
CHAPTER - IV

**SPECTROPHOTOMETRIC DETERMINATION OF
GOLD (III) WITH 4'-BROMO-PTPT**

CHAPTER - I V

RAPID EXTRACTION OF GOLD(III) WITH 1-(4'-BROMOPHENYL)-
4,4,6-TRIMETHYL (1H, 4H) -2-PYRIMIDINETHIOL

Introduction :

Gold in massive form is a soft, yellow metal with highest ductility and malleability. 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 on an average about 0.004 ppm. It is the most beautiful of the chemical elements. The beauty and rarity of gold has led to its use in jewellery and other decorative uses. It is also used in coinage and as a standard for monetary systems throughout the world. Gold has high thermal and electrical conductivity, hence is used in electronics. The infra-red refractivity 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 various 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 rheumatoid arthritis and radioactive Au¹⁹⁸ in radiotherapy. Hence, it was felt

necessary to develop a simple, rapid and selective method of determining Au(III) in presence of largely associated metals.

Beamish published in 1965 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 metals². In reviewing the work upto early 1964, Beamish comments on the deficiency of the methods for the more common of the noble metals, namely gold and platinum. Recently Bhattacharya et al have reviewed the reagents and methods used for the determination of gold.³ The monograph describing the chemistry of gold has appeared recently.⁴

Numerous reagents have been proposed for the photometric determination of Au(III). However, very few have analytical value. Gold(III) forms well defined complexes with halide ions. Hence the simplest method, is to convert Au(III) into AuBr_4^- with subsequent measurement of its absorbance. Several spectrophotometric procedures based on the formation of colloidal precipitate of elemental gold using e.g. stannous chloride⁵, dimethyl aminobenzylidinerhodanine⁶, variamine-blue⁷, etc. have been reported. The colloidal suspensions are unstable thereby rendering the method less reliable.

Among the various oximes, di-2-pyridylketoxime,⁸ furil- α -dioxime,⁹ 4-heptanone oxime¹⁰, bipyridyl ketoxime¹¹, and

syn-phenyl-2-pyridyl ketoxime¹² have been proposed as extractive photometric reagents for gold(III).

Some ketones including HTTA¹³, STTA¹⁴, thio-Michler's ketone¹⁵⁻¹⁷, thiodibenzylmethane acetophenone¹⁸, 4,4-bis-(dimethylamino) thiobenzophenone¹⁹, 3-methyl-1-phenyl-4-trifluoroacetylpyrazoline-5-one²⁰ are recommended as selective extractants for Au(III). These reagents coextract large number of elements and require longer time for quantitative recovery of Au(III).

Au(III) has 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 B²¹, methyl violet²², ethyl violet²³, methyl blue²⁴, acridine orange²⁵, PAR²⁶, acradine yellow²⁷, chrompyrazol-I²⁸, etc.

The reagents mercaptoquinoline²⁹, 8-hydroxyquinoline³⁰, bismuthiols³¹, thionaphthanic acid³², dithizone³³, trioctylamine³⁴, sodium diethyldithiocarbamate³⁵, 2-nonylpyridine-1-oxide³⁶, 5-(4-dimethylaminocinnamylidene)-1-phenyl-2-thio-barbituric acid³⁷, N-phenylbenzohydroxamic acid³⁸ and zephiramine³⁹ have been used for the extractive photometric determination of gold (III). The 5-(4-sodium sulphonate phenylazo)-8-aminoquinoline⁴⁰ forms blue coloured complex with gold (III) in basic medium. But method requires waiting period for full colour development and reagent blank is also

required. 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 green⁴¹, o-toluidine⁴², o-dianisidine⁴³, lumicol⁴⁴, etc. But such methods are unspecific.

Ascorbic acid⁴⁵ forms complex which is stable for one hour. O-aminobenzene arsonic acid⁴⁶ forms complex after 40 to 90 minutes. Complexes of O-toluidine⁴⁷, NNN'N'-tetramethyl-O-toluidine⁴⁸ and azide⁴⁹ 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 acid⁵⁰, solution is kept in dark for colour development. Ammonium pyrrolidine-1-carbodithioate⁵¹ forms complex after heating on boiling water bath, but many cations and anions interfere seriously in this method. 1,2,4-triazole-3-thione⁵² forms complex of gold which is measurable at 250 nm.

Sanke Gowda et al have reported the use of promethazine hydrochloride and fluphenazine hydrochloride⁵³, triflupromazine, promethazine, mepazine⁵⁴ for photometric determination of Au(III) in aqueous medium, but platinum metals interfere.

Au(III) was determined recently spectrophotometrically by the reagents such as 1,2,4,6-tetraphenyl pyridinium perchlorate⁵⁵, 4,4'-bisdiethylamino thiobenzophenone dodecyldi-

methyl ammonium acetate⁵⁶, 4,4'-bis diethylamino diphenyl thioketone⁵⁷, thio-Michler's ketone⁵⁸⁻⁶², O-amino benzoic acid⁶³, trypan blue dye⁶⁴, 4,4'-bis-(diethylamino) diphenyl thioketone and zephiramine⁶⁵, crystal violet⁶⁶, polyurethane foam⁶⁷, 5-(4-sodium-sulphonate phenylazo) 8-aminoquinoline⁶⁸, azastyrene Schiff bases⁶⁹, N-methylaniline carbodithionate⁷⁰, pentacyanoaminoferrate and 2,2'-bipyridine⁷¹, 7-(2-pyridylazo)-5-chloro-8-hydroxyquinoline⁷² and victoria blue B⁷³.

Recently, for the extractive spectrophotometric determination of gold, various reagents are used such as anisaldehyde-4-phenyl-3-thiosemicarbazone⁷⁴, astrazon blue-5 GL⁷⁵, malachite green⁷⁶, naphthyl bismuthiol⁷⁷, methyl green⁷⁸, N-phenyl-N-octylbenzamidine⁷⁹, methylene blue⁸⁰ and methyl violet and brilliant green⁸¹.

Spectrophotometric determination of gold was studied with the systems such as Au(III)-thiocyanate-nile blue⁸², Au(III)-tin(II) chloro-crystal violet⁸³, Au(III)-thiocyanate-rhodamine B⁸⁴ and Au(III) - SnCl₂- malachite green⁸⁵.

Catalytic photometry for the determination of gold was studied with the reagents dimethyl formide⁸⁶ and phosphomolybdic acid⁸⁷. Tris-(2-ethylhexyl) phosphate⁸⁸ extract Au(III) from 4 M HCl medium with 5 ml of 30 percent of the reagent. After stripping with 2 & 5 ml portion of water, gold(III) was determined by SnCl₂ method spectrophotometrically. Recently highly sensitive colour reaction of meso-tetrakis (4-acetylo-

xyl phenyl) porphyrin⁸⁹ sodium dodecyl sulphate-Triton-X-100 system has been developed for Au(III), but method requires heating the reaction mixture on boiling water bath for six minutes.

The proposed reagent in chloroform extract Au(III) quantitatively from acidic medium within 5-10 sec. The method is rapid, simple, reproducible. The reagent allow the enrichment of Au(III) at the trace level from a large volume of aqueous medium even in the presence of base metals.

EXPERIMENTAL

Standard Au(III) Solution :

Standard solution of Au(III) was prepared by dissolving 100 mg of pure metal (99.99%) in aquaregia, fuming with portions of hydrochloric acid to remove oxides of nitrogen and diluting to 100 ml with 0.1 M HCl. The solution was standardised gravimetrically⁹⁰. Working solutions of lower concentration were made from it by diluting the stock solution with distilled water.

Reagent Solution :

A stock solution (0.01 M) was prepared by dissolving 0.312 gm of reagent in 100 ml chloroform.

Stannous Chloride Solution :

- 10 percent solution of the stannous chloride dihydrate in 1 M hydrochloric acid was used. This solution should be prepared fresh weekly.

Standard solutions of diverse ions were prepared by dissolving AR grade reagents in distilled water or dilute hydrochloric acid. All the organic solvents were used after double distillation. Mineral acid solutions were of AR grade.

Apparatus :

An Elico digital spectrophotometer model CL-27 with a set of 1 cm quartz cells was used for absorbance measurements

Extraction Procedure for Au(III) :

The acidity of Au(III) solution was adjusted to 2 M in HCl. The gold was extracted with 10 ml of 0.01 M reagent in chloroform for 5-10 sec. The organic layer was separated and evaporated to dryness on steam bath. The Au(III) pyrimidine-thiol complex was destroyed by treatment with 1-2 ml of a concentrated perchloric and hydrochloric acids. The residue was dissolved in few ml of aquo regia, evaporated, then 2 ml of 2% sodium chloride solution and concentrated hydrochloric acid were added and again evaporated. The procedure of evaporation was repeated to remove oxides of nitrogen, taking care not to evaporate to dryness and so avoid loss of gold⁹¹. The

residue was dissolved in dilute hydrochloric acid and determined gold photometrically by the stannous chloride method⁹³.

• Preparation of Calibration Curve for Gold(III) :

Take an aliquot of sample solution which is preferably slightly acidic. Dilute with water to about 20 ml in a 25 ml volumetric flask and add all at once 2 ml of stannous chloride solution. Make up the volume to the mark with water, mix, and allow to stand 20 min. Then determine absorbance. Prepare the calibration curve for determination of gold(III). (Fig.1)

RESULTS AND DISCUSSION

Characteristics of Extracted Species :

4'Bromo PTPT extracts Au(III) from acidic medium within 5-10 sec shaking in a single extraction. Extracted complex is colourless and hence is not suitable for determination of gold(III) spectrophotometrically. The gold(III) pyrimidinethiol II complex is destroyed as per recommended procedure and gold content is determined photometrically with stannous chloride method.

Effect of Acidity :

The optimum acidity range for the quantitative extraction of Au(III) was determined by varying HCl concen-

tration over the range 0 - 10 M acid using 0.150 mg of Au(III) and 10 ml of 0.01 M 4'-bromo PTPT reagent. The complex was extracted as per recommended procedure. The optimum acid range was between 0.5 - 8 M HCl, 0.5 - 5 M HNO₃, 0.5 - 5 M HClO₄, 0.5 - 5 M H₂SO₄, for pyrimidinethiol II but HCl was recommended for further studies because of high distribution coefficients of chloro complex.

Effect of Reagent Concentration :

The capacity of 4'-bromo PTPT for Au(III) extraction at acidity range 0.5 - 8 M HCl with 10 ml of 0.01 M of reagent in chloroform was 5.5 mg. Hence, for extraction of 0.150 mg of Au(III), 10 ml of 0.01 M reagent in chloroform was used to ensure the complete extraction (Fig.2), (Table 1).

Effect of Time of Shaking :

The complexation reaction of the pyrimidinethiol with Au(III) is quite rapid. Gold(III) in acidic medium gets extracted with pyrimidinethiol II with 5 to 10 sec shaking. There is no adverse effect when shaking is carried out upto 5 min for the reagent.

Effect of Solvent :

Various solvents were examined as extractants for Au(III) (4'-bromo PTPT) pyrimidinethiol complex developed as

• Table - 1 : Effect of Reagent Concentration

Au(III) = 150 μ g HCl = 2 M

Pyrimidinethiol II, 10 ml of = 1.0×10^{-3} M

Pyrimidinethiol in ml	Pyrimidinethiol	
	% Extraction	Distribution ratio
0.5	8	0.217
1.0	26	0.878
1.5	50	2.5
2.0	68.5	5.436
3.0	85.05	14.1
4.0	92.67	31.62
5.0	100	∞
6.0	100	∞
8.0	100	∞
• 10.0	100	∞

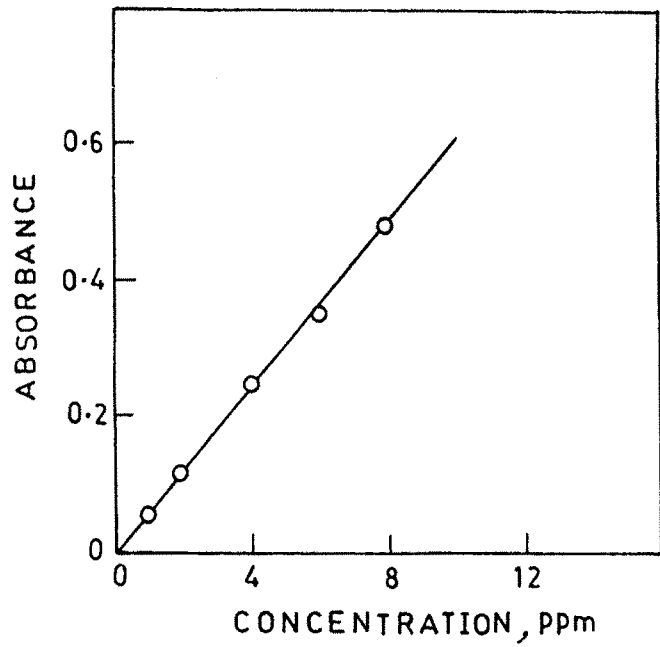


FIG. 1 —
THE CALIBRATION
CURVE FOR DETERMINATION
OF Au (III) WITH STANNOUS
CHLORIDE .

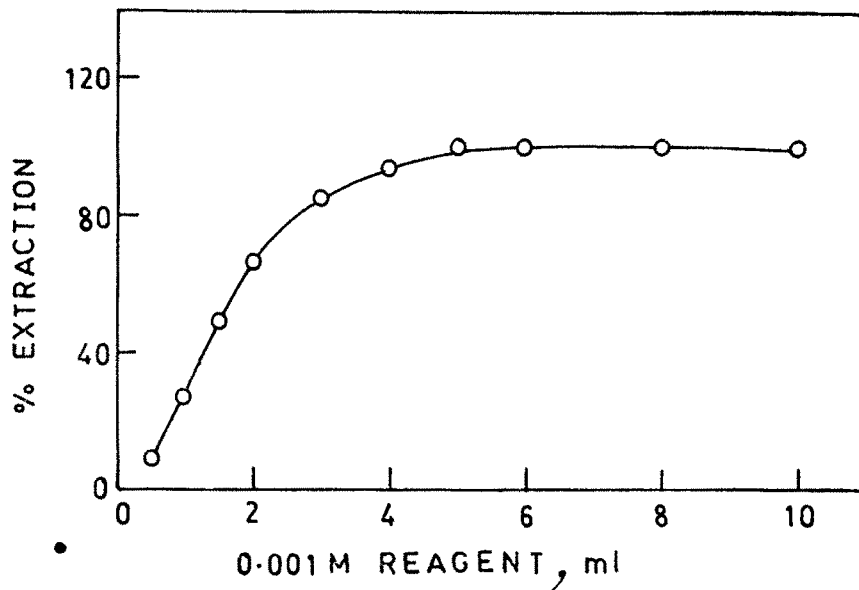


FIG. 2
EFFECT OF
REAGENT CONC.
Au (III) = 150 μ g

per the extraction procedure. The results in Table 2 show the 100% extraction of the complex in chloroform over the range 0.5 - 8 M HCl for pyrimidinethiol. The extraction of complexes were found to be incomplete in carbontetrachloride, toluene, n-butanol, benzene, amyl alcohol, MIBK, 4-methyl-2-pentanol and amyl acetate. Hence chloroform was preferred as an extractant for the complex.

Composition of Extracted Species :

The plot of $\log D - \log C$ (pyrimidinethiol II) for 2 M HCl concentration gave slope 2.0. Fig. 3 indicates that the probable extracted species has the formula 1:2 (Metal:ligand).

Effect of Diverse Ions :

The effect of large number of diverse ions on the determination of Au(III) with pyrimidinethiol II was investigated, following the recommended procedure. Initially the foreign ion was added to the Au(III) solution in large excess : 100 fold for cations and 500 fold for anions. When the interference was intensive, the tests were repeated with successively smaller amount of foreign ion. The tolerance for foreign ion was taken as the largest amount that could be present to give an error less than 2% in the extraction. The tolerance limits for ion tested are shown in Table 3. Upto 15 to 20 mg each of Cu(II), Ni(II), Zr(II), Co(II), Cd(II), Mo(VI), Zn(II), Sn(II), W(VI), Ti(IV), Ca(II) gave no interference

Table - 2 : Distribution ratio of Au(III) Pyrimidinethiol II complex between organic solvents and aqueous solutions.

Au(III) = 150 μ g HCl = 2 M

Solvent	Pyrimidinethiol	
	% Extraction	Distribution ratio
Chloroform	100	∞
Carbontetrachloride	25.8	0.86
Toluene	47.7	2.28
n-butanol	88.6	19.42
Benzene	66.47	4.95
Amyl alcohol	96.8	75.6
MIBK	95.0	47.5
4-methyl-2-pentanol	95.0	47.5
Amyl acetate	96.02	60.3

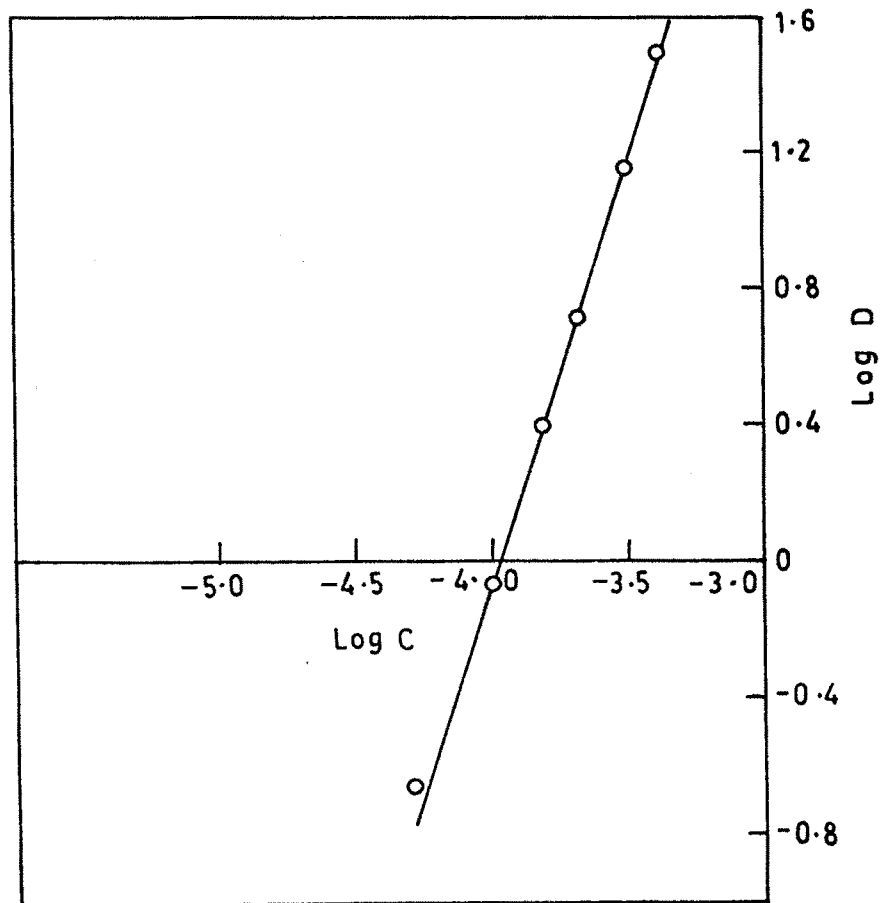


FIG. 3 — Log D — Log C

Table - 3 : Effect of Foreign Ions on the Extraction
of Au(III) with Pyrimidinethiol II.

Au(III) = 150 μ g

Aqueous phase = 2 M HCl

Tolerance limit in mg	Foreign ions added
15-20	Cu(II), Ni(II), Zr(II), Co(II), Cd(II), Mo(VI), Zn(II), Sn(II), W(VI), Ti(IV), Ca(II).
5-10	Mn(II), Cr(VI), K(I), V(VI), Mg(II), Hg(II), Pb(II), Ba(II).
2-3	UO ₂ (II), Te(IV), Se(IV)

while there is no interference from 5 to 10 mg each of Mn(II), Cr(VI), K(I), Mg(II), V(VI), Hg(II), Pb(II), Ba(II), 2 to 3 mg each of UO_2 (II), Te(IV), Se(IV). Silver is tolerated in 1:1 ratio. The concentration of Pd(II) and Os(VIII) was removed by using the separation scheme⁹²⁻⁹³. Many ions except thiosulphate, thiourea, ascorbic acid, and iodide did not interfere in fairly large concentration.

Enrichment Studies of Gold(III) :

Extraction of different amounts of gold(III) at trace level from 25, 50, 100, 1000 and 2500 ml solution 2 M in hydrochloric acid containing 20 mg amounts of iron(III), copper(II), nickel(II) and cobalt(II) each and with subsequent determination showed that the recovery of the gold(III) was quantitative and results are reproducible. Results of recovery of gold(III) from 2500 ml solution, 2 M in HCl with 10 ml of 0.01 M pyrimidinethiol II in chloroform with 30 min shaking are shown in Table 4.

Table - 4 : Determination of Gold(III) of the
ppb Level in 2500 ml of water.

Au(III), taken ppb	Au(III) found ppb	Au(III) recovery %	Au(III) relative error, %
65	64.7	99.5	0.46
70	69.8	99.7	0.29
80	80.5	100.6	0.75

(six determinations)

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