

Chapter-V

Extraction of Gold(III) with  
2,4-Dichloro PTPT

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## EXTRACTION OF GOLD (III) WITH 2,4-DICHLORO PTPT

INTRODUCTION

Gold in the 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 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 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. 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. The various gold (I) thiol complexes are used in the treatment of rheumatoid arthritis and radioactive Au<sup>198</sup> in radiotherapy. Hence, it is 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 metals(2). 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 Bhattacharaya 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. Au(III) forms well defined complexes with halide ions. Hence the simplest method, is to convert Au(III) into  $(\text{AuBr}_4)^-$  with subsequent measurement of its absorbance. Several spectrophotometric procedures based on the formation of colloidal precipitate of elemental gold using e.g. stannous chloride(5), dimethylaminobenzylidenerhodanine (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 eg. oxidation of leuco compound of malachite green(8), o-toluidine(9), o-dianisidine (10), luminol(11), etc. But such methods are unspecific.

Among the various oximes, 2,2'-bipyridylketoxime (12) Di-2-pyridylglyoxime (13), furil- $\alpha$ -aldoxime(14), quinoline-2-aldoxime(15) 4-heptanone oxime(16), 2-pyridyl-2-thenyl-2-ketoxime(17) and

2-phenyl-2-pyridylketoxime(18) have been proposed 2,2'-bipyridyl-ketoxime and di-2-pyridylketoxime form a complex with Au(III) in ethanolic medium at pH 2 to 5.0 which is measured after extraction into dichloroethane. The method require 10 min for full colour development. Palladium(II) and Co(II) must be absent. Fural- $\alpha$ -dioxime and 4-heptanone oxime methods demand the separation of interfering ions before the extraction of Au(III). Moreover, the furil - $\alpha$ -dioxime complex is stable only for 30 min. Hence, the results are less reliable. With 4-heptanoneoxime the recovery of Au(III) is incomplete. In the determination of Au(III)with quino-line-2-aldoxime, the elements which are precipitated in alkaline medium must be absent. 2-Pyridyl-2-thienyl- $\beta$ -ketoxime has been recently reported as a sensitive reagent for Au(III) but the base metals interfere. The method needs 10 min waiting for full colour attainment and also measurements of absorbance must be done within 30 min.

Some ketones including HTTA (19), STTA(20), thio-Michler's ketone(21-23), thiodibenzoylmethane acetophenone (24) are recommended for the selective extraction of Au(III). These reagents coextract large number of the elements and require longer time for quantitative recovery of Au(III). Various modifications of thio-Michler's ketone method have been proposed.

Voluminous work is seen in the literature on the photometric determination of Au(III), 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 which are reported are, Rhodamine-B(25), methyl violet(26), ethyl violet(27) methylene blue(28), acridine orange(29), PAR(30), gentin violet-B and Basic

magneta(31), substituted triphenylmethane dyes(32-33), tetrahydrofuran and tetraphenylarsonium chloride (34) etc. Ascorbic acid(35) form a complex which is stable for 1 h only and is less sensitive ( $S, 100 \text{ ng Cm}^{-2}$ ), mercaptoquinoline (36), requires 30 min for shaking. The method is tedious and time consuming. With 8-hydroxyquinoline(37) the colloidal gold formed must be measured immediately. Bismuthiol (38) forms 1:3 complex with Au(III) at pH 6 to 8 which is extractable into chloroform and measured at 330 nm. The error is high. Thionaphthenic acid (39), requires 15 min shaking for complete transfer of the complex. In dithizone method (40), the scrubbing of the organic phase with ammonia is necessary to minimise the reagent blank. Trioctylamine(41) in chloroform extracts quantitatively Au(III) from acidic medium and the complex is measured at 325 nm. Many metal ions interfere 4-(4-Hydroxy-3-methoxybenzylidene)-3-methylisoxalolin-5-one(42), reagent is highly specific for Au(III) but requires heating of the aqueous phase and rigid control of condition for its determination in presence of Co(II) and nickel(II). Sodium diethyldithio carbamate (43) complex of Au(III) is extractable into TABP but it is stable for only 15 min. Many metal ions interfere. Morpholinium morpholine-4-carbodithiolate (44) requires heating for 3 min and the tolerance limit is low.

Sanke Gowda et al. have reported the use of promethazine hydrochloride and fluphenazine hydrochloride (45), triflupromazine, promethazine, mepazine(46) for photometric determination of Au(III) in aqueous medium but platinum metals interfere.

Solvent extraction separation of Au(III) with hexanoic acid (47) in the presence of pyridine or benzylamine in chloroform from macro levels of nickel and cobalt is achieved. The sulphide of Gold(III) can be extracted with 100 percent efficiency from 4N mineral acid with butanol(48). The solution of Au(III) is made 0.5-3M in HCl and is extracted into a solution of triphenyl guanidium chloride (49) in dichloroethane. The method is applied for separation of gold(III) from palladium, platinum and iridium. Gold(III) can be preconcentrated from its ores by extraction with Zephiramine(49) into chloroform-dichloroethane(1:1).

The proposed reagents in chloroform extract Au(III) quantitatively from acidic medium within 5-10 sec. The method is rapid, simple, reproducible and permits the separation of Au(III) from other noble and base metals. The reagents allow the enrichment of Au(III) at the trace level from a large volume of aqueous medium even in the presence of base metals. The method can also be used for the determination of gold(III) in alloys.

Summary of the methods reported for Au(III) extraction and determination is given in Table No.1.

Table 1 : Summary of the Methods Reported for Gold (III)

Reagent	Medium	Conditions	$\lambda_{max}$ , molar absorptivity $\epsilon$ , Beer's range and sensitivity	Interferences	Remarks	Ref No.
1	2	3	4	5	6	7
Variamine blue	Aqueous	pH=3	$\lambda_{max}=580$ nm, $\epsilon < 1$ mg, S= 20ng $\text{cm}^{-2}$	-	Gum acacia is necessary	7
2-2'-Bipyridyl ketoxime	-	pH=3 to 3.5	$\lambda_{max}=459$ nm 20 to 200 $\mu\text{g}$	Pd(II),Co(II) interfere	Shaking 10 min	12
Di(2-pyridyl) glyoxime	Dichloro ethane; pentanol(4:1)	pH=2.5 to 5.0	$\lambda_{max}=448$ nm, 25 to 275 $\mu\text{g}$	Sn(II), Pd(II), Co(II), Rh(III), $\text{I}^-$ , $\text{CN}^-$ , $\text{SCN}^-$ interfere	Waiting 10 min	13
Furil-aldoxime	Chloroform	pH=1.7 to 2.0	$\lambda_{max}=330$ nm $\epsilon = 31600$ , upto 45 $\mu\text{g}$ , S = 6 ng $\text{cm}^{-2}$	-	Shaking 5 min	14
Quinoline-2-aldoxime	-	pH=10.12	$\lambda_{max}=570$ nm, 1.5 to 11.5 ppm	-	Heating 50°-60°	15
4-Heptanone oxime	Chloroform	1M HCl	-	-	Recovery of gold is incomplete	16
2-Pyridyl-2-thienyl-2-ketoxime	-	pH=2.5 to 4.0	$\lambda_{max}=477$ nm, 0.1 to 1.2 ppm	Many metal ions interfere	Stability 5 to 30 min	17
Thiothenoyltrifluoro acetone	$\text{CCl}_4$	pH=6.2	$\lambda_{max}=500$ nm, 1.5 to 5.5 $\mu\text{g}$	Many metal ions interfere	Shaking 10 min	20

Contd.

1	2	3	4	5	6	7	8
9	4,4'-Bis(dime-thylamino)-thiobenzophenone	-	pH=3.0	$\lambda_{\max}=545 \text{ nm}$ , 0.02 to 3.0 ppm	-	C.V.=4.8 to 26%	21
10	Thiodibenzoylme-thane acetophenone	Alkaline medium	-	$\lambda_{\max}=350 \text{ nm}$ , 0.12 to 12 $\mu\text{g}$	Ag(I), Pd(II) Os(VIII), $\text{CN}^-$ $\text{S}_2\text{O}_3^{2-}$ etc. interfere	-	24
11	Rhodamine-B	Benzene	-	$\lambda_{\max}=565 \text{ nm}$ , upto 10 $\mu\text{g}$	-	Stability 30 min	25
12	Methyl violet	Trichloroethane	pH=1	$\lambda_{\max}=600 \text{ nm}$	Pt(IV) interfere	-	26
13	Ethylviolet	Benzene	-	$\lambda_{\max}=551 \text{ nm}$ and 606 nm upto 50 $\mu\text{g}$ per 10 ml	Many metal ions interfere	Stability 3 hr.	27
14	Acridine orange	Ethylacetate dichloroethane (9:1)	pH=1	$\lambda_{\max}=495 \text{ nm}$ , 1.25 to 30 $\mu\text{g}$ per ml	Ions interfere	Stability 2 hr	29
15	4-(2-Pyridylazo)resorcinol	t-Butanol	-	$\lambda_{\max}=540 \text{ nm}$ $\epsilon=8295$ , 3.5 to 18 $\mu\text{g}/\text{ml}$ $S=51 \text{ ng cm}^{-2}$	-	-	30
16	Ascorbic acid	-	pH=5.5 to 9.0	$\lambda_{\max}=550 \text{ nm}$ , 20 to 50 $\mu\text{g}/\text{ml}$ $S=100 \text{ ng cm}^{-2}$	-	Stability 1 hr.	35
17	Mercaptoquinoline	Chloroform	$\text{H}_2\text{SO}_4$ + trichloroacetic acid	-	-	Shaking 30 min. Au (III) determined by malechite green method	36
18	8-Hydroxyquinoline	Alkaline medium	Ethanollic reagent	$\lambda_{\max}=680 \text{ nm}$ , 1 to 20 $\mu\text{g}/\text{ml}$	-	Less stable	37



Contd..

1	2	3	4	5	6	7	
19	Bismthiols	Chloroform	pH= 6 to 8	$\lambda$ max=330 nm, upto 12.5 $\mu$ g per ml $\epsilon = 17400$	-	The error is high	38
20	Thionaphth- enic acid	CCl <sub>4</sub>	0.5 M -HCl	$\lambda$ max=465 nm, 5 to 350 $\mu$ g/ml	-	Shaking 15 min	39
21	Dithizone	CCl <sub>4</sub>	-	$\lambda$ max=420 nm, upto 40ppm	Ag(I), Hg(II), Pd(II), Pt(IV) interfere	Waiting 5 min	40
22	Trioctyl- amine	CHCl <sub>3</sub>	1.2M-H <sub>2</sub> SO <sub>4</sub> or 3M-HCl 5%-R	$\lambda$ max=330 nm	-	Separation from platinum	41
23	4-(4-Hydroxy 3-methoxybenzylidene) 3-methyliso- xalolins-one	Alkaline medium	-	$\lambda$ max=400 or 525 nm	-	Heating 10 min	42
24	Sodiumdieth- ylalithio- carbamate	TBP	pH=8.5 to 9.5	$\lambda$ max=420 nm, 0.4 to 97 ppm	Many metal ions interfere	Waiting 10 min, stability 15min error is high	43
25	Morpholiniam morpholine-4 Carbodi-thiolate	-	4M-HCl	$\lambda$ max=317 nm, 4 to 30 ppm	Platinum & base metals interfere	Heating 3 hr, tolerance limit is less	44
26	Promazine Hydrochloride	-	1M-HCl	$\lambda$ max=516nm, $\epsilon = 24150$ 0.2 to 7.0 ppm	Rh(III), Os(VIII) Fe(III) interfere	-	45
27	Fluphenazine hydrochloride	-	3M-HCl	$\lambda$ max=500nm, $\epsilon = 13340$ 0.2 to 17 ppm	I <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , EDTA, Ru <sup>III</sup> , Ir <sup>III</sup>	-	45
28	Triflupromazine	-	2 to 4M-HCl	$\lambda$ max=503nm, 0.8to 14.1 ppm	interfere Ce(IV), Cr(VI), Mn(VII), Mn(VII), V(V), Ag(I) & platinum base metal interfere	-	46

Contd..

1	2	3	4	5	6	7	8
29	Promethazine	-	2.5 to 4M-HCl	$\lambda_{\text{max}}=517 \text{ nm}$ , 0.75 to 11.6ppm	Platinum and base metals interfere	-	46
30	Mepazine	-	1.8 to 2.1M-HCl	max=514 nm 0.6 to 12.3 ppm	platinum metals interfere	-	46

### EXPERIMENTAL

#### Standard Au(III) solution :

Standard solution of Au(III) was prepared by dissolving 100mg of pure metal (99.99%) in aqua-regia, fuming with portions of hydrochloric acid to remove oxides of nitrogen and diluting to 100 ml with 0.1M HCl. The solution was standardised gravimetrically (50). Working solutions of lower concentration were made from it by diluting the stock solution with distilled water as required.

#### Reagent Solution :

A stock solution (0.01 M) was prepared by dissolving 0.301 of pyrimidinethiol in chloroform.

#### Stannous Chloride Solution :

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

#### Apparatus :

All absorbance measurements were carried out with Beckman DU-2 spectrophotometer equipped with 1 cm quartz cells.

#### Extraction Procedure for Au(III):

The acidity of an Au(III) solution was adjusted to 0.5-8M HCl. The gold (III) was extracted with 10 ml of 0.01M pyrimidinethiol in chloroform for 5-10 sec. The organic layer was separated and evaporated to dryness on steam bath. The Au(III)pyrimidinethiol complex was destroyed by treatment with 1-2 ml of a concentrated perchloric and hydrochloric acids. The residue was dissolved in few ml of aqua-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 gold(51). The residue was dissolved in dilute hydrochloric acid and gold was determined photometrically by the stannous chloride method(52).

#### Preparation of Calibration Curve for Gold (III):

The sample solution of gold(III) in a volume of 20 ml and should preferably be only slightly acidic (0.05 M in HCl). 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).

### Results and Discussion

#### Characteristics of Extracted Species:

Pyrimidinethiol in chloroform extracts Au(III) from acidic medium with 5-10 sec shaking in a single extraction. Extracted complex is colourless and hence is not suitable for determination of gold(III). The gold(III)pyrimidinethiol 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 concentration over the range 0-10 M acid using 0.3 mg of Au(III) and 10 ml of 0.01 M pyrimidinethiol. The complex was extracted as per recommended procedure. The optimum acid range was between 0.5-8M HCl.

Effect of Reagent Concentration :

The capacity of pyrimidinethiol for Au(III) extraction at acidity range 0.5 -8M HCl with 10 ml of 0.01M of reagent in chloroform was 5 mg. Hence, for extraction of 0.3 mg of Au(III), 10 ml of 0.01 M pyrimidinethiol in chloroform was used to ensure the complete extraction (Fig.1) (Table-2).

Effect of Time of Shaking:

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

Effect of the Solvent :

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

Composition of the Extracted Species:

The plot of  $\log D - \log C$  pyrimidinethiol for 2M HCl concentration gave a slope 2.60 (fig.2) indicates that the probable extracted species having the formula 1:3 with respect to metal and ligand.

Table 2 : Effect of Reagent Concentration Au(III) taken, 300  $\mu$ g;  
HCl = 2M

Pyrimidinethiol ml ( 0.001M)	% Extraction	Distribution ratio
0.5	25.00	0.83
1.0	70.14	5.87
1.5	87.51	17.51
2.0	96.15	62.41
2.5	100.00	$\infty$
3.0	100.00	$\infty$
5.0	100.00	$\infty$
10.0	100.00	$\infty$

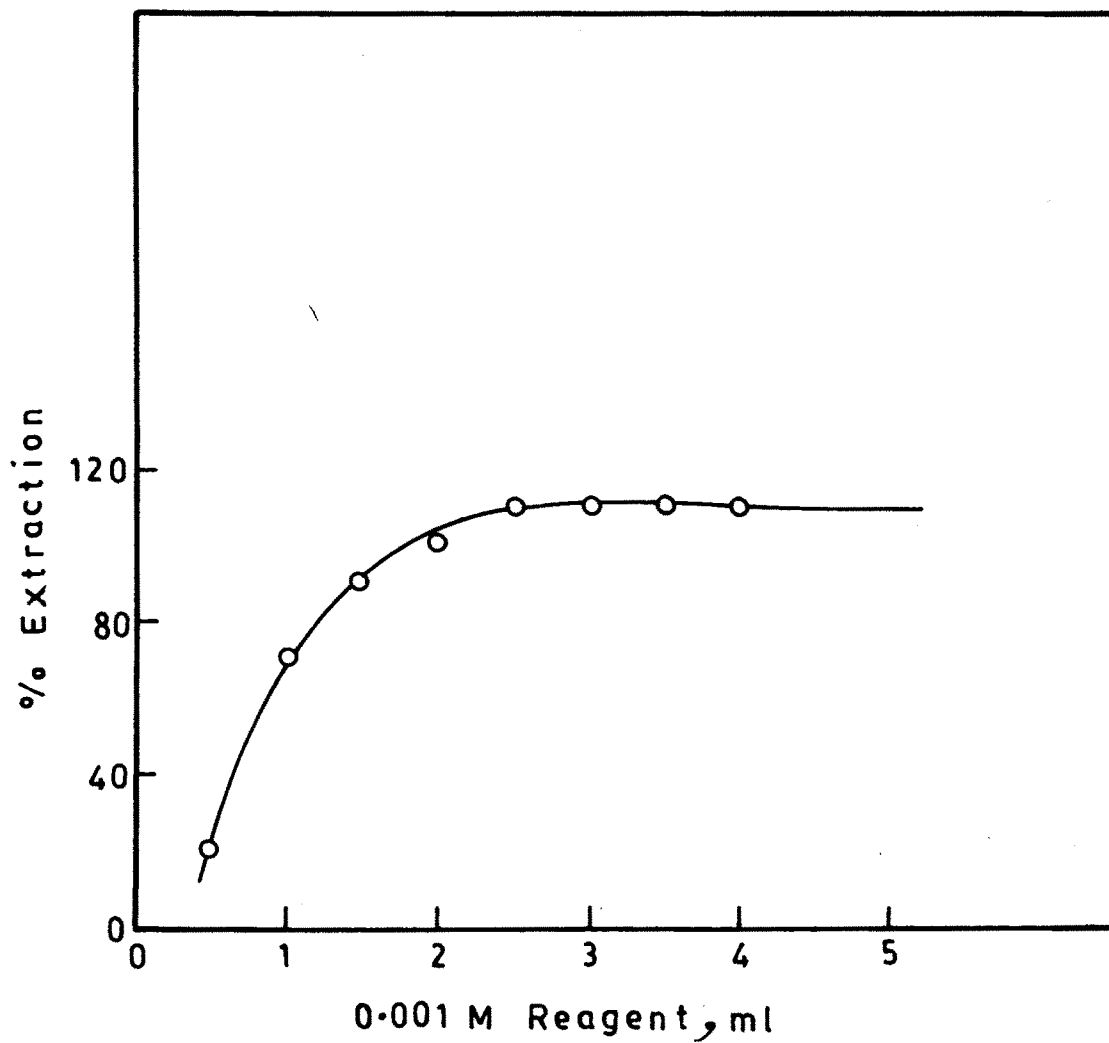


Fig. 1 — EFFECT OF REAGENT CONCENTRATION .

Au (III) = 300  $\mu$ g

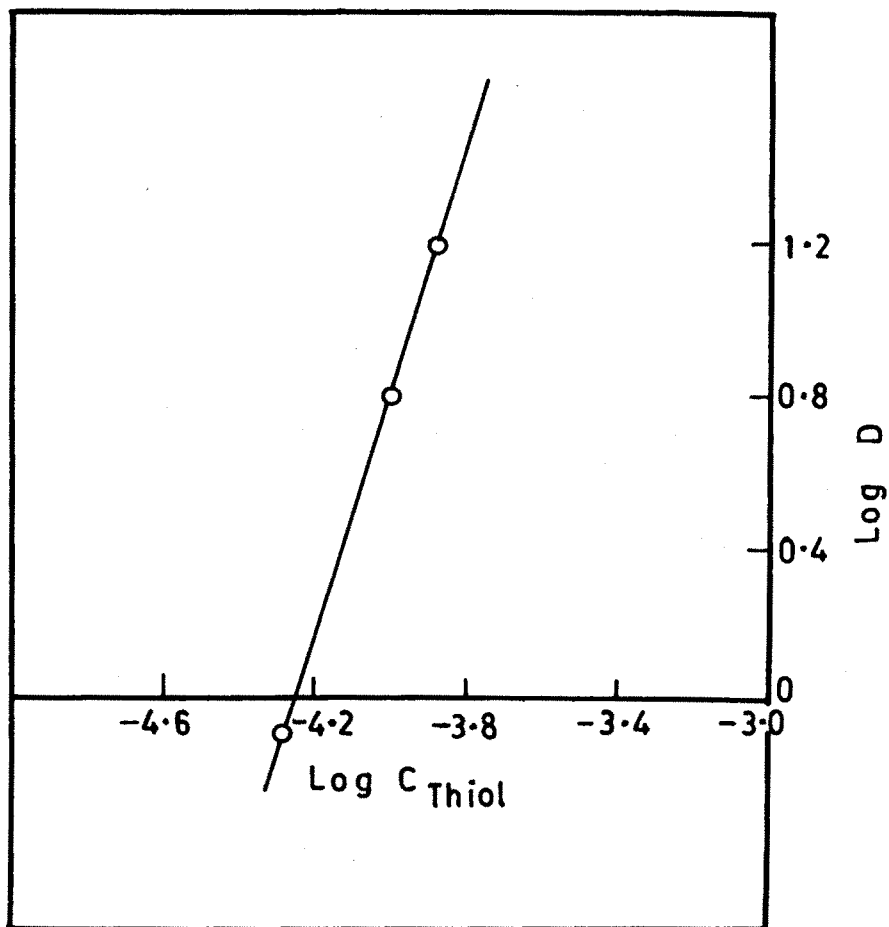


Fig. 2 - Log D - Log C PYRIMIDINE THIOL



#### Effect of the Diverse Ions:

The effect of large number of diverse ions on the determination of Au(III) with pyrimidinethiol 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. The coextraction of Pd(II) and Os(VIII) was removed by using the separation scheme. (52-53). Many ions except thiosulphate, thiourea and ascorbic acid 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 2M 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 2M in HCl with 10 ml of 0.01M pyrimidinethiol in chloroform with 30 min shaking are shown in Table-4.

Table 3 : Effect of Diverse Ions Au(III) = 300 g; HCl = 2 M

Foreign ion	Amount tolerated in mg	Foreign ion	Amount tole- rated in mg.
V(V)	5.0	Te(IV)	3.0
Cr(VI)	1.0	Se(IV)	5.0
Mn(II)	15.0	Ti(I)	3.0
Fe(III)	20.0	Ce(IV)	3.0
Co(II)	20.0	Ti(IV)	5.0
Ni(II)	20.0	Th(IV)	10.0
Cu(II)	20.0	Bi(III)	5.0
Zn(II)	10.0	Thiosulphate	Int.
Ga(III)	10.0	Iodide	100.0
Mo(VI)	3.0	Thiourea	100.0
Ru(III)	1.0	Sulphasalicylic acid	100.0
Rh(III)	5.0	EDTA	100.0
Pd(II)	Coextract	Phosphate	100.0
Cd(II)	10.0	Oxalate	100.0
W(VI)	15.0	Thiocynate	100.0
Os(VIII)	Coextract	Acetate	100.0
Ir(III)or(IV)	10.0	H <sub>2</sub> O <sub>2</sub>	100.0
Pt(IV)	20.0	MnO <sub>4</sub>	100.0
Hg(II)	16.0	Tartrate	100.0
Pb(II)	5.0	Citrate	100.0
U(VI)	20.0	Ascorbic acid	Int.
Ag(I)	0.2	Nitrate	100.0
Zr(IV)	10.0		
Al(III)	5.0		

Table 4 : Determination of Gold(III) of the pp<sup>b</sup> level in  
2500 ml of water

Pyrimidinethiol			
Au(III), taken pp <sup>b</sup>	Au(III) found pp <sup>b</sup>	Au(III) recovery %	Au(III) relative error %
60	59.7	99.5	0.5
90	89.8	99.8	0.2
100	101.0	101.0	1.0

( six determinations )

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