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Synergistic liquid–liquid extractive spectrophotometric determination of gold(III) using 1-(2′,4′-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol

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ABSTRACT

Synergistic liquid–liquid extractive spectrophotometric determination of gold(III) using 1-(2′,4′-dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydro pyrimidine-2-thiol [2′,4′-dinitro APTPT] has been described. Equal volumes (5 cm^3) of the 2′,4′-dinitro APTPT (0.02 mol L^{-1}) in the presence of pyridine (0.5 mol L^{-1}) form an orange-red coloured ternary complex with gold(III) of molar ratio 1:1:1 at pH 1.8–2.4 with 5 min of shaking. The absorbance of coloured organic layer in 1,2-dichloroethane is measured spectrophotometrically at 445 nm against reagent blank. A pronounced synergism has been observed by the binary mixture of 2′,4′-dinitro APTPT and pyridine, which shows that the enhancement in the absorbance is observed in the presence of pyridine by the adduct formation in the organic phase. Beer's law was obeyed in the concentration range 2.5–20.0 μg mL^{-1}, with molar absorptivity and Sandell's sensitivity values of 8.7×10^3 dm^3 mol^{-1} cm^{-1} and 0.023 μg cm^{-2} respectively. A repetition of the method was checked by finding relative standard deviation (R.S.D.) ($n = 10$) which was 0.17%. The composition of the gold(III)–2′,4′-dinitro APTPT–pyridine adduct was established by slope analysis, molar ratio and Job's method. The ternary complex was stable for more than 48 h. The influence of various factors such as pH, 2′,4′-dinitro APTPT concentration, solvent and pyridine on the degree of complexation has been established. A number of foreign ions tested for their interferences and use of suitable masking agents wherever necessary are tabulated, which show that selectivity of the method has been enhanced. The method is successfully employed for the determination of gold(III) in binary, synthetic mixtures and ayurvedic samples. The reliability of the method is assured by inter-comparison of experimental values, using an atomic absorption spectrometer.

1. Introduction

The abundance of gold in the earth's crust is 0.004 μg mL^{-1} [1]. Gold is the most important noble metal due to its wide application in industry and economic activity. A wide variety of spectrophotometric methods for the determination of gold have been reported by Sandell [2] and Marczenko [3] in their monographs. Gold could be determined colorimetrically by reduction to the metal, which under suitable conditions gives fairly stable colloidal suspensions. Stannous chloride is as good as any other methods proposed for this purpose. However, this method has many limitations such as colour development is highly sensitive to hydrochloric acid concentration, for full colour development 20 min waiting time is required. Platinum, Pd, Ru, Te, Se, Ag, Hg and W which gave fairly intense coloured reduction products under these conditions. The method has very low sensitivity (0.05 μg Au/cm^3). The coloured species has no specific λ_{max} value which changes with acid concentration. The proposed method when compared with other spectrophotometric methods is found to be more sensitive and selective [4–18] (Table 1).

Solvent extraction is one of the most efficient methods for separation technology because of its simplicity, speed and applicability to both tracer and macro-amounts of metal ions. The primary cause of synergism is generally accepted to an increase in hydrophobic character of the extracted metal complex upon addition of the adduct, although proposed mechanism involved replacement of the metal ion–water molecule by the adduct molecule or expansion of the coordination sphere of the metal ion upon the addition of the adduct molecule [19–21]. Furthermore, synergistic extraction of metal ions has various advantages over ordinary liquid–liquid solvent extraction system, such as enhancement of extractability, widening the optimum concentration, pH range, stabilization of extracted species by forming an adduct [22].

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Table 1
Comparison of the present method with other spectrophotometric methods for the determination of gold(III).

Reagent	λ_{max}/nm	Acidity/pH	Beer's law validity range/ppm	Molar absorptivity L mol^{-1} cm^{-1} ε	M:L[a]	Remarks	Ref. No.
5-(2-Hydroxy-5-nitrophenylazo)thior-hodanine	520	0.05–0.5 mol L^{-1} H_3PO_4	0.01–3	1.37 × 10^5	1:3	Use of surfactants. Absorption increases in the presence of surfactants	[4]
Amberlite XAD-2000		1.5 mol L^{-1} HCl	–	–	–	Column preparation	[5]
Sudan Red III	520	H_2SO_4	0–20	–	–	Column preparation	[6]
2-Carboxyl-1-naphthalthiorhodanine	540	0.05–0.5 mol L^{-1} H_3PO_4	0.01–2	1.35 × 10^5	1:3	Use of surfactants. Absorption increases in the presence of surfactants	[7]
Thamine and phloxine	570	4.3–4.9	0.2–8.0	2.1 × 10^5	1:2	Heated for 25 min at 40 °C	[8]
Tetrabutylammonium cation	292, 360	4–7	0.5–5	2.18 × 10^4 1.40 × 10^4	1:1	Many metal ions interfere	[9]
5-p-Dimethylamino cinnamylidene-1-phenyl-2-thiobarbituric acid	622	0.02–0.07 mol L^{-1} HCl	0.1–0.9	1.1 × 10^5	1:2	Many metal ions interfere strongly	[10]
4-(2-Quinolyazo)phenol	550	8.0–9.5	0.0–6.30	2.0 × 10^4	1:1	Colour stability 45 min, many metal ions interfere seriously	[11]
Ethopropazine hydrochloride and	513	–	0.5–14.1	2.0 × 10^4	1:1	Many metal ions interfere	[12]
Isothipendyl hydrochloride	512	–	0.5–14.5	2.1 × 10^4	1:1		
5-(4-Sulphophenylazo)-8-aminoquinoline	605	0.5% NaOH	0–75	1.48 × 10^5	1:1	Use of surfactants, high sensitivity	[13]
3-Hydroxy-2-methyl-1-phenyl-4-pyridone	365	2.25–2.75 1.4–2.75	0.95–18	1.65 × 10^4	–	Equilibrium time 20 min	[14]
5-(p-Dimethylamino-benzylidine) rhodanine	550	4.0	1–3	–	–	Many metal ions interfere	[15]
Dowex 1X 4	–	0.2 mol L^{-1} HBr	0–2.0	–	–	Column preparation, $K_2S_2O_8$, H_2O_2 used for the oxidation of gold	[16]
Amberlite XAD-7	–	0.5 mol L^{-1} HCl	–	–	–	Column preparation	[17]
Naflon 811X	–	6.0–7.0	–	–	–	Dialysis for 10 min	[18]
2′,4′-Dinitro APTPT	445	1.7–2.4.	5–20	8.70 × 10^3	1:1	Sensitive and selective	P.M.[b]

[a] Metal:ligand.

[b] Present method.

We have reported from this laboratory the extractive spectrophotometric determination of gold(III) by using the derivative of pyrimidine-2-thiol in the presence of tri-*iso*-octyl amine to stabilize the colour of the complex. However, many metal ions co-extracted [23]. Extraction of colourless complex of gold(III) with the amine has also been studied [24]. The extracted complex was decomposed before the spectrophotometric determination with stannous chloride method.

The object of the present work is to study the synergistic solvent extraction and spectrophotometric determination of gold(III) with mixture of 2′,4′-dinitro APTPT and pyridine in 1,2-dichloroethane.

2. Experimental

2.1. Apparatus

Absorption spectra were obtained with an Elico digital spectrophotometer model CL-27 using 1 cm quartz cell. The pH values were determined with an Elico digital pH meter model LI-120.

2.2. Reagents

A stock solution of gold(III) was prepared by dissolving 1.0 g $HAuCl_4$ (AR, Johnson Matthey, UK) in 250 cm^3 of double distilled water and was standardized gravimetrically [25]. Working solutions were prepared by diluting the stock solution suitably.

2.2.1. 1-(2′,4′-Dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol solution, 0.02 M

1-(2′,4′-Dinitro aminophenyl)-4,4,6-trimethyl-1,4-dihydropyrimidine-2-thiol [2′,4′-dinitro APTPT] was synthesized and recrystallized as reported by Mathes [26]. A 0.02 M stock solution was prepared by dissolving 0.324 g of 2′,4′-dinitro APTPT in a 50 cm^3 1,2-dichloroethane.

Other standard solutions of different metals used to study the effect of foreign ions were prepared by dissolving weighed quantities of their salts in double distilled water or dil. HCl. Solutions of anions were prepared by dissolving the respective alkaline metal salts in water. Different synthetic mixtures containing gold(III) were prepared by combining with commonly associated metal ions in definite composition. All of the chemicals used were of AR grade. Doubly distilled water was used throughout.

2.3. Recommended procedure

An aliquot of the sample solution containing 10 $\mu g\,mL^{-1}$ gold(III) solution was taken and pH was adjusted to 2.2 with dil. HCl and NaOH in 25 cm^3 volume. The solution was transferred into a 125 cm^3 separatory funnel and thoroughly mixed with 5 cm^3 of a 0.02 $mol\,L^{-1}$ 2′,4′-dinitro APTPT and 5 cm^3 of 0.5 $mol\,L^{-1}$ pyridine in 1,2-dichloroethane solution for 5 min. The two phases were allowed to separate and dried over anhydrous Na_2SO_4. The organic layer having an orange-red colour was transferred to a 10 cm^3 standard flask and made up to the mark with 1,2-dichloroethane. The absorbance of the organic phase was measured at 445 nm against reagent blank in 1,2-dichloroethane. Unknown amount of gold(III) was determined from the calibration graph prepared in the same manner.

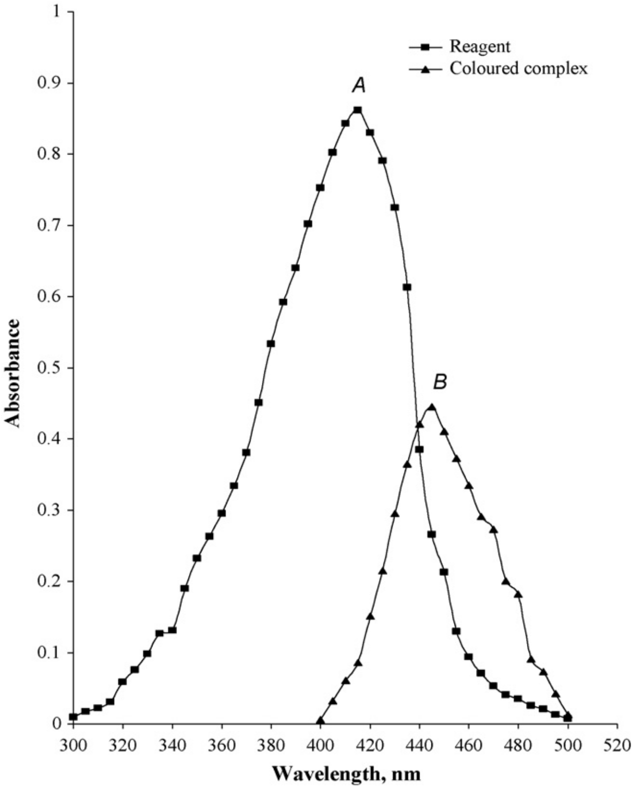

Fig. 1. (A) Absorption spectra of 2′,4′-dinitro APTPT vs. 1, 2-dichloroethane blank (B) Absorption spectra of Au(III)-2′,4′-dinitro APTPT complex vs.2′,4′-dinitro APTPT blank: Au(III) = 10 $\mu g\,mL^{-1}$, 2′,4′-dinitro APTPT = 5 cm^3 of 0.02 $mol\,L^{-1}$, pyridine = 5 cm^3 of 0.5 $mol\,L^{-1}$, pH = 2.2, shaking time = 5 min, λ_{max} = 445 nm.

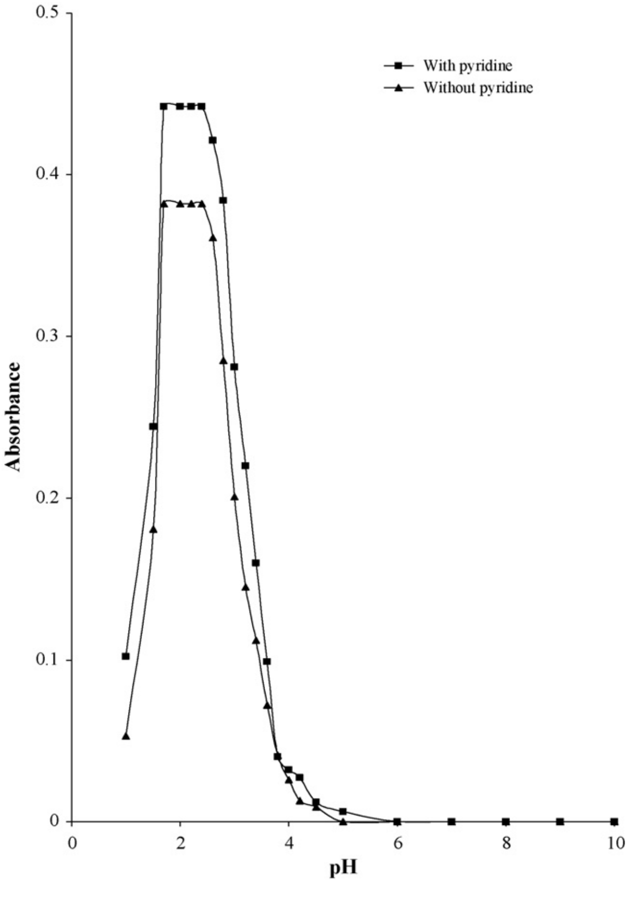

Fig. 2. Effect of pH on the extraction of Au(III)-2′,4′-dinitro APTPT complex: Au(III) = 10 $\mu g\,mL^{-1}$, 2′,4′-dinitro APTPT = 5 cm^3 of 0.02 $mol\,L^{-1}$, pyridine = 5 cm^3 of 0.5 $mol\,L^{-1}$, shaking time = 5 min, λ_{max} = 445 nm.

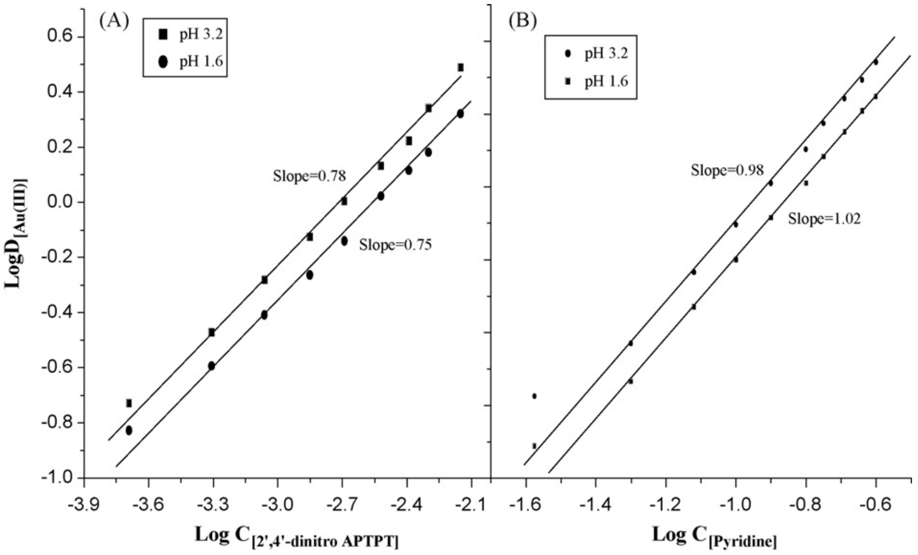

Fig. 3. Slope ratio method: (A) Au(III) = 10 μg mL^{-1}, 2′,4′-dinitro APTPT = 2×10^{-4} to 7×10^{-3} mol L^{-1}, pyridine = 5 cm^3 0.5 mol L^{-1}, shaking time = 5 min, λ_{max} = 445 nm. (B) Slope ratio method: Au(III) = 10 μg mL^{-1}, 2′,4′-dinitro APTPT = 5 cm^3 of 0.02 mol L^{-1}, pyridine = 0.025 to 0.250 mol L^{-1}, shaking time = 5 min, λ_{max} = 445 nm.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of the gold(III)–2′,4′-dinitro APTPT complex and the reagent in 1,2-dichloroethane have the maximum absorbance at 445 and 415 nm, respectively. Thus, further absorbance measurements of the complex were made at 445 nm against reagent blank solution (Fig. 1).

3.2. Effect of the pH

The extraction of gold(III) with 2′,4′-dinitro APTPT in 1,2-dichloroethane was carried out in the presence and absence of pyridine at different pH as shown in Fig. 2. In the absence of pyridine, the extraction of gold(III) took place in the pH range from 1.7 to 2.4. However, in the presence of 5 cm^3 of 0.5 mol L^{-1} pyridine there was enhancement in the absorbance in the same pH range. Thus, pyridine shows a synergistic effect on the extraction of gold(III)–2′,4′-dinitro APTPT complex from acidic medium. Hence, pH 2.2 was employed for further studies.

3.3. Effect of solvent

Various organic solvents were examined for the extraction of gold(III) with 2′,4′-dinitro APTPT complex in the presence of 5 cm^3 of 0.5 mol L^{-1} pyridine. It was observed that, the percentage extraction (%*E*) values increased in the order of kerosene (8.8) < amyl alcohol (9.5) < n-butanol (10.9) < xylene (30.5) < toluene (35.7) < amyl acetate (75.3) < methyl-*iso*-butyl ketone (88.0) < carbon tetrachloride (88.5) < chloroform (94.6) < 1,2-dichloroethane (99.9). Among these, 1,2-dichloroethane was used for further extraction.

3.4. Effect of 2′,4′-dinitro APTPT concentration

The concentration of 2′,4′-dinitro APTPT in 1,2-dichloroethane was varied from 0.0007 to 0.01 mol L^{-1} for full colour development in the presence of 5.0 cm^3 of 0.5 mol L^{-1} pyridine at pH

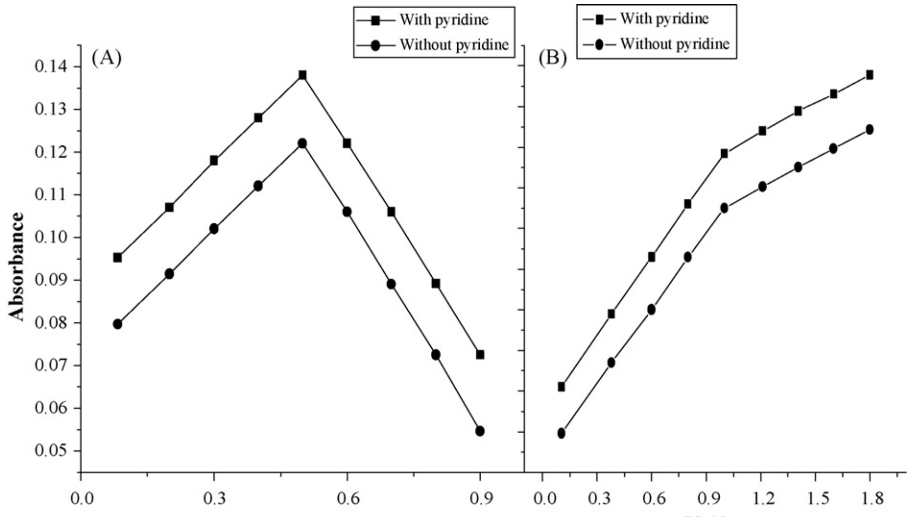

Fig. 4. (A) Mole ratio method: Au(III) = 2′,4′-dinitro APTPT = 1.52×10^{-3} mol L^{-1}, Pyridine = 5 cm^3 of 0.5 mol L^{-1}, pH = 2.2, shaking time = 5 min, λ_{max} = 445 nm. (B) Job's continuous variation graph: Au(III) = 2′,4′-dinitro APTPT = 1.52×10^{-3} mol L^{-1}, Pyridine = 5 cm^3 of 0.5 mol L^{-1}, pH = 2.2, shaking time = 5 min, λ_{max} = 445 nm.

2.2. In the absence of pyridine, absorbance was lowered. Therefore, the extraction of gold(III) was complete and reproducible with 0.007 mol L^{-1} 2′,4′-dinitro APTPT in the presence of pyridine. However, 5 cm^3 of 0.02 mol L^{-1} reagent was recommended in order to ensure the complete complexation. There was no significant change in the absorption with excess of the reagent concentration.

3.5. *Effect of shaking time*

The optimum shaking time of 4 min was determined by varying the shaking time from 0.5 to 10 min in the absence and presence of pyridine. Prolonged shaking has no adverse effect on the extraction of gold(III) in the presence of pyridine. Hence, a shaking time of 5 min was selected for subsequent experiment.

3.6. *Effect of nature and concentration of auxiliary ligand*

The effect of the concentration of pyridine, 3-picoline and 4-picoline was studied by measuring the absorbance of gold(III) with 5 cm^3 of 0.02 mol L^{-1} 2′,4′-dinitro APTPT. The volume of 0.5 mol L^{-1} pyridine, 3-picoline and 4-picoline in 1,2-dichloroethane was varied from 0 to 5 cm^3 to obtain the maximum colour development. It was observed that the colour of gold(III) complex into organic phase increases as the pyridine concentration increases and remains constant from 4 cm^3 of 0.5 mol L^{-1} pyridine. However, in the presence of 3-picoline, 4-picoline there was no significant enhancement in the absorbance. Therefore, 5 cm^3 of 0.5 mol L^{-1} pyridine in 1,2-dichloroethane was used for further studies.

Table 2

Influence of foreign ions for the determination of 10 μg mL^{-1} gold(III) with 2′,4′-dinitro APTPT at 445 nm.

Coexisting ions	Added as	Amount tolerated (mg)	Without masking agent absorbance at 445 nm	With masking agent absorbance at 445 nm	Masking agent
None	–	–	0.424		
Zn(II)	$ZnSO_4{\cdot}7H_2O$	25.0	0.424		
Mn(II)	$MnCl_2{\cdot}6H_2O$	25.0	0.424		
Sn(II)	$SnCl_2{\cdot}2H_2O$	25.0	0.424		
Al(III)	$AlCl_3{\cdot}6H_2O$	25.0	0.424		
Tl(I)	$TlNO_3$	25.0	0.424		
Te(IV)	Na_2TeO_3	25.0	0.424		
Ca(II)	$CaCO_3$	25.0	0.424		
Ce(IV)	$Ce(SO_4)_2$	25.0	0.424		
Se(IV)	SeO_2	15.0	0.424		
Ga(III)	$GaCl_3$	10.0	0.424		
Mo(VI)	$(NH_4)_6Mo_7O_{24}{\cdot}2H_2O$	10.0	0.424		
Fe(III)	$(NH_4)Fe(SO_4)_2{\cdot}12H_2O$	5.0	0.424		
Ir(III)	$IrCl_3{\cdot}xH_2O$	5.0	0.424		
Y(III)	$Y(NO_3)_3$	5.0	0.424		
Cr(III)	$CrCl_3$	3.0	0.424		
Sn(IV)	$SnCl_4$	3.0	0.424		
In(III)	$InCl_3{\cdot}4H_2O$	3.0	0.424		
Sr(II)	$Sr(NO_3)_2$	3.0	0.424		
Ba(II)	$BaCl_2{\cdot}2H_2O$	3.0	0.424		
Gd(III)	Gd_2O_3	3.0	0.424		
Th(IV)	$Th(NO_3)_4$	3.0	0.424		
Mg(II)	$MgCl_2{\cdot}6H_2O$	3.0	0.424		
Fe(II)	$Fe(SO_4)_2{\cdot}7H_2O$	1.0	0.424		
Ru(III)	$RuCl_3{\cdot}6H_2O$	1.0	0.424		
Nb(V)	NH_4NbF_6	0.2	0.424		
Zr(IV)	$ZrOCl_2$	0.2	0.424		
U(VI)	$UO_2(NO_3)_2{\cdot}6H_2O$	0.2	0.424		
Pt(IV)	H_2PtCl_6	0.2	0.424		
Ni(II)	$NiCl_2{\cdot}6H_2O$	15	1.835	0.424	5 mg NH_4SCN
Hg(II)	$HgCl_2$	15	1.534	0.424	5 mg NH_4SCN
Co(II)	$CoCl_2{\cdot}6H_2O$	5.0	0.932	0.424	5 mg NH_4SCN
Pb(II)	$Pb(NO_3)_2$	5.0	0.236	0.424	5 mg Na_2EDTA
Cd(II)	$Cd(NO_3)_2{\cdot}2H_2O$	5.0	1.532	0.424	5 mg Na_2EDTA
Sb(III)	Sb_2O_3	5.0	0.172	0.424	5 mg Na_2EDTA
Os(VIII)	OsO_4	1.0	0.023	0.424	5 mg NH_4SCN
Cu(II)	$CuSO_4{\cdot}5H_2O$	1.0	1.321	0.424	5 mg Na_2EDTA
Mn(VII)	$KMnO_4$	1.0	0.186	0.424	5 mg Na_2EDTA
Bi(III)	$Bi(NO_3)_3{\cdot}5H_2O$	1.0	0.182	0.424	100 mg $Na_3C_6H_5O_7$
Iodide	NaI	100	0.424		
Citrate	$Na_3C_6H_5O7$	100	0.424		
Sulphate	K_2SO_4	100	0.424		
Tartarate	$C_2H_2O_6$	100	0.424		
Bromide	KBr	50	0.424		
Phosphate	Na_3PO_4	50	0.424		
Malonate	$C_3H_3O_4$	50	0.424		
Fluoride	NaF	25	0.424		
Nitrate	$NaNO_3$	25	0.424		
Acetate	CH_3COONa	25	0.424		
Thiourea	$CS(NH_2)_2$	5	0.424		
EDTA	Na_2EDTA	5	0.424		
Thiocynate	NH_4SCN	5	0.424		
Nitrite	$NaNO_2$	1	0.424		

Table 3
Separation of gold(III) from associated metals.

Metal ion	Amount taken (μg)	Average% Recovery[a]	R.S.D.%	Chromogenic ligand	Reference number
Au(III)	100	99.9	0.09		
Cu(II)[b]	1000	99.8	0.17	4′-Chloro PTPT	[29]
Au(III)	100	99.9	0.10		
Co(II)[c]	500	99.9	0.05	Thiocyanate	[3]
Au(III)	100	99.8	0.24		
Os(VIII)[c]	500	99.8	0.15	Thiourea	[2]
Au(III)	100	99.7	0.27		
Pt(IV)	300	99.9	0.09	$SnCl_2$	[2]
Au(III)	100	99.8	0.20		
Sb(III)	250	98.7	1.32	Ascorbic acid + KI	[3]
Au(III)	100	99.9	0.06		
Ru(III)	200	99.6	0.42	Thiourea	[2]
Au(III)	100	99.7	0.23		
Ir(III)	150	99.6	0.41	HBr + $SnCl_2$	[3]
Au(III)	100	99.7	0.30		
Bi(III)[d]	100	99.6	0.37	Ascorbic acid + KI	[3]
Au(III)	100	99.9	0.15		
Pd(II)[b]	100	99.7	0.26	4′-Chloro PTPT	[30]
Au(III)	100	99.8	0.15		
Hg(II)[b]	100	99.9	0.07	PAR	[31]
Au(III)	100	99.5	0.49		
Ni(II)[c]	75	98.4	1.51	DMG	[3]
Au(III)	100	99.8	0.22		
Fe(III)	50	98.6	1.39	Thiocyanate	[3]

[a] Average of five determinations.
[b] Masked with 5 mg EDTA.
[c] Masked with 5 mg thiocyanate.
[d] Masked with 100 mg citrate.

3.7. Effect of colour stability of complex

The absorbance of the gold(III)–2′,4′-dinitro APTPT complex in 1,2-dichloroethane solution was stable for more than 48 h in the presence of pyridine. But in the absence of pyridine, significant extraction was not obtained and colour stability decreases after 5 h and remains constant. Hence the time of measurement of absorbance of complex in the presence of pyridine was not critical.

3.8. Beer's law and sensitivity

The system obeyed Beer's law over the concentration range of 2.5–25 μg mL^{-1} of gold(III) as evaluated by Ringbom's plot method [27] was 5–20 μg mL^{-1}. The sensitivity of the method defined by Sandell was 0.023 μg cm^{-2} and molar absorptivity was 8.7×10^3 dm^3 mol^{-1} cm^{-1}. The standard deviation calculated from 10 determinations on a solution containing 10 μg mL^{-1} of gold(III) is 0.02 and relative standard deviation of the method is 0.17%.

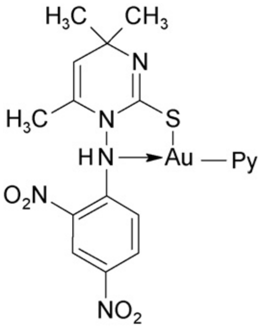

Fig. 5. Structure of Au(III)-1-(2′,4′-dinitro aminophenyl)-4,4,6-trimethyl 1,4-dihydropyrimidine-2-thiol-pyridine complex.

3.9. Stoichiometry of the complex

The synergistic extraction of precious metals by mixtures of an acidic chelating extractant and an organic amine has been investigated. In order to apply this kind of extraction system to the separation of gold(III) and to evaluate its extraction properties, the synergistic extraction with 2′,4′-dinitro APTPT and a pyridine (py) was studied at pH 2.2.

Table 4
Determination of gold(III) in a synthetic mixtures.

Composition (μg)	Average% Recovery[a]	R.S.D.%
Au, 100; Pd[b] 100; Pt, 300	99.9	0.14
Au, 100; Cu[b], 1000; Hg[b], 100	99.8	0.18
Au, 100; Bi[c], 100; Fe,200	99.8	0.15
Au, 100; Ru, 200; Os[d], 200	99.8	0.17
Au, 100; Ni[d], 1000; Hg[b], 100	99.8	0.20
Au, 100; Sb[e], 50; Ru, 100	99.9	0.14
Au, 100; Co[d], 500; Ni[d], 1000	99.5	0.50
Au, 100; Ir, 200; Pt, 300	99.8	0.21
Au, 100; Ag[f], 100; Pt, 300	99.8	0.20
Au, 100; Ag[f], 100; Cu[b], 1000	99.9	0.10

[a] Average of five determinations.
[b] Masked with 5 mg EDTA.
[c] Masked with 100 mg citrate.
[d] Masked with 5 mg thiocyanate.
[e] Masked with 25 mg flouride.
[f] Precipitate out by 10 M HCl (10 cm^3).

Table 5
Determination of gold(III) from ayurvedic samples.

Name of medicine	Certified value of gold(III) (mg/gm)	Amount found by AAS (mg/gm)	Amount found by proposed method[a] (mg/gm)	Confidence limit $\alpha = 0.95$	R.S.D.%
Vasantkumar Rasa	26.1	25.25	24.72	0.068	0.20
Brahatshwas Kas Cintamani Rasa	72.1	69.15	69.15	0.086	0.09
Garbhcintamani Rasa (Brihat)	14.0	13.82	13.82	0.040	0.24
Brahmi Vati	3.0	3.10	3.10	0.001	0.03
Makardhwaja Vati	1.0	1.24	1.22	0.002	0.12

[a] Average of five determinations.

The probable composition of extracted species was ascertained by plotting graphs of $\log D_{[\mathrm{Au(III)}]}$ against $\log C_{[2',4'\text{-dinitro APTPT}]}$ at fixed pyridine concentration ($0.5\,\mathrm{mol\,L^{-1}}$). The plots were linear having the slopes 0.75 and 0.78 at pH 3.2 and 1.6, respectively. Also plots of $\log D_{[\mathrm{Au(III)}]}$ against $\log C_{[\mathrm{pyridine}]}$ at fixed 2′,4′-dinitro APTPT concentration ($0.02\,\mathrm{mol\,L^{-1}}$) were linear with slopes of 1.02 and 0.98 at pH 3.2 and 1.6, respectively (Fig. 3). The probable composition of extracted species was calculated to be 1:1:1 (metal:thiol:pyridine). The composition was also verified by Mole ratio and Job's method of continuous variation (Fig. 4).

As 2′,4′-dinitro APTPT is a weak organic acid, its degree of dissociation increases with decreasing acidity in the aqueous phase. At the given acidity, gold(III) reacts with 2′,4′-dinitro APTPT in the presence of auxiliary ligand pyridine, giving an uncharged chelate which is distributed between two phases according to the following equations,

$$\mathrm{HAu^{III}Cl_4} + 3\mathrm{R{-}SH} \rightleftarrows \mathrm{Au^{I}SR} + \mathrm{R{-}S{-}S{-}R} + 4\mathrm{HCl} \qquad (1)$$

$$\mathrm{Au^{I}SR} + \mathrm{py} \rightleftarrows \mathrm{Au(py)SR_{adduct}} \qquad (2)$$

The sulphur containing ligands first reduce the metal ion [Au(III) Au(I)] and then complex formation takes place [28]. Due to multidentate behavior of the ligand, thiol group ($\mathrm{R{-}S^-}$) and nitrogen from –NH– group coordinate with gold(III) to form five-membered chelate and then interact with pyridine to enhance the extractability by adduct formation. Based on this investigation the structure is recommended for the complex (Fig. 5).

3.10. Influence of foreign ions

The effect of foreign ions on the determination of gold(III) was investigated by adding the known amount of test ion to a standard gold(III) solution and by comparing the final absorbance with the standard. The tolerance limits of other ions which do not cause a deviation of more than ±2% in the absorbance in the determination of gold(III) is given in Table 2. The result shows that most common ions do not interfere with the determination. Selectivity of this method is increased by the use of suitable masking agent. In the presence of ascorbate, oxalate, salicylate and thiosulphate extraction of gold(III) is not possible.

3.11. Applications

3.11.1. Separation of gold(III) from associated metals

The method permits the separation and determination of gold(III) from associated metals containing Cu(II), Co(II), Os(VIII), Pt(IV), Sb(III), Ru(III), Ir(III), Bi(III), Pd(II), Hg(II), Ni(II) and Fe(III).

Gold(III) separated from Pt(IV), Sb(III), Ru(III), Ir(III), Fe(III) by its extraction with $5\,\mathrm{cm^3}$ of $0.02\,\mathrm{mol\,L^{-1}}$ 2′,4′-dinitro APTPT and $5\,\mathrm{cm^3}$ of $0.5\,\mathrm{mol\,L^{-1}}$ pyridine in 1,2-dichloroethane at pH 2.2. Under these conditions the added metal ions remain quantitatively in the aqueous phase. The aqueous phase was evaporated to moist dryness by treating with $5\,\mathrm{cm^3}$ conc. $\mathrm{HNO_3}$ followed by HCl. The residue was dissolved in water and diluted to appropriate volume. The metal ions were determined by standard methods [2,3]. Gold(III)–2′,4′-dinitro APTPT complex was estimated spectrophotometrically at 445 nm against reagent blank.

Copper(II), Pd(II), Hg(II), Co(II), Os(VII), Ni(II) and Bi(III) were co-extracted and affect the colour stability of gold(III) complex. Therefore, separation of these metal ions can be achieved by use of masking agent. Copper(II), Pd(II), and Hg(II) were masked by each of 5 mg of $\mathrm{Na_2EDTA}$ while Co(II), Os(VIII), Ni(II) were masked by each of 5 mg of ammonium thiocyanate and Bi(III) was masked with 100 mg sodium citrate, under these conditions the added metal ions remained in the aqueous phase quantitatively and were subsequently demasked by evaporation to moist dryness by treating with $2\,\mathrm{cm^3}$ of conc. $\mathrm{HClO_4}$ The residue was dissolved in water, diluted to appropriate volume and metal ions were determined by standard methods [2,3,29–31] (Table 3). The absorbance of gold(III)–2′,4′-dinitro APTPT complex from organic phase was measured at 445 nm against reagent blank.

3.11.2. Determination of gold(III) in a synthetic mixtures

A solution containing $10\,\mu\mathrm{g\,mL^{-1}}$ of gold(III) was taken and known amount of different compositions of metal ions was added followed by suitable masking agents. The results were obtained in good agreement with the amount added (Table 4).

3.11.3. Determination of gold(III) from ayurvedic samples

The proposed method was applied for the determination of gold(III) in ayurvedic samples such as Vasantkumar Rasa, Brhatshwas Kas Cintamani Rasa, Garbhacintamani Rasa, Brahmi Vati, Makardhwahaja Vati. Each weight of (1 tablet) sample was dissolved in $5\,\mathrm{cm^3}$ of *aqua regia*. The organic matter was destroyed by treatment with $2\,\mathrm{cm^3}$ of conc. $\mathrm{HClO_4}$. The solution was evaporated to moist dryness. The residue was dissolved in hot dil. HCl and filtered through Whatmann filter paper No. 1. The filtrate was diluted to required volume with water. An aliquot of this solution was analyzed for gold(III) content. The results were in good agreement with those obtained by atomic absorption spectroscopy (Table 5).

4. Conclusion

2′,4′-Dinitro APTPT has been proved to be a sensitive and selective spectrophotometric reagent for gold(III). The developed method is simple, reproducible and rapid; requires less time for separation and determination of gold(III). The important features of the proposed method: (i) It permits selective separation and determination of gold(III) from other associated metals such as Cu(II), Co(II), Os(VIII), Pt(IV), Sb(III), Ru(III), Ir(III), Bi(III), Pd(II), Hg(II), Ni(II), Fe(III). (ii) Low reagent concentration is required for quantitative recovery of gold(III). (iii) The extraction occurs in a single stage. (iv) It is free from interference of a large number of foreign ions which are associated with gold(III) in its natural occurrence. The selectivity was enhanced by the use of suitable masking agents. (v) 2′,4′-Dinitro APTPT forms complex with gold(III) in acidic medium in the presence of auxiliary ligand pyridine which showed synergistic effect in extraction. (vi) The probable stoichiometry of the extracted species calculated to be 1:1:1 (metal:thiol:pyridine). The orange-red coloured complex is stable for more than 48 h. (vii) It is successfully applicable to the determination of gold(III) in analysis of binary, synthetic mixtures and ayurvedic samples.

Novelty Statement

Synergistic liquid-liquid extraction and spectrophotometric determination of gold(III) from weakly acidic aqueous solutions has been observed with a mixture of 2′,4′-dinitro APTPT and pyridine. There was enhancement of absorbance in the pH range 1.8–2.4 and stability of the complex was increased by chelate formation. The method allowed large tolerance limit for foreign ions. Proposed method is simple, rapid, selective and sensitive for extractive spectrophotometric determination of gold(III) as compared with reported one.

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