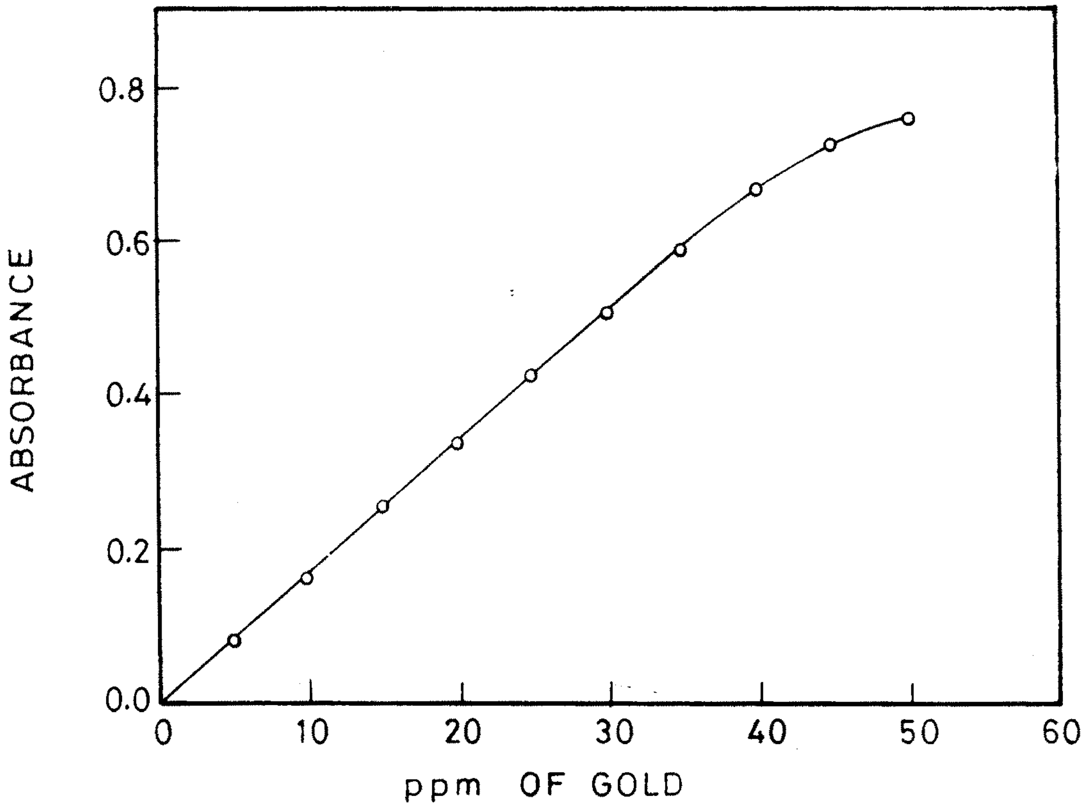


FIG. 2·3 – VALIDITY OF BEER'S LAW.

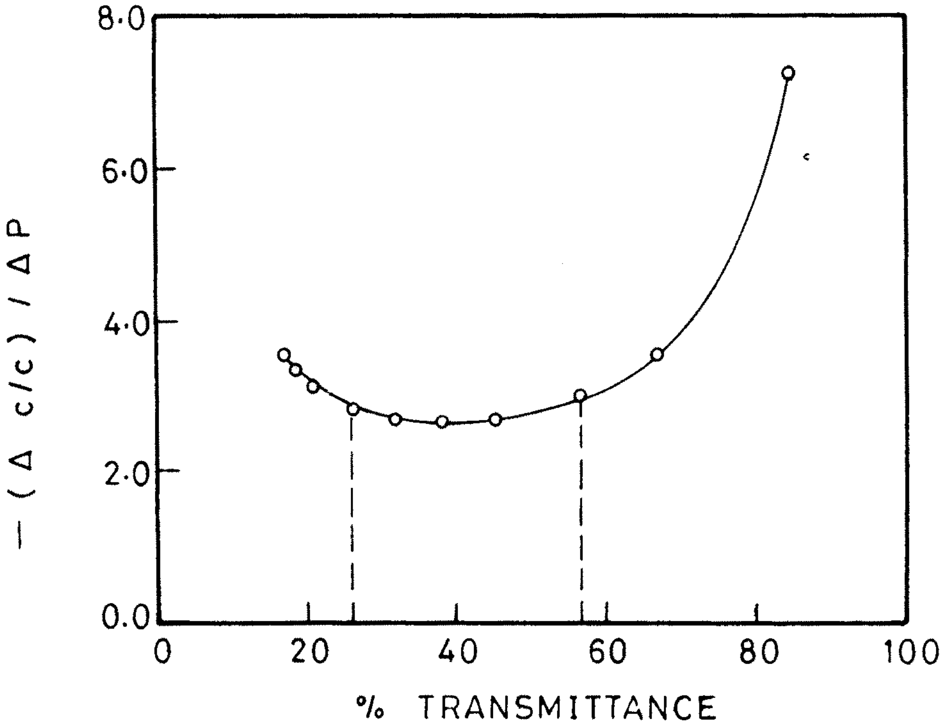


FIG. 2·4 — RINGBOM PLOT.

2.3.6 Composition of the Complex :

The empirical formula of Au(III)-BPG complex was determined by Job's method of continuous variation[70], mole ratio method[71] and slope ratio method[72]. For Job's method of continuous variation, a series of solutions were prepared by keeping the sum of molar concentrations of gold and ligand constant, while their ratios were varied in different solutions. For this purpose, equimolar solutions of gold and ligand were used.

The plots of absorbances at 395 nm and 420 nm wavelengths against mole fraction of the reagent indicate that ligand forms 1:1 complex (Table 2.5; Figure 2.5).

In a mole ratio method, gold concentration (1.0×10^{-4}M) was maintained constant and different concentrations of reagent ranging from 0.5×10^{-4}M to 4.0×10^{-4}M were used. The absorbances were measured at 395 nm and 380 nm wavelengths (Table 2.6). Mole ratio plot indicates and confirms the formation of 1:1 complex at pH 10.5 (Figure 2.6).

In slope ratio method, a series of solutions were prepared by keeping the metal concentration variable and a very large excess of ligand concentration and vice versa. Slope ratio method also confirms the 1:1 complex of Au(III)-BPG.

Table 2.5 : Job's continuous variation method

$[\mathrm{Au(III)}] = [\mathrm{BPG}] = 1.47 \times 10^{-4}\mathrm{M}$

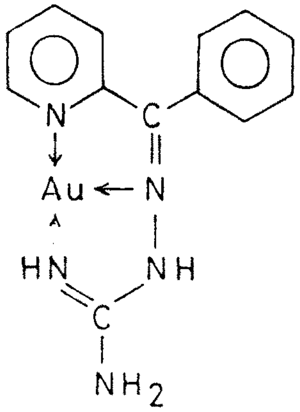
$[\mathrm{Au(III)}]$, ml	$[\mathrm{BPG}]$ ml	$\frac{[\mathrm{BPG}]}{[\mathrm{Au(III)}] + [\mathrm{BPG}]}$	Absorbance at λ 395 nm	Absorbance at λ 420 nm
4.0	0.0	-	-	-
3.6	0.4	0.1	0.30	0.23
3.2	0.8	0.2	0.58	0.48
2.8	1.2	0.3	0.77	0.68
2.4	1.6	0.4	0.89	0.78
2.0	2.0	0.5	0.94	0.80
1.6	2.4	0.6	0.76	0.66
1.33	2.66	0.66	0.62	0.55
1.2	2.8	0.7	0.53	0.45
1.0	3.0	0.75	0.42	0.34
0.8	3.2	0.8	0.28	0.23
0.4	3.6	0.9	0.15	0.11
0.0	4.0	1.0	-	-

Table 2.6 : Mole ratio method

$[Au(III)] = [BPG] = 1.0 \times 10^{-4} M$

[Au(III)] ml	[BPG] ml	$\frac{[BPG]}{[Au(III)]}$	Absorbance at λ	
			395 nm	380 nm
2.0	0.0	-	-	-
2.0	0.5	0.25	0.21	0.15
2.0	1.0	0.50	0.39	0.28
2.0	1.5	0.75	0.53	0.40
2.0	2.0	1.00	0.64	0.50
2.0	2.5	1.25	0.72	0.55
2.0	3.0	1.50	0.78	0.60
2.0	3.5	1.75	0.82	0.62
2.0	4.0	2.00	0.83	0.64

Hence, the probable structure for Au(III)-BPG complex may be shown as :



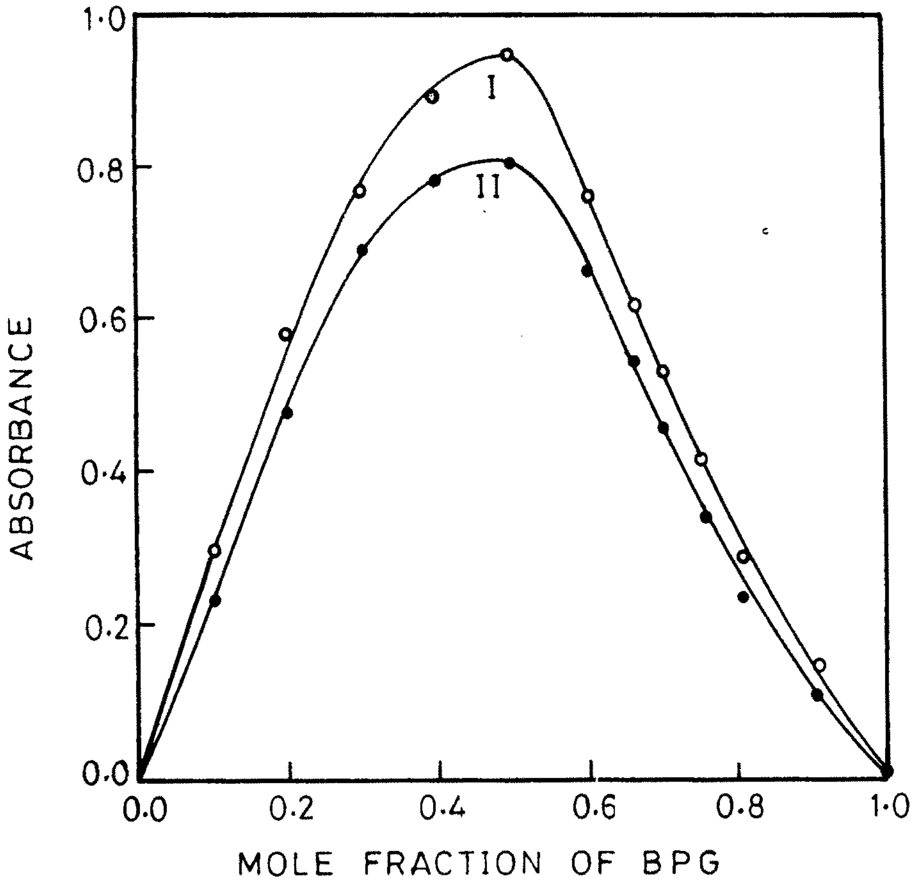


FIG. 2·5 – JOB'S CONTINUOUS VARIATION METHOD.

I — 395 nm ; II — 420 nm .

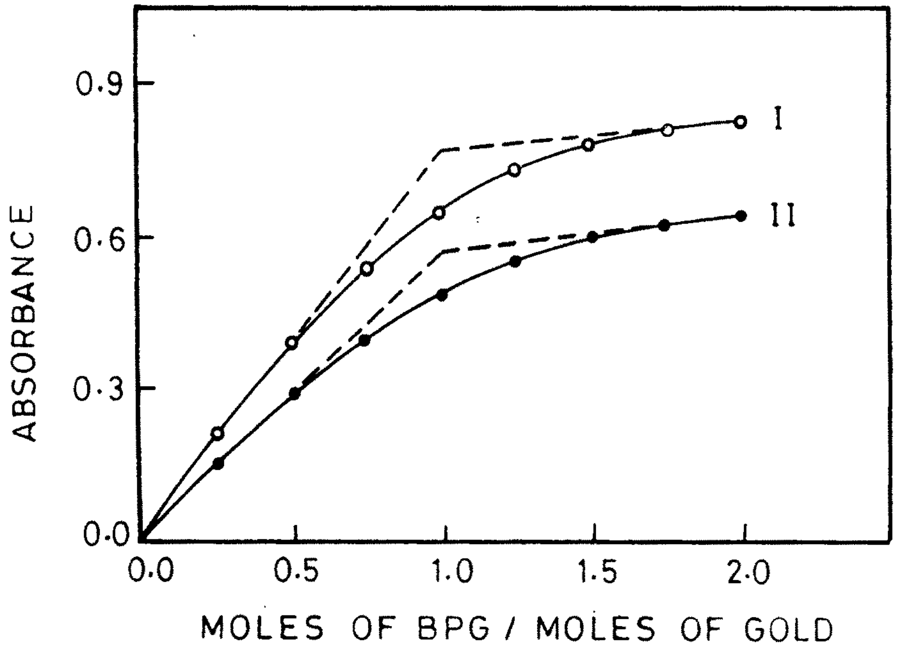


FIG. 2·6 — MOLE RATIO METHOD.

I – 395 nm ; II — 380 nm .

2.3.7 Sensitivity :

The complex of gold is not sensitive to the light. The photometric sensitivity was calculated by the method of Sandell[73] and was found to be 0.1525 $\mu g/cm^2$.

2.3.8 Degree of Dissociation and Instability Constant :

The instability constant[74] is calculated from the mole ratio plot (Figure 2.6). The equatiion is :

$$K = \frac{(m \alpha c)^m \ (n \alpha c)^n}{c\ (1 - \alpha)}$$

where K = Instability constant

α = Degree of dissociation

c = Concentration of the complex in moles per litre.

m & n = 1 and 1 respectively

The degree of dissociation, α, is calculated from the relationship

$$\alpha = \frac{dE - do}{dE}$$

where

dE = Optical density when complex is completely formed (extrapolated value of O.D.).

do = Optical density observed actually at stoichiometric molar ratio.

The degree of dissociation of the complex at 395 nm was found to be 0.1766.

The apparent instability constant was calculated as 7.519 x 10^{-6}.

2.3.9 Reproducibility of the Method :

The reproducibility of the method was studied by determining gold in sets of six observations for each concentration. The table 2.7 summarises the results and shows that the results are reproducible.

Table 2.7 : Reproducibility of the method

Gold(III), ppm	Mean absorbance of six observations	Standard deviation	Coefficient of variation, %
8.0	0.140	0.0017	1.214
16.0	0.275	0.0035	1.273
24.0	0.415	0.005	1.205
32.0	0.550	0.007	1.273

2.3.10 Effect of Diverse Ions :

The effect of diverse ions, was studied using fixed amount of gold (10.0 ppm) and measuring the colour intensity as per recommended procedure. An error upto ± 2% in absorbance was considered to be tolerable.

It was found, that Cu(II), Fe(III), Ni(II), Pb(II), Zr(II), Bi(III), thiosulphate ion, thiourea and $EDTA^{-4}$ interfere seriously. While the tolerance limits of Mg(II) and oxalate ion are 80 ppm and 55 ppm respectively. Fe(III) can be eliminated by phosphate, while Mn(II) is masked with fluoride. The tolerance limits for the ions are listed in table 2.8.

Table 2.8 : Effect of diverse ions

[Au(III)] = 10.0 ppm; [BPG] = 2.5 x 10^{-4}M

Foreign ions	Added as	Tolerance limit, ppm
Cations :		
Zn(II)	$ZnSO_4.\ 7H_2O$	20
Ba(II)	$BaCl_2.\ 2H_2O$	12
V(V)	V_2O_5	8
Cu(II)	$CuSO_4.\ 5H_2O$	None
Fe(III)	$FeCl_3.\ 6H_2O$	None
Tl(I)	TlCl	14
Ni(II)	$NiSO_4.\ 6H_2O$	None
Sn(II)	$SnCl_2.\ 2H_2O$	12
Mg(II)	$MgCl_2.\ 6H_2O$	80
Pb(II)	$Pb(NO_3)_2$	None
Mn(II)	$MnSO_4.\ H_2O$	7
In(III)	$InCl_3.\ 4H_2O$	3
U(VI)	$UO_2(NO_3)_2.\ 6H_2O$	5
Zr(IV)	$ZrSO_4$	None
Bi(III)	$BiCl_3$	None
Cr(VI)	$Cr(NO_3)_3.\ 9H_2O$	6
Se(IV)	Na_2SeO_3	8
Anions :		
Phosphate	Potassium hydrogen phosphate	14
Thiosulphate	Sodium thiosulphate	None
Oxalate	Potassium oxalate	55
$EDTA^{-4}$	Disodium salt	None
Borate	Sodium borate	6
Thiourea	Thiourea	None
Acetate	Sodium acetate	9

2.4 APPLICATIONS

Determination of Gold in Gold-copper-silver Alloy :

The sample of alloy 50 mg was transferred into 100 ml conical flask, covered with stem-cut funnel and heated gently with 10 ml of aqua-regia to dissolve the alloy. The solution was treated with 10.0 ml of concentrated hydrochloric acid. (each time with the addition of 2.0 ml portions) and being evaporated almost to dryness on water bath. The residue was dissolved in dilute hydrochloric acid. The precipitate of silver chloride was removed by filtration. As the alloy contains large amount of copper, it was removed by extraction with acetyl acetone. The solution was transferred into 100 ml volumetric flask and was diluted upto the volume with distilled water.

A suitable aliquot of the solution was used for determination of gold as per recommended procedure. The results of the analysis are summarised in table 2.9.

Table 2.9 : Analysis of gold-copper-silver alloy

Alloy	Certified value of Au(III), %	Experimental value of Au(III), %	Relative standard deviation for five observations
Gold-copper-silver alloy	43.4	43.1	0.056

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