# CHAPTER - II

## DETERMINATION OF GOLD (III)

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## 2.1 INTRODUCTION

Gold is the most beautiful of the chemical elements. On account of its brilliance and stability, gold has attracted attention of the primitive man. It is one of the first metals known to man.

Gold occurs in nature in the native state associated with other metals. 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.

Gold is mainly used for ornamental purposes and in jewellery, since it retains its bright surface untarnished. Gold is also used for gold-plating. Colloidal gold is used in colouring glass and enamels. Gold has high thermal and electrical conductivity, hence it is used in electronics. The infrared 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. There is an increasing interest in the development of new gold complexes for use in the treatment of arthritis. The use of gold in microelectronic circuit is increasing rapidly.

Being a precious metal, determination of gold at microlevels is of great importance. Several photometric methods involve the reduction of gold(III) to a purple colloidal elemental gold. Hence, it was felt necessary to develop a simple, rapid and selective method of determining Au(III). The reagent 2-acetyl thiophene guanylhydrazone (ATG) can be used for the determination of gold.

Beamish[1,2] published a critical review of the methods for photometric determination of noble metals. Recently Bhattacharya and Das[3] have reviewed the reagents and methods used for determination of gold. The monograph describing the chemistry of gold[4] has appeared recently.

Numerous reagents are available for trace determination of gold(III). However very few have analytical value. Several spectrophotometric procedures based on the formation of colloidal precipitate of elemental gold using e.g.stannous chloride[5], p-dimethyl aminobenzylidinerhodanine[6], variamine blue[7] etc. have been reported. The colloidal suspensions are unstable, thereby rendering the method less reliable.

Among the various oximes, di-2-pyridyl ketoxime[8], furil-$\alpha$-dioxime[9], 4-heptanone oxime[10], bipyridyl ketoxime[11] and syn-phenyl-2-pyridyl ketoxime[12] have been proposed as extractive photometric reagents for gold (III).

Some ketones including HTTA[13], STTA[14], thiomichler's ketone[15-17], thiodibenzoyl methane acetophenone[18], 4-4'-bis-(dimethylamino) thiobenzophenone[19], 3-methyl-1-phenyl-4-trifluoroacetyl-pyrazoline-5-one[20] are recommended as selective extractants for Au(III). These reagents coextract large number of elements and require longer time for quantitative recovery of gold.

Gold is a strong oxidising agent. It oxidises various organic substances to intensely coloured products in mineral acid solutions and several methods for determination of gold based on this principle have been described, e.g. oxidation of leuco compound of malachite green[21], o-toluidine[22], o-dianisidine[23], luminol[24] etc. But such methods are unspecific.

The analytical reagents mercaptoquinoline[25], 8-hydroxyquinoline[26], bismuthiols[27], thionaphthanic acid[28], dithizone[29], trioctylamine[30], sodium diethyldithiocarbamate[31], 2-nonylpyridine-1-oxide[32], 5-(4-dimethyl aminocinnamylidene)-1-phenyl-2-thiobarbituric acid[33], N-phenylbenzohydroxamic acid[34] and zephiramine[35] have been used for the extractive photometric determination of gold(III).

Au(III) forms complex with ascorbic acid[36], which is stable for one hour. o-Aminobenzene arsonic acid[37] forms complex after 40 to 90 minutes. Complexes of O-toluidine[38], NNN'N'-tetramethyl-o-toluidine[39] and azide[40] 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[41], solution is kept in dark for colour development. Ammonium Pyrrolidine-1-carbodithioate[42] forms complex after heating on boiling water bath, but many cations and anions interfere seriously in this method. 1,2,4-Triazole-3-thione[43] forms complex of gold which is measurable at 250 nm

Au(III) have been determined photometrically based on the formation of easily extractable ion association complex with the acid form of the dye or the cation forming species of the reagent. The dyes reported are rhodamine-B[44], methyl violet[45], ethyl violet[46], methylene blue[47], acridine orange[48], PAR[49], acridine yellow[50], chrompyrazol-I[51] etc.

Sanke Gowda et al. have reported the use of promethazine hydrochloride and fluphenazine hydrochloride[52] triflupromazine, promethazine, mepazine[53] for photometric determination of Au(III) in aqueous medium, but platinum metal interfere.

Recently, gold (III) was determined spectrophotometrically by the reagents such as 1,2,4,6-tetraphenyl pyridinium perchlorate[54], 4,4'-bisdiethylamino thiobenzophenone dodecyldimethyl ammonium acetate[55], 4-4'-bis-diethylamino diphenyl thioketone[56], thio-michler's ketone[57-61], o-amino benzoic acid[62], trypan blue dye[63], 4-4'-bis-

(diethylamino) diphenyl thioketone and zephiramine[64], crystal violet[65], polyurethane foam[66], 5-(4-sodium sulfonate-phenylazo) 8-aminoquinoline[67], azastyrene schiff bases[68], N-methylaniline carbodithioate[69], Pentacyano aminoferrate and 2,2'-bipyridine[70], 7-(2-pyridylazo)-5-chloro-8-hydroxy quinoline[71] and Victoria blue B[72].

For the extractive spectrophotometric determination of gold, various reagents are used such as anisaldehyde-4-phenyl-3-thiosemicarbazone[73], astrazone blue-5GL[74], malachite green[75], naphthyl bismuthiol[76], methyl green[77], N-phenyl-N-octylbenzamidine[78], methylene blue[79] and methyl violet and brilliant green[80].

Determination of gold was also studied spectrophotometrically with the systems such as Au(III)-thiocyanate-nile blue[81], Au(III)-tin(II) chloride-crystal violet[82], Au(III)-thiocyanate-rhodamine B[83] and Au(III)-$SnCl_2$-malachite green[84].

Catalytic photometry for the determination of gold was studied with the reagents dimethyl formide[85] and phosphomolybdic acid[86].

The proposed reagent, 2-acetyl thiophene guanylhydrazone (ATG) forms complex instantaneously. The method has the desired sensitivity for photometric determination of gold in µg level.

## 2.2 EXPERIMENTAL

### 2.2.1 Standard Solutions:

**Standard gold(III) solution:**

A stock solution of Au(III) (1 mg/ml i.e. $5.076\times10^{-3}$ M) was prepared by dissolving 100.0 mg of pure gold in a few ml of aqua-regia and was evaporated just to dryness on water bath. 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 hydrochloric acid and made upto the mark in 100 ml volumetric flask with distilled water. The solution was standardised gravimetrically[87]. Working solutions of lower concentrations were prepared by diluting it with distilled water.

**Reagent (ATG) solution:**

A stock solution of the reagent, 2-acetyl thiophene guanylhydrazone (ATG) was prepared by dissolving 182 mg of it in 100.0 ml 50% ethanol (1.82 mg/ml i.e. 0.01M)

**Buffer solution:**

Buffer solution was prepared by mixing appropriate amounts of sodium hydroxide and borax.

All other reagents used were of analytical grade.

### 2.2.2 Recommended procedure:

An aliquot of the solution containing 20 µg of gold(III) was taken in a 10 ml volumetric flask. Then 1.5 ml of $1.0\times10^{-3}$ M reagent (ATG) solution was added. The pH of the solution was adjusted to 10.0 by adding 1.0 ml buffer solution and was diluted upto the mark with distilled water. The absorbances of the complex were measured at 375 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 Au(III)-ATG complex containing $1.0154\times10^{-4}$ M of gold(III) and excess of the reagent (ATG) of $1.5\times10^{-4}$ M at pH 10.0 was recorded against reagent blank. The spectral curve of the yellow complex has an absorption peak at 375 nm. There is negligible absorption due to the reagent at 375 nm. The molar extinction coefficient of the complex is $0.3131 \times 10^{4}$ l $\text{mole}^{-1}$ $\text{cm}^{-1}$ at 375nm. The observations of absorbance 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)-ATG complex and reagent (ATG)

| Wavelength $\lambda$,nm | Absorbance | | Molar extinction coefficient, $\epsilon$ | |
|---|---|---|---|---|
| | Au(III)-ATG $1.0154 \times 10^{-4}$ M | ATG, reagent $1.5 \times 10^{-4}$ M | Au(III)-ATG complex $\epsilon \times 10^4$ l $mole^{-1}$ $cm^{-1}$ | ATG, reagent $\epsilon \times 10^4$ l $mole^{-1} cm^{-1}$ |
| 350 | 0.083 | 0.064 | 0.0817 | 0.0426 |
| 360 | 0.141 | 0.053 | 0.1388 | 0.0353 |
| 370 | 0.300 | 0.033 | 0.2954 | 0.0220 |
| 375 | 0.318 | 0.005 | 0.3131 | 0.0033 |
| 380 | 0.306 | 0.002 | 0.3013 | 0.0013 |
| 390 | 0.276 | - | 0.2718 | - |
| 400 | 0.246 | - | 0.2422 | - |
| 410 | 0.212 | - | 0.2087 | - |
| 420 | 0.193 | - | 0.1900 | - |
| 430 | 0.180 | - | 0.1772 | - |
| 440 | 0.167 | - | 0.1644 | - |
| 450 | 0.156 | - | 0.1536 | - |
| 460 | 0.147 | - | 0.1447 | - |
| 480 | 0.131 | - | 0.1290 | - |
| 500 | 0.118 | - | 0.1162 | - |
| 520 | 0.106 | - | 0.1043 | - |
| 540 | 0.090 | - | 0.0886 | - |
| 560 | 0.077 | - | 0.0758 | - |
| 580 | 0.067 | - | 0.0659 | - |
| 600 | 0.059 | - | 0.0581 | - |
| 620 | 0.051 | - | 0.0502 | - |

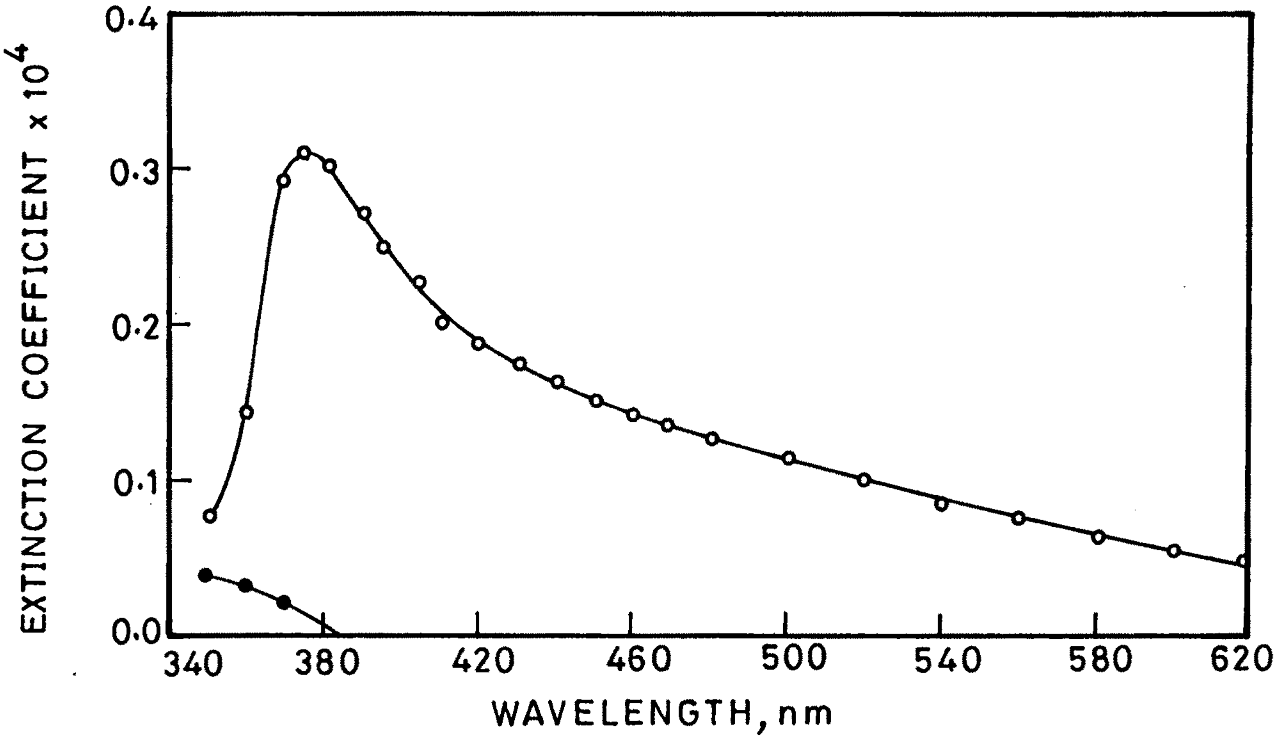


FIG. 2·1- o—o ABSORPTION SPECTRUM OF GOLD (III)-ATG COMPLEX
●—● ABSORPTION SPECTRUM OF REAGENT (ATG)

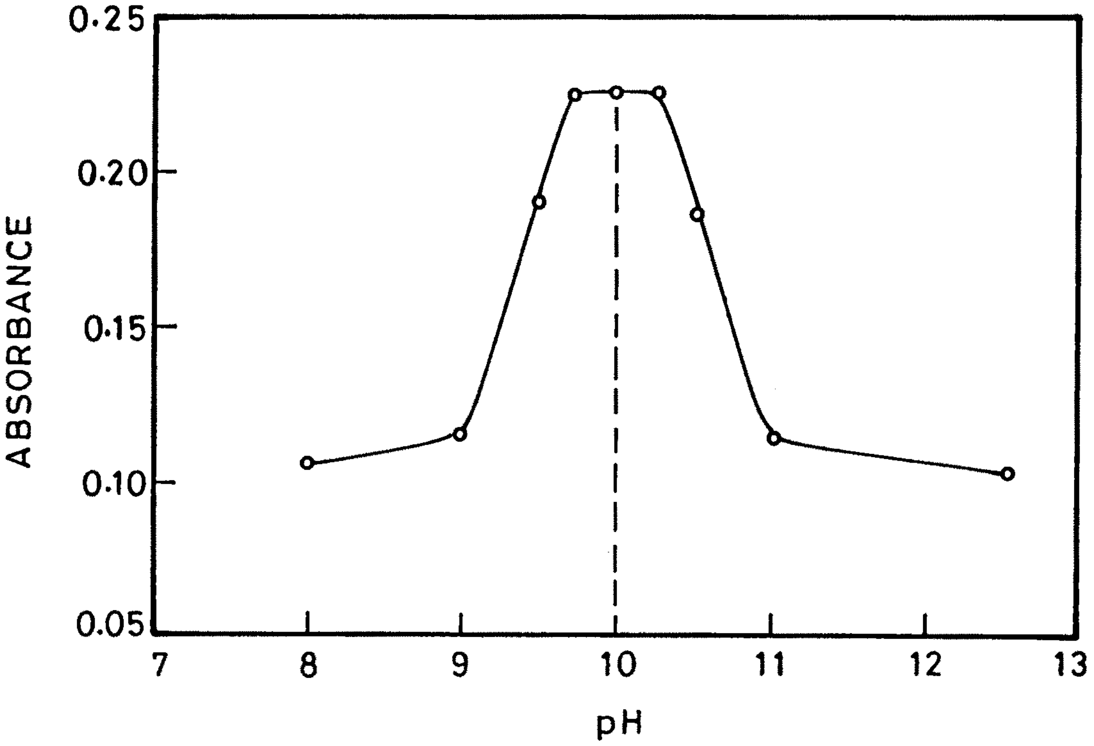


FIG. 2·2 – EFFECT OF pH

### 2.3.2 Effect of pH:

A series of solutions varying in pH were prepared as per recommended procedure. The complex has maximum and constant absorbance over the range 9.7 to 10.3. It falls below pH 9.5 and after pH 10.5. Hence, the pH value 10.0 was selected for the study of Au(III)-ATG complex. The observations are given in table 2.2. The plot of observations is shown in figure 2.2.

Table 2.2: Effect of pH
[Au(III)] = 20 ppm; [ATG] = $1.5 \times 10^{-4}$ M

| pH | Absorbance at 375 nm |
|---|---|
| 8.00 | 0.105 |
| 9.00 | 0.115 |
| 9.50 | 0.190 |
| 9.75 | 0.225 |
| 10.00 | 0.225 |
| 10.25 | 0.225 |
| 10.50 | 0.185 |
| 11.10 | 0.115 |
| 12.50 | 0.105 |

### 2.3.3 Effect of Reagent Concentration:

A series of solutions were prepared in which the volume of $1.0\times10^{-3}$ M reagent was varied from 0.5 to 3.5 ml, while the concentration of gold was kept constant at $1.0154\times10^{-4}$ M. The pH value of each solution was adjusted and each solution was made upto the mark in 10 ml volumetric flask. The absorbances were measured at 375nm wavelength against reagent blank. The results are given in table 2.3 which shows that about two-fold molar excess of the reagent is sufficient for full colour development of 20.0 ppm gold.

Table 2.3: Effect of reagent concentration
[Au(III)] = 20 ppm; [ATG] = $1.0 \times 10^{-3}$ M

| Amount of reagent, ml | Absorbance at 375 nm |
|---|---|
| 0.5 | 0.228 |
| 1.0 | 0.270 |
| 1.2 | 0.282 |
| 1.4 | 0.299 |
| 1.5 | 0.306 |
| 1.6 | 0.302 |
| 1.8 | 0.291 |
| 2.0 | 0.283 |
| 2.5 | 0.271 |
| 3.0 | 0.279 |
| 3.5 | 0.269 |

### 2.3.4 Stability and Reaction Rate:

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

### 2.3.5 Validity of Beer's Law:

The solutions containing different amounts of gold and same amount of reagent (ATG), 1.0 ml of $1.0\times10^{-2}$ M at pH 10.0 were used to study the validity of Beer's law. It was found that Beer's law is valid upto 28.0 ppm of gold (Table 2.4, Figure 2.3).

The optimum concentration range for the determination of gold was calculated from Ringbom plot[88] and was found to be 16.0 to 40.0 ppm (Figure 2.4).

Table 2.4: Validity of Beer's law
[ATG] = $1.0\times10^{-3}$ M

| Amount of Gold(III), ppm | Absorbance at 375 nm | Transmittance, % | $-(\Delta c/c)/\Delta p$ |
|---|---|---|---|
| 4.0 | 0.070 | 85.1 | 7.20 |
| 8.0 | 0.138 | 72.8 | 4.64 |
| 12.0 | 0.210 | 61.7 | 3.26 |
| 16.0 | 0.275 | 53.1 | 3.04 |
| 20.0 | 0.346 | 45.1 | 2.78 |
| 24.0 | 0.405 | 39.3 | 2.73 |
| 28.0 | 0.474 | 33.6 | 2.72 |
| 32.0 | 0.518 | 30.3 | 2.77 |
| 36.0 | 0.551 | 28.1 | 2.77 |
| 40.0 | 0.587 | 25.9 | 2.89 |

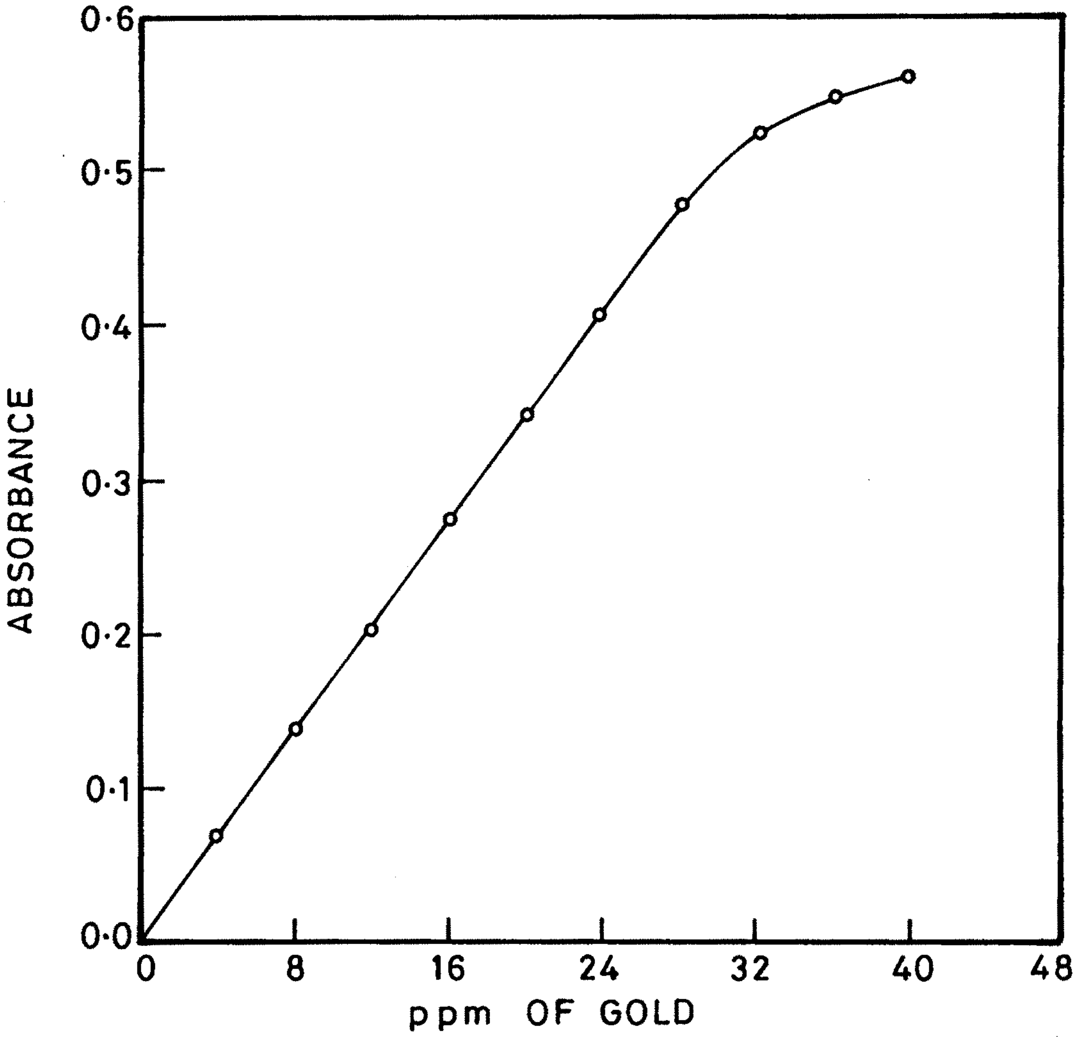


FIG. 2·3 – VALIDITY OF BEER'S LAW

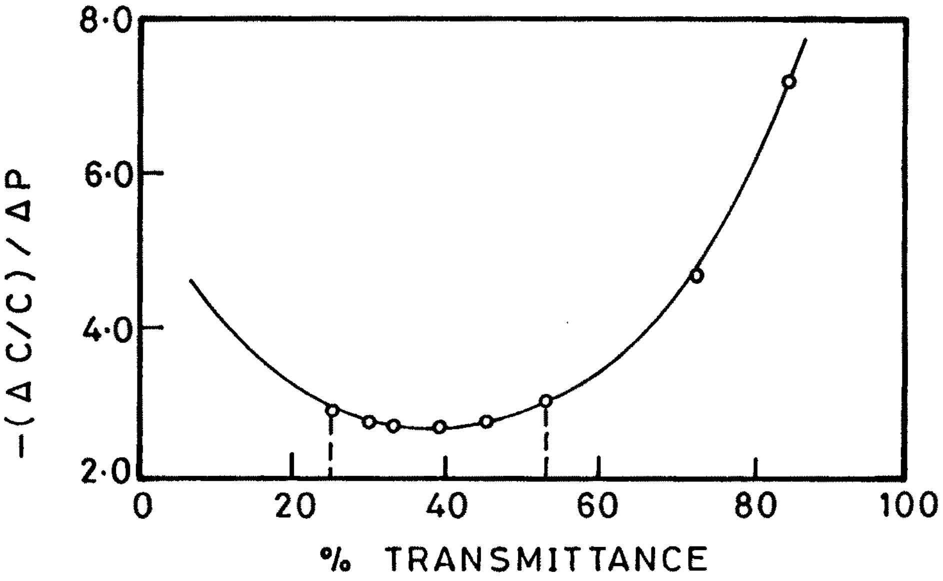


FIG. 2·4 – RINGBOM PLOT

### 2.3.6 Composition of the Complex:

The empirical formula for Au(III)-ATG complex was determined by Job's continuous variation method[89], mole ratio method[90] and slope ratio method[91].

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 are used. The plots of absorbances at 375 nm and 410 nm wavelengths against mole fraction of the reagent indicate that ligand forms 1:1 complex with metal (Table 2.5, Figure 2.5).

In a mole ratio method, gold concentration ($2.03\times10^{-4}$ M) was maintained constant and different concentrations of reagent ranging from $1.0 \times10^{-4}$ M to $5.0 \times 10^{-4}$ M were used (Table 2.6). The absorbances were measured at 375 nm wavelength. Mole ratio plot indicates and confirms the formation of 1:1 complex at pH 10.0. (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)-ATG.

Table 2.5: Job's continuous variation method
$[Au(III)]=[ATG]=1.0\times10^{-3}$ M

| [Au(III)], ml | [ATG], ml | $\frac{[ATG]}{[Au(III)]+[ATG]}$ | Absorbance at λ | |
|---|---|---|---|---|
| | | | 375 nm | 410 nm |
| 2.0 | 0.0 | 0.0 | - | - |
| 1.8 | 0.2 | 0.1 | 0.112 | 0.076 |
| 1.6 | 0.4 | 0.2 | 0.174 | 0.112 |
| 1.4 | 0.6 | 0.3 | 0.221 | 0.145 |
| 1.2 | 0.8 | 0.4 | 0.239 | 0.159 |
| 1.0 | 1.0 | 0.5 | 0.248 | 0.168 |
| 0.8 | 1.2 | 0.6 | 0.240 | 0.156 |
| 0.66 | 1.33 | 0.66 | 0.210 | 0.128 |
| 0.6 | 1.4 | 0.7 | 0.194 | 0.124 |
| 0.5 | 1.5 | 0.75 | 0.183 | 0.111 |
| 0.4 | 1.6 | 0.8 | 0.141 | 0.095 |
| 0.2 | 1.8 | 0.9 | 0.074 | 0.059 |
| 0.0 | 2.0 | 1.0 | - | - |

Table 2.6: Mole ratio method
$[Au(III)] = [ATG] = 1.0\times10^{-3}$ M

| [Au(III)], ml | [ATG], ml | $\frac{[ATG]}{[Au(III)]}$ | Absorbance at λ | |
|---|---|---|---|---|
| | | | 375 nm | 360nm |
| 2.0 | 0.0 | 0.0 | - | - |
| 2.0 | 1.0 | 0.5 | 0.275 | 0.140 |
| 2.0 | 2.0 | 1.0 | 0.472 | 0.261 |
| 2.0 | 3.0 | 1.5 | 0.602 | 0.355 |
| 2.0 | 4.0 | 2.0 | 0.645 | 0.408 |
| 2.0 | 5.0 | 2.5 | 0.679 | 0.438 |

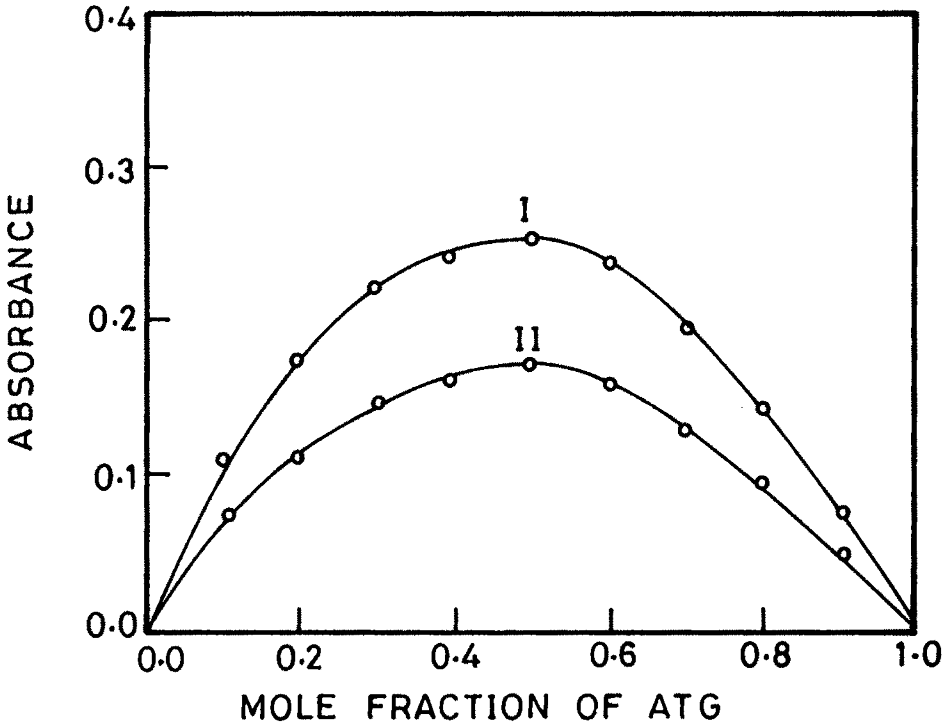


FIG. 2·5 — JOB'S CONTINUOUS VARIATION METHOD

I — 375 nm ; II — 410 nm

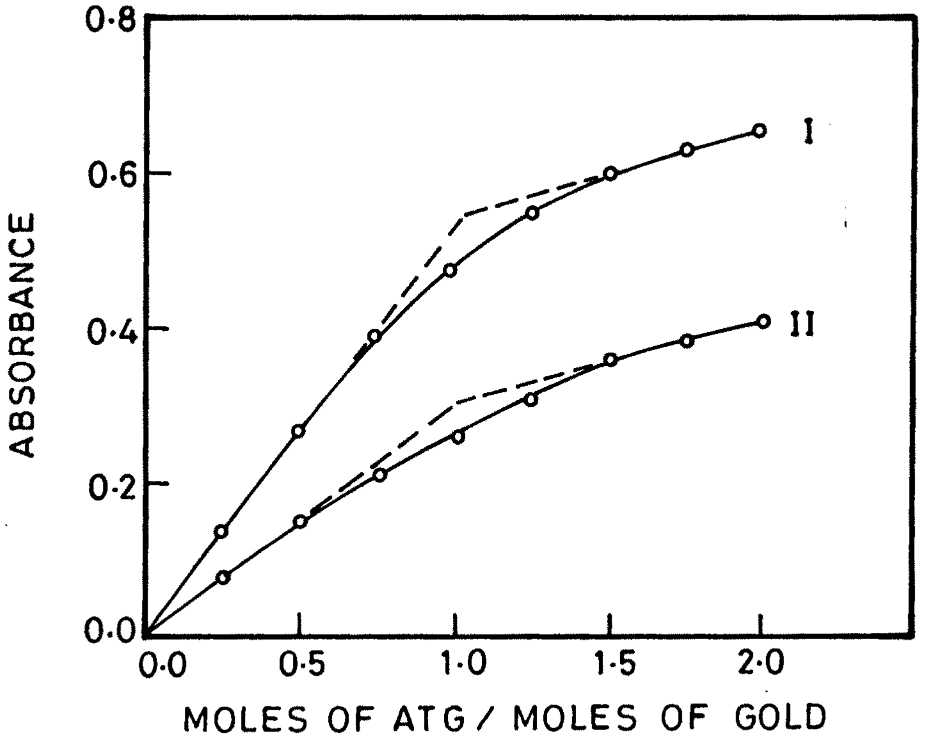
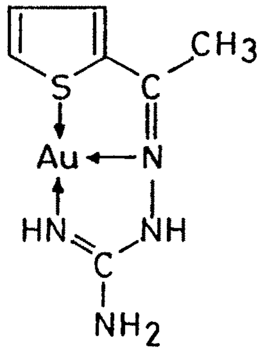


FIG. 2·6 — MOLE RATIO METHOD

I — 375 nm ; II — 360 nm

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



## 2.3.7 Sensitivity:

The complex of gold is not sensitive to the light. The photometric sensitivity was calculated by the method of Sandell[92] and was found to be 0.1210 µg/cm$^2$.

## 2.3.8 Degree of Dissociation and Instability Constant:

The instability constant[93] was calculated from the mole ratio plot (Figure 2.6). The equation is

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

Where

K = Instability constant

$\alpha$ = Degree of dissociation

c = Concentration of the complex in moles per litre

m & n = 1 and 1 respectively.

The degree of dissociation $\alpha$, 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 375 nm was found to be 0.1296.

The apparent instability constant was calculated as $3.9207 \times 10^{-6}$.

### 2.3.9 <u>Reproducibility of the Method</u>:

The reproducibility of the method was tested by determining different amounts of gold as per recommended procedure. The results are tabulated in table 2.7 which show that the method is reproducible. The standard deviations of the method calculated for six observations and the coefficient of variation are also given in table 2.7.

Table 2.7: Reproducibility of the method

| Au(III), ppm | Mean absorbance of six observations | Standard deviation | Coefficient of variation, % |
|---|---|---|---|
| 6.0 | 0.108 | 0.0010 | 1.01 |
| 10.0 | 0.176 | 0.0006 | 0.35 |
| 14.0 | 0.246 | 0.0007 | 0.31 |
| 18.0 | 0.310 | 0.0007 | 0.24 |

### 2.3.10 Effect of Diverse Ions:

The effect of a large number of diverse ions on the determination of 10.0 ppm of gold(III) with the reagent (ATG) was investigated, following the recommended procedure. The tolerance for the foreign ion was taken as the largest amount that could be present to give an error of ± 2.0 % in the absorbance at 375 nm. The tolerance limits for the ions tested are shown in table 2.8.

It is found that, the ions showing strong interferences are $EDTA^{-4}$ and thiocyanate ions. Iron(III) was masked with phosphate. Many anions did not interfere in the determination of gold. The tolerance limits of Ba(II),Mg(II) and borate ions are 900.0, 250.0 and 170.0 ppm respectively.

Table 2.8: Effect of diverse ions
[Au(III)]=10.0 ppm, [ATG] = $8.0 \times 10^{-5}$ M

| Foreign ions | Added as | Tolerance limit, ppm |
|---|---|---|
| **Cations:** | | |
| Pt(IV) | $H_2PtCl_6$ | 40.0 |
| Y (III) | $Y(NO_3)_3.6H_2O$ | 75.0 |
| Mo(VI) | $(NH_4)_2MoO_4$ | 2.0 |
| Sn(II) | $SnCl_2.2H_2O$ | 30.0 |
| Al(III) | $AlCl_3.6H_2O$ | 10.0 |
| Pb(II) | $Pb(NO_3)_2$ | 3.0 |
| Ba(II) | $BaCl_2.2H_2O$ | 900.0 |
| Zn(II) | $ZnSO_4.7H_2O$ | 25.0 |
| Mg(II) | $MgSO_4.7H_2O$ | 250.0 |
| Cd(II) | $CdSO_4.8/_3H_2O$ | 30.0 |
| Be(II) | $BeSO_4.4H_2O$ | 15.0 |
| Bi(III) | $Bi(NO_3)_3.5H_2O$ | 7.0 |
| Tl(I) | $TlNo_3$ | 120.0 |
| Cu(II) | $CuSO_4.5H_2O$ | 5.0 |
| Th(III) | $Th(NO_3)_3$ | 23.0 |

| Foreign ions | Added as | Tolerance limit, ppm |
|---|---|---|
| **Anions:** | | |
| Thiosulphate | Sodium thiosulphate | 1.0 |
| Citrate | Citric Acid | 20.0 |
| Thiourea | Thiourea | 6.0 |
| Tartrate | Tartaric acid | 14.0 |
| $EDTA^{-4}$ | Disodium salt | None |
| Acetate | Sodium acetate | 5.0 |
| Thiocyanate | Potassium thiocyanate | None |
| Phosphate | Sodium phosphate | 9.0 |
| Oxalate | Potassium oxalate | 4.0 |
| Urea | Urea | 45.0 |
| Bromate | Potassium bromate | 5.0 |
| Persulphate | Potassium persulphate | 19.0 |
| Borate | Boric acid | 170.0 |

## 2.4 APPLICATION

### Analysis of Gold-Copper-Silver Alloy:

A known weight 0.08 g of the sample of gold-copper-silver alloy was taken and transferred into a 250 ml conical flask covered with stem cut funnel and heated gently with 10.0 ml aqua-regia to dissolve the alloy. The solution was treated with 10.0ml of concentrated hydrochloric acid in 2.0 ml portions. The solution was evaporated almost to dryness on steam-bath after each addition. The residue was dissolved in dilute hydrochloric acid and the precipitated silver chloride was removed by filtration. The precipitate was washed with dilute hydrochloric acid.

The filtrate and washings were transferred into a 250 ml volumetric flask and made upto volume with distilled water.

A suitable aliquot of the sample solution was taken. Acidity of the solution was adjusted to 2.0 M in 25 ml volume with hydrochloric acid. Gold (III) was determined by proposed method. Results are reported in table 2.9. The recovery of gold(III) in alloys shows an agreement with the certified values.

Table 2.9: Analysis of gold-copper-silver alloy*

| Sample | Composition of the alloy, % | Gold(III) found, % | Relative standard deviation |
|---|---|---|---|
| I | Au(III) = 50.0<br>Cu(II) = 30.0<br>Ag(I) = 20.0 | 49.50 | 0.0007 |
| II | Au(III) = 40.0<br>Cu(II) = 35.0<br>Ag(I) = 25.0 | 39.20 | 0.00037 |

* Triplicate analyses

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