ORIGINAL ARTICLE

Extraction and separation studies of gold(III) with 4-(4-methoxybenzylideneimino)-5-methyl-4*H*-1,2,4-triazole-3-thiol in hydrochloric acid medium

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Abstract A novel method is proposed for the extraction of microgram level concentration of gold(-III) from hydrochloric acid medium with 4-(4-methoxybenzylideneimino)-5-methyl-4*H*-1,2,4-tria-zole-3-thiol (MBIMTT) dissolved in chloroform as an extractant. The gold(III) from the organic phase is stripped with ammonia buffer solution (pH-10.1) and determined spectrophotometrically with stannous chloride. The method affords the binary separation and determination of gold(III) from the alloys and synthetic mixtures. The method is applicable for the determination and separation of gold from Ayurvedic samples. The method is highly selective, simple and reproducible.

1. Introduction

The beauty and rarity of gold has led to its use in jewelry and coinage, and as a standard for monetary systems throughout the world. Gold has also one of the most important noble metals due to its wide applications in industry and economic activity. In medieval times, gold was often seen as beneficial for health, in the belief that something that rare and beautiful could not be anything but healthy. Even some modern esoter-

icists and forms of alternative medicine assign metallic gold with a healing power. Some gold salts do have anti-inflammatory properties and are used as pharmaceuticals in the treatment of arthritis and other similar conditions. However, only salts and radioisotopes of gold are of pharmacological value, as elemental (metallic) gold is inert to all the chemicals it encounters inside the body.

There is wide application of gold in the industrial process next to their extremely scarcity due to their natural abundance and the complexity of the process used for its extraction and refining, therefore, it is of paramount importance to develop separation methods to recover these metals to meet the future demand. Liquid–liquid extraction is one of the most efficient methods used to separate, concentrate and purify metal ions and organic compounds (De et al., 1970; Freiser, 1970; Marcus-sand and Kertes, 1996; Morrison and Freiser, 1957; Gedye et al., 1989). Solvent extraction has become an effective

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technique in the recovery and separation of gold (Mirza 1980; Biswas et al., 1996; Yukhin et al., 1985; Kolekar and Anuse, 2001). The aqueous chemistry of these metals is extremely complex. The important tendency of these metals is to form chlorocomplex in chloride medium. Solvent extraction technique of separation uses the difference in kinetic behavior for the formation of extractable species as well as the strength of electrostatic interactions of their chlorocomplexes with liquid anion exchanger. The inertness of the chlorocomplex of palladium in aqueous medium plays an important role in the extraction from acidic solution by an anion exchange mechanism. Other extractants reported for gold(III) are *N-n*-octylaniline (Kolekar and Anuse, 2001), cynex 923 (Alguacil et al., 1998), tributylphosphate (Chen et al., 1998), phospholene (Madi et al., 1996), tri-*n*-octylamine (Jianzhun et al., 2005), tri-*n*-butyl phosphate (Yang et al., 2007) alamine (Torgov et al., 2005). The methods reported are not so reliable for routine application because these methods suffer due to the drawbacks such as operating condition (emulsion formation leading to problem for the separation, slow equilibrium) and ionic exchanger, nature of diluents, critical pH range etc.

One coordination chemistry property of Au(III) is that it prefers to coordinate most strongly with polarizable atoms such as sulfur, phosphorous and nitrogen. These ligands are 'soft' bases according to the empirical Pearson classification (Pearson, 1963). Sulfur containing ligands are highly selective for the extraction of Au(III), and have been widely used in the extraction of this species (Alguacil, 2003; Lachowicz and Czapiuk, 1990; Fontas et al., 2007; Domínguez et al., 2002). 4-(4-Methoxybenzylideneamino)-5-methyl-4*H*-1,2,4-triazole-3-thiol (MBIMTT) is sulfur containing ligand and it is highly water repellent. It does not form an emulsion at the time of extraction. Because the determination of small amounts of noble metals in minerals containing large amount of base metals is difficult; the effectiveness of MBIMTT has been evaluated as an extractant for gold(III) from a variety of gold bearing materials and process solutions. MBIMTT has been employed successfully in this laboratory for the extraction of Rh(III) (Vidhate et al., 2008). We report here the use of MBIMTT as an extractant for gold(III) from hydrochloric acid medium.

2. Experimental

2.1. Instrumentation

A Shimadzu UV–Visible spectrophotometer (UV-1601) with 1 cm quartz cells was used for measurement, pH measurements were carried out with an Elico digital pH meter model LI-120($\pm$0.01). A Perkin Elmer (Germany) atomic absorption spectrophotometer with a deuterium lamp back ground corrector, equipped with graphite furnace, with gold hollow cathode lamps. The experimental conditions were: slit width, 1.3 nm; lamp current, 10.0 mA; wavelength, 242.8 nm; cuvette, cup; carrier gas (argon), 200 ml min^{-1}; sample volume, 10 μL.

2.2. Chemicals and reagents

A stock solution of gold(III) was prepared by dissolving 1 g of HAuCl$_4$ in dilute hydrochloric acid (1 M) and diluting to

100 ml with distilled water and further standardizing it (Beamish and Van Loon, 1977). A working solution 100 μg ml^{-1} was prepared from it by diluting the stock solution with distilled water. The reagent MBIMTT was synthesized by the known literature method (Vidhate et al., 2008). MBIMTT (0.1 M) solution was prepared in chloroform.

The solutions of different metal ions used to study the effect of foreign ions were prepared by dissolving weighed quantities of respective salts in distilled water or dilute hydrochloric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in double distilled de-ionized water. All the chemicals used were of AR grade. Double distilled de-ionized water was invariably used throughout the measurements.

2.3. General procedure

An aqueous solution containing 100 μg of gold(III) and enough hydrochloric acid and water were added to give final concentration of 1 M with respect to hydrochloric acid in a total volume of 25 ml. The resulting solution was transferred to 125 ml separating funnel. The aqueous phase was equilibrated once with 10 ml of 0.1 M MBIMTT solution in chloroform for 30 s. The phase was allowed to separate and the metal from the organic phase was backstripped with two 5-ml portions of ammonia buffer solution (pH-10.1). The extract was evaporated to moist dryness and leached with dilute hydrochloric acid to form the solution. Gold(III) was estimated spectrophotometrically with stannous chloride at 540 nm (Sandell, 1965).

3. Results and discussion

3.1. Extraction of gold(III) as a function of acid concentration

The extraction of 100 μg gold(III) was carried out from different acid medium with 0.1 M MBIMTT in chloroform keeping the aqueous to organic volume ratio 2.5:1. The extraction was found to be quantitative from hydrochloric acid. The extraction was found to be quantitative in very high concentrations of nitric acid but was incomplete in sulfuric acid. Hence the use of hydrochloric acid is recommended for further studies.

3.2. Effect of reagent concentration

The concentration of MBIMTT in chloroform was varied from the 1×10^{-5} to 0.2 M over the acid range 1–10 M hydrochloric acid. It was found that 0.1 M reagent in chloroform was needed for the quantitative extraction of gold(III) from 1 M hydrochloric acid.

3.3. Effect of equilibration time

Variation of the shaking period from 5 s to 5 min showed that a minimum 10 s equilibration time is adequate for quantitative extraction of gold(III) from hydrochloric acid media. As a general procedure, 30 s of equilibration time is recommended in order to ensure complete extraction of gold(III) hydrochloric acid medium. Prolonged shaking up to 5 min has no adverse effect on the efficiency of extraction.

Table 1 Effect of diverse ions on the extraction of gold(III).

Tolerance limit (mg)	Foreign ion added
100	Fluoride, citrate, oxalate, acetate, EDTA, malonate, bromide, iodide
20	Ca(II), Ba(II), Be(II), Mg(II), Fe(III)
15	Mn(II), Fe(II), Cr(III), Co(II)
10	Mo(VI), Sr(II), Ti(IV), Ce(IV)
5	U(VI), Mn(VII), Sb(III), Zn(II), Pb(II), Hg(II), Ni(II), Sn(II), Cu(II)
0.5	Pt(IV), Rh(III), Pd(II), Ru(III)

Gold(III) = 100 μg; aqueous phase = 1 M HCl; Aq/Org = 25:10; extractant = 0.1 M MBIMTT in chloroform.

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

Composition of metal ions (μg)	Gold(III) found[a] (μg)	Recovery ± s (%)
Au(III),100; Fe(III), 15,000	99.7	99.4 ± 0.5
Au(III), 100; Co(II) 10,000	99.5	99.5 ± 0.3
Au(III), 100; Ni(II) 5000	99.7	99.6 ± 0.6
Au(III), 100; Cu(II) 5000	99.5	99.5 ± 0.4

[a] Average of six determinations.

Table 3 Analysis of synthetic mixtures.

Composition (μg)	Gold found[a] (μg)	Recovery ± s (%)
Au, 100; Pt, 500	99.4	99.7 ± 0.0
Au, 100; Pd, 500	99.6	99.8 ± 0.2
Au, 100; Ru, 500	99.6	99.8 ± 0.4
Au, 100; Rh, 500	99.8	99.6 ± 0.5
Au, 100; Pt, 500; Ru, 500	99.3	99.7 ± 0.0
Au, 100; Pt, 500; Pd, 500	99.5	99.6 ± 0.6
Au, 100; Pt, 500; Rh, 500	99.6	99.5 ± 0.0
Au, 100; Pt, 500; Ru, 500; Pd, 500	99.7	99.8 ± 1.0
Au, 100; Pt, 500; Rh, 500; Pd, 500	99.4	99.5 ± 1.2
Au, 100; Pt, 200; Ru, 200; Pd, 200; Fe, 2000; Co, 2000; Ni, 2000; Cu, 2000	99.2	99.7 ± 1.0

[a] Average six determination.

3.4. Effect of diluents

The extractions were performed from 1 M hydrochloric acid medium using 0.1 M MBIMTT in various solvents as diluents. It was found that 0.1 M MBIMTT solution in carbon tetrachloride, chloroform, xylene, toluene and benzene provides quantitative extraction of gold(III). The extraction of gold(III) was found to be incomplete in isobutyl methyl ketone, isoamylalcohol, n-butanol and 4-methyl-2-pentanol. Chloroform is recommended for further extraction procedure because it offers better phase separation.

3.5. Nature of extracted species

The composition of complex was confirmed by using $\log D$–$\log C$ plot. The graph $\log D_{[Au(III)]}$ versus $\log C_{[MBIMTT]}$ at 4 M hydrochloric acid was found to be linear and having slope of 1.3. Hence the probable composition of extracted species in chloroform has been found to be 1:1, [Au(III):MBIMTT].

3.6. Loading capacity of MBIMTT

The concentration of gold(III) was varied to determine the loading capacity of MBIMTT. The loading capacity of 10 ml of 0.1 M MBIMTT was found to be 6.5 mg of gold(III).

3.7. Effect of diverse ions

Various ions were used in order to asses the tolerance of these ions on the extraction of gold(III). Gold(III) was extracted in the presence of different diverse ions (Table 1). The tolerance limit was set as the amount of foreign ions cause ± 2% errors in the recovery of gold. The results showed that in the extraction and determination of 100 μg of gold, these ions did not interfere at the level tested. The reproducibility of gold extraction investigated from six replicate measurements was found to be 99.00 ± 0.95%.

4. Applications

4.1. Binary separation of gold(III) from base metals

The method allowed for separation and determination of gold(III) from a binary mixture containing either iron(III), cobalt(II), nickel(II), and copper(II). The separation of gold(III) from iron(III), cobalt(II), nickel(II), and copper(II) by its extraction with 0.1 M MBIMTT in chloroform at 1 M hydrochloric acid. Under this condition all the base metals remain quantitatively in the aqueous phase and these base metals were determined spectrophotometrically with thiocyanate (Vogel, 1978), 1-nitroso-2 naphthol (Vogel, 1978), DMG (Vogel, 1978), and pyrimidine-2-thiol (Kuchekar et al., 1986) respectively. Gold is stripped from the organic phase with two 5 ml portions of ammonia buffer solution (pH-10.1). The extract was evaporated to moist dryness and leached with 1 M hydrochloric acid to form the solution. Gold(III) was estimated spectrophotometrically with stannous chloride. The recovery of gold(III) and that of added ions was 99.7% and results are reported in Table 2.
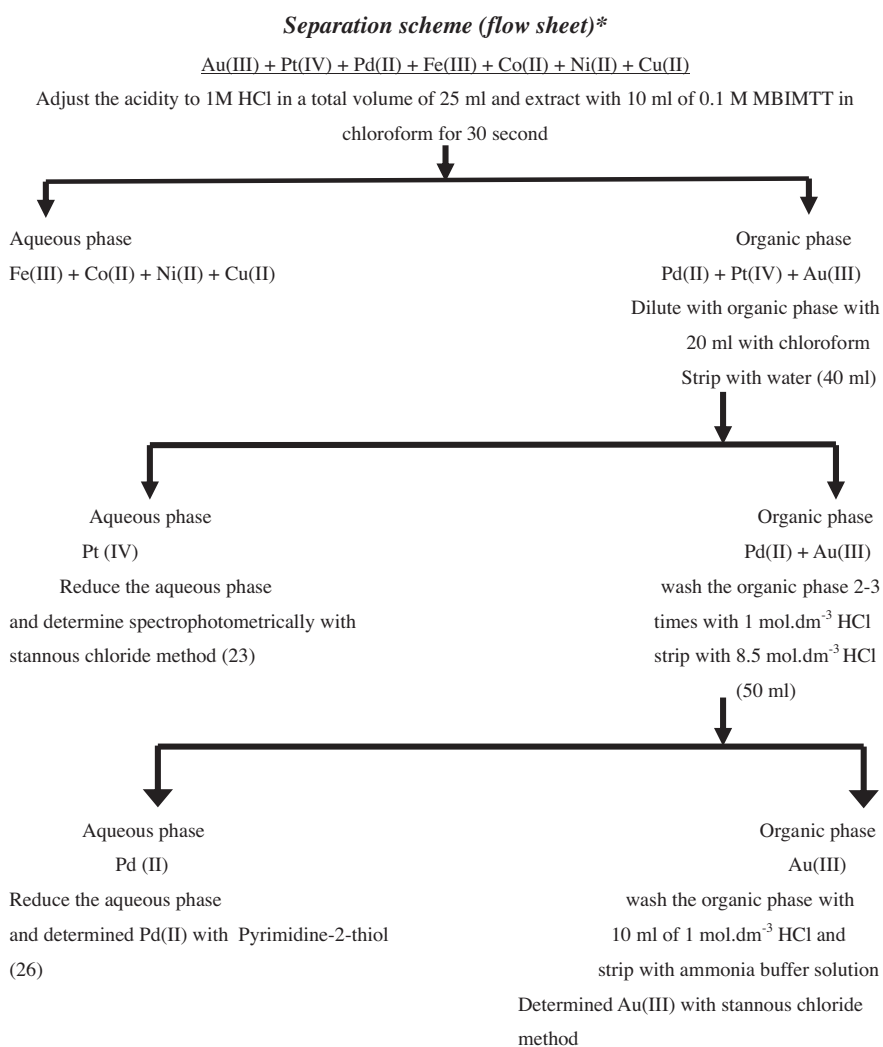
4.2. Separation of gold(III) from multicomponent synthetic mixture

In its natural occurrence gold is always associated with the noble and base metals, hence its separation from these metals is of great importance. Under the optimum conditions for the extraction of gold(III), there is quantitative extraction of Pd(II), Pt(IV) and Rh(III). But the co-extracted metal ions cannot be back stripped by ammonia buffer solution (pH-10.1). Thus the MBIMTT reagent is made selective toward gold(III) by taking advantage of the strippent used. The proposed method allows the selective separation and determination of gold from many metal ions (Table 3).

Table 4 Analysis of alloys.

Alloys	Composition of alloys (%)	Gold(III) found by AAS%	Gold(III) found by proposed method[a] (%)	Recovery ± s (%)
Copper–silver–gold alloy	(i) Cu, 49.35; Ag, 7.25; Au, 43.4	43.4	43.3	99.7 ± 0.0
	(ii) Cu, 35; Ag, 5; Au, 60	59.9	59.8	99.8 ± 0.6
Low melting dental alloy	Pd, 25; Au, 10; Co,22 Ni, 34	9.9	9.7	99.6 ± 0.4
Jewelry alloy(Pd–Au alloy)	Pd, 50; Au, 50	49.9	49.8	99.8 ± 0.0
Solder alloy	Pt, 10; Pd, 30; Au, 60	59.9	59.8	99.7 ± 0.2
Alloy for electrical contact	Pt, 10; Pd, 35; Ag, 30; Cu, 14; Au, 10; Zn, 1.0	9.9	9.8	99.8 ± 1.2

[a] Average six determination.

Separation scheme (flow sheet)*

Au(III) + Pt(IV) + Pd(II) + Fe(III) + Co(II) + Ni(II) + Cu(II)

Adjust the acidity to 1M HCl in a total volume of 25 ml and extract with 10 ml of 0.1 M MBIMTT in chloroform for 30 second

Aqueous phase

Fe(III) + Co(II) + Ni(II) + Cu(II)

Organic phase

Pd(II) + Pt(IV) + Au(III)

Dilute with organic phase with

20 ml with chloroform

Strip with water (40 ml)

Aqueous phase

Pt (IV)

Reduce the aqueous phase

and determine spectrophotometrically with

stannous chloride method (23)

Organic phase

Pd(II) + Au(III)

wash the organic phase 2-3

times with 1 mol.dm^{-3} HCl

strip with 8.5 mol.dm^{-3} HCl

(50 ml)

Aqueous phase

Pd (II)

Reduce the aqueous phase

and determined Pd(II) with Pyrimidine-2-thiol

(26)

Organic phase

Au(III)

wash the organic phase with

10 ml of 1 mol.dm^{-3} HCl and

strip with ammonia buffer solution

Determined Au(III) with stannous chloride

method

* Au(III), 100 μg + Pd(II), 100 μg + Pt(IV), 100 μg + 3000 μg each of Fe(III), Co(II), Ni(II) and Cu(II)

Scheme 1 Separation scheme (flow sheet).

4.3. Analysis of alloys

To ascertain the selectivity of the reagent the proposed method was successfully used in the determination of gold(III) in alloys. The dissolution of the sample was carried out by using the literature method (Anuse and Chavan, 1984). This brings the metals present into the proper oxidation states for the extraction of gold(III) with MBIMTT. An aliquot of the

Table 5 Analysis of gold(III) in Ayurvedic samples.

Name of medicine	Amount found by AAS (µg/ml)	Amount found by proposed method[a] (µg/ml)	Recovery ± s (%)
Vita-Ex-Gold (Shree Baidyanath, Nagpur)	82	81.7	99.7 ± 0.0
Suvarna Sootashekar (Ayurvedic Rasashala, Pune)	40	39.9	99.8 ± 0.2
Makardwaja Vati (Ayurvedic Rasashala, Pune)	38	37.8	99.6 ± 0.5

[a] Average six determination.

sample solution was taken and gold(III) was determined using the procedure described above. The results of analysis are given in Table 4. The average recovery of gold(III) has been found to be 99.6%.

4.4. Determination of gold(III) from Ayurvedic samples

The proposed method is applicable for the determination of gold content in the pharmaceutical samples. Dissolution of the sample is carried out by using the literature method (Kolekar and Anuse, 2001). An appropriate aliquot of the solution was taken for the analysis of gold content. The results of the analysis are reported in Table 5. The average recovery of gold(III) was 99.7%. The accuracy of the results was confirmed using atomic absorption spectroscopy (AAS).

4.5. Extraction scheme for separation of gold(III), platinum(IV), palladium(II), and base metals and its application to alloys

It is possible to extract and separate gold(III) from platinum(IV), palladium(II) and base metals. The extraction scheme is presented in the form of flow chart (Scheme 1), hence the separation can be achieved by the use of different striping agents. The analysis of results of synthetic mixture containing gold(III), palladium(II), platinum(IV) and base metals, corresponding to the various alloy are given in the Table 4. Gold(III) was estimated spectrophotometrically by the standard stannous chloride method.

5. Conclusion

In the present work, a simple, sensitive, inexpensive and selective method was developed for the extraction and separation of gold(III) from synthetic mixtures, alloys and Ayurvedic samples. The proposed method has several remarkable analytical characteristics:

(i) It is free from interference from the large number of diverse ions which are associated with gold(III) in its natural occurrence.
(ii) The important features of this method are that low reagent concentration is required, and the time required for the equilibrium is very short (30 s).
(iii) The method is effective to determine and separate gold from the alloys, synthetic mixtures and Ayurvedic samples.
(iv) The method is very simple, selective and reproducible.

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