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Liquid-liquid extraction of gold(III) with 4-(4-ethoxybenzylideneamino)-5-methyl-4*H*-1, 2, 4-triazole-3-thiol (EBIMTT) from hydrochloric acid media

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ABSTRACT

The solvent extraction of gold (III) from hydrochloric acid media using 4-(4-ethoxybenzylideneamino)-5-methyl-4H-1,2,4-triazole-3-thiol (EBIMTT) in chloroform was studied as a function of several variables, such as reagent, acid and metal ion concentration, effect of various diluents, and diverse ions. The gold (III)-EBIMTT complex was stable for more than 24 hours with molar absorptivity and Sandell's sensitivity of (1.8×10^4 L mol^{-1} cm^{-1}) and (0.058μg cm^{-2}), respectively, which indicates applicability of the method. Present method is effective, rapid, reproducible, and free from interference of almost all metal ions tested. The proposed method was further applied for the separation of gold (III) from binary mixtures, synthetic mixtures, alloys and commercially available samples.

KEYWORDS

Gold(III);
EBIMTT;
Liquid-liquid extraction;
Gold alloys.

INTRODUCTION

The abundance of gold in the earth's crust is 0.004μgmL^{-1}[1]. It is widely used in various industries (e.g., electrical systems, fuel cells, catalysts, biomedical area, etc.), due to its unique physical and chemical properties. Some gold salts do have anti-inflammatory properties and are used as pharmaceuticals (ayurvedic samples) in the treatment of arthritis and other similar conditions. Gold nanoparticals are used in treatment of cancer[2]. Taking into account all these applications it is imperative on the part of the analytical chemist to investigate newer methods through which gold can be recovered from natural resources as well as secondary sources.

Though several techniques are in use for the determination of trace and ultra trace quantities of gold[3-7], the spectrophotometric technique still has the advantage in respect of simplicity and low operating costs. Hence, separation and preconcentration of trace level quantities of gold is necessary prior to actual quantitative analysis. Several preconcentration procedures are available for this purpose, however, most of these are time consuming and costly, but, liquid-liquid extraction method still remains a standard method of separation and preconcentration, because of its simplicity, speed and applicability to both tracer and macro-amounts of metal ions.

Over past few years, in a considerable number of studies, several extractants have been used for the extraction of trace amount of gold[8-16]. Most of these show longer equilibration time and difficult to synthesize. Sulphur containing Schiff bases showed promising effects in the field of analytical chemistry for the separation and estimation of platinum group metals[17]. As a soft acid, gold has a great affinity for soft base ligand containing sulfur. A significant number of sulphur reagents has been proposed for use in the extractive separation of gold such as, tetrathiododecane[18], mercaptobenzothiazole[19], dialkyl sulphides[20], thioamide derivatives[21] N-substituted alkylthiourea[22], 3,3-diethylthietane[23].

EXPERIMENTAL

Instrumentation

A Jasco V-530 UV-Vis spectrophotometer with 1 cm quartz cells was used for absorbance measurement; pH measurements were carried out with an Elico digital pH meter model LI-120 (± 0.01).

Reagents

A stock solution of gold (III) was prepared by dissolving of 1g of $HAuCI_4$ in analytical reagent grade hydrochloric acid (1M) diluted to 100 ml with distilled water and standardized gravimetrically[24]. A working solution of 200μg ml^{-1} was prepared by diluting the stock solution with distilled water. Other standard solutions of different metal ions were screened to study the effect of foreign ions which were prepared by dissolving weighed quantities of respective salts in dilute hydrochloric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in distilled water. All the chemicals used were of AR grade. Double distilled water was invariably used throughout the measurements. The extractant (EBIMTT) was prepared according to previously published procedure[25].

General procedure

An aqueous solution containing 200μg of gold (III) mixed with a sufficient quantity of hydrochloric acid and water so as to maintain the pH value of the solution to 1.0. The solution was transferred into a 125 ml separation funnel containing 10 ml of 0.1M EBIMTT in chloroform and shaken for 30 seconds. After equilibration, the mixture was allowed to separate and the metal was stripped from the organic phase with two 10 ml portions of ammonia solution (pH-10). The collected extract was evaporated to moist dryness. The residue was dissolved in 5ml of concentrated hydrochloric acid to afford a clear gold (III) solution. It was then estimated spectrophotometrically by standard stannous chloride method[26] at 400nm as λ_{max}.

RESULTS AND DISCUSSION

Gold (III) reacts with extractant and forms 1:1 metal-ligand complex. The complex has maximum absorption at 400 nm and is stable for over 24 hours. The molar absorptivity (1.8×10^4 L mol^{-1} cm^{-1}) and Sandell's sensitivity (0.058μg cm^{-2}) of the complex suggests that trace and ultra trace level quantities of gold can be quantified with required accuracy and precision. The influence of various factors like pH, reagent concentration, choice of solvent and effect of foreign ions on the extraction efficiency of gold (III) has been studied for optimizing the conditions for the selective and rapid extraction at trace level quantities.

Effect of acid media

The extraction of 200 μg of gold(III) was carried out from different acid media with 0.1 M EBIMTT in chloroform keeping the aqueous to organic volume ratio 2.5:1. The extraction was found to be quantitative from hydrochloric, and hydrobromic acid media. The extraction is incomplete in nitric acid, sulphuric acid and acetic acid. Among the HCl and HBr, HCl gives better phase separation, hence, the use of hydrochloric acid system is recommended for further studies.

Effect of pH

The effect of pH on the extraction of gold (III)-EBIMTT complex into the organic phase was studied in order to select a suitable pH that could be adopted in the determination of gold (III) which was extracted in the pH range of 0.1- 9 using 1M hydrochloric acid. A

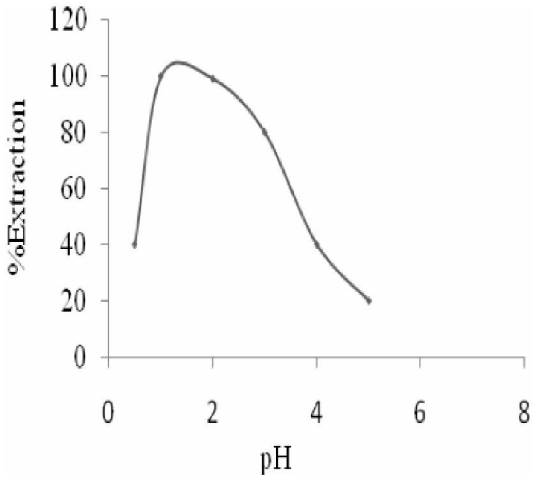

Figure 1 : Effect of pH on the extraction of gold (III) with EBIMT

plot between pH and % extraction has been shown in figure 1. It is observed that the quantitative extraction is possible in the pH range 1-2. The extraction of gold (III) is quantitative in the pH range 1-2 which may be due to the protonation of the ligand in acidic medium. The maximum absorption is observed at pH 1.

Effect of concentration of extractant (EBIMTT)

In order to optimize the conditions for extraction of gold (III), chloroform solutions of EBIMTT with varying concentrations (0.01- 0.20 M) were employed and found that 10 ml of 0.06 M EBIMTT is just sufficient for quantitative extraction of 200µg gold (III) from hydrochloric acid media, however, to ensure complete extraction of metal ion, excess of ligand concentration was used (0.1M). But, a decrease in concentration of extractant resulted in lower distribution ratio, D

Effect of solvent

Among organic solvents (benzene, chloroform, xylene, toluene, carbon tetrachloride, isobutyl methyl ketone, ethanol, and N, N dimethylformamide (DMF)) were examined for the extraction of gold(III) with EBIMTT from hydrochloric acid media, chloroform medium extracts the complex effectively without third phase formation.

Effect of diverse ions

Extraction of gold (III) was carried out in the presence of diverse ions, as mentioned in the TABLE 1. Tabulated results show that sizeable amounts of diverse ions do not interfere in the extraction of gold (III). In order to test the precision of the method the extraction process was repeated six times and the results obtained are 99.00±0.95%. The tolerance limit was set as the amount of foreign ions cause ± 2% error in recovery of gold (III).

TABLE 1 : Effect of foreign ions on extraction of gold (III) from hydrochloric acid media with 0.1M EBIMTT

Foreign ions added	Amount tolerated
Pd^{II} Ru^{III} Pt^{IV} Rh^{II}	0.5
Zn^{II} Mo^{VI} U^{VI} Mn^{VII} Sb^{III} Cd^{II} Cu^{II} Sn^{II} Ni^{II}	05
Mn^{II} Sr^{II}	10
Fe^{III} Bi^{III} Ca^{II} Mg^{II} Be^{II} Ba^{II}	20
Acetate, Iodide, EDTA	100
Oxalate, Fluorides	200

Effect of time

Variation of the shaking period from 5 seconds to 10 minutes showed that a minimum 10 second equilibrium time is just sufficient for quantitative extraction of gold (III) from hydrochloric acid medium however in a general procedure 30 second of time is recommended in order to ensure complete extraction of gold (III). Prolonged shaking has no adverse effect on the efficiency of extraction.

Effect of stripping agents

Stripping is the reverse of extraction, so it should be promoted by those factors that affect extraction negatively. The stripping percentage was calculated relative to the initial amount of gold (III) in the loaded organic solutions. Gold (III) was stripped with different stripping agents such as mineral acids, bases, and salts after its extraction. The stripping of Gold (III) was quantitative with 7M ammonia solution (PH-10), however, the stripping was found to be incomplete with nitric acid, sulphuric acid, hydrochloric acid and with sodium chloride, whereas gold (III) cannot be stripped with water.

APPLICATIONS

Binary separation of gold (III), from iron (III), cobalt (II), nickel (II) and copper (II)

The method allowed separation and determination of gold (III) from a binary mixture containing either iron (III), cobalt (II), nickel (II) and copper (II). In a typical experiment, solution containing 200µg of gold (III) was taken and known amounts of other metal ions were added. The separation of gold (III) from iron(III), cobalt(II), nickel(II) and copper(II) was accomplished with 0.1 mol/dm^3 EBIMTT in chloroform from hy-

TABLE 2 : Binary separation of gold (III) from iron (III), cobalt (II), nickel (II) and copper (II)

Composition of metal ions, (µg)	Average % recovery[a] Rh(III)	R.S.D (%)	Average % Recovery added metal ions	R.S.D. (%)
Au(III)100, Fe(III)1500	99.4	0.15	99.7	0.07
Au(III)100, Co(II)10000	99.5	0.19	99.6	0.13
Au(III)100, Cu(II)5000	99.6	0.25	99.5	0.16
Au(III)100, Ni(II)5000	99.5	0.17	99.6	0.19

[a] **Average of six determination.**

drochloric acid medium. The recovery of gold (III) and those added ions was 99.5% and results are reported in (TABLE 2).

Determination of gold (III) from synthetic mixtures

The separation of gold (III) from the platinum group metals and other metals is very difficult. A solution containing 200μg of gold (III) was taken and known amount of different compositions of metal ions were added followed by suitable masking agents. Under the optimum extraction conditions of gold (III), a quantitative extraction of palladium (II), platinum (IV), ruthenium (III) and rhodium (III) was also observed however co-extracted metal ions cannot be back-stripped by 7M ammonia solution. Thus, the reagent (EBIMTT) is made selective towards gold (III) by taking an advantage of the stripping agent used. (TABLE 3)

Analysis of alloys

To 50–100 mg of the alloy of known composition, 10 ml of aqua regia was added and the solution evaporated to moist dryness. Ten milliliters of concentrated hydrochloric acid was added. The solution was warmed, transferred to a 500-ml standard flask, and made up to mark with distilled water. An aliquot of this solution was taken and gold was determined by the general procedure and the results are shown in TABLE 4. The average recovery of gold (III) was 99.5%.

TABLE 3 : Analysis of synthetic mixtures

Composition of metal ions (μg)	Average % Recovery[a]	R.S.D (%)
Au(100)+Pd(500)	99.6	0.07
Au(100)+Rh(500)	99.8	0.05
Au(100)+Pt(500)	99.7	0.07
Au(100)+Ru(500)	99.8	0.05
Au(100)+Pd(500)+Ru(200)	99.9	0.06
Au(100)+Pd(500)+Rh(200)	99.7	0.07
Au(100)+Pt(500)+Rh(200)	99.7	0.07
Au(100)+Pt(500)+Pd(200)+Rh (200)	99.6	0.06

[a] Average of five determinations.

TABLE 4 : Analysis of alloys

Alloy	Composition (%)	Gold taken (μg)	Gold found[a] (μg)	Recovery (%)	R.S.D (%)
Gold 22 carat	91Au, 4Ag, 4Cu	200	198.83	99	0.07
Coinage alloy	90Au, 10Cu	200	198.81	99	0.07
Jewelry alloy	84Au, 16Cu	200	199.86	99.8	0.03
White gold	75-85Au, 8-10Ni, 2-9Zn	200	198.6	99	0.07

[a] Average of six determinations

CONCLUSION

EBIMTT has proved to be an effective extractant for gold (III), it can be synthesized at low cost with high yield and in the best purity and recovered for reuse without loss of extraction efficiency. The novelty of the method possesses various advantages such as; shorter equilibration time, no third phase formation, better efficiency of extractant, method can be used successfully for the quantitative analysis of gold (III) from alloys, natural sources, secondary sources it is simple and rapid, hence, can be used for routine separation of gold(III) from real samples. It is free from interference from a large number of diverse ions which are associated with gold (III) in its natural occurrence.

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