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Liquid anion exchange chromatographic extraction and separation of gold(III) with 4-(4-methoxybenzylideneimino)-5-methyl-4*H*-1,2,4triazole-3-thiol in malonate medium

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ABSTRACT

A novel method is proposed for the extraction of microgram level concentration of gold(III) from malonate medium with 4-(4-methoxybenzylideneimino)-5-methyl-4H-1,2,4-triazole-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.

INTRODUCTION

The abundance of gold in the earth's crust is 0.004 ppm. It is a highly sought-after precious metal which, for many centuries, has been used as money, a store of value and in jewelry. The metal occurs as nuggets or grains in rocks, underground "veins" and in alluvial deposits. Modern industrial uses include dentistry and electronics, where gold has traditionally found use because of its good resistance to oxidative corrosion. Gold compounds are widely used in photography, medicine, electroplating industry and with sulfurized venice turpentine as an ink or paint. It commands a premium price because its low abundance in nature. The economy of a nation depends to a significant extent on the size of its gold reserves. Due to wide application of the 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 in the development of separation method to recover the gold to meet the future demand. Solvent extraction has become an effective technique in the recovery and separation of gold [1-4]. The aqueous chemistry of these metals is extremely complex. The important tendency of gold 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 gold 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[5], cynex 923[6], tributylphosphate [7], phospholene[8], tri-n-octylamine[9], tri-nbutyl phosphate [10] alamine [11]. 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.

In present investigations, extraction behavior of gold(III) using 4-(4-methoxybenzylideneimino)-5-methyl-4H-



Kaluram N. Vidhate

1,2,4-triazole-3-thiol(MBIMTT) dissolved in chloroform as an extractant presence of malonate media. MBIMTT has been employed successfully in this laboratory for the extraction of Rh(III), Ru (III) and Au(III), Pd(II), Pt(IV), Ir(III) and Os(VIII) in hydrochloric acid media and Pt(IV) in malonate medium. [12-19].

Equipment's and reagents

A Shimadzu UV-Visible spectrophotometer (UV-1601) with 1cm quartz cells was used for measurement. pH measurements were carried out with an Elico digital pH meter model LI- $120(\pm 0.01)$

A stock solution of gold(III)was prepared by dissolving 1g of HAuCI₄ in dilute AnalaR hydrochloric acid (1M) and diluting to 100ml with distilled water and further standardizing it [20]. A working solution 100 μ g ml⁻¹ was prepared from it by diluting the stock solution with distilled water. The reagent MBIMTT synthesized by known literature method [12]. MBIMTT (0.1M) solution was prepared in chloroform.

Other standard 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 distilled water. All the chemicals used were of AR grade. Double distilled de-ionized water was invariably used throughout the measurements.

General procedure

An aqueous solution containing 100 μ g of gold(III) and sufficient quantity of sodium malonate to make its concentration 1 M in a total volume of 25 ml. then the pH of the solution adjusted to 1.0 using dilute hydrochloric acid and sodium hydroxide. The resulting solution was transferred to 125 ml separating funnel. The aqueous phase was equilibrated once with 10 ml of 0.1M MBIMTT solution in chloroform for 30 second. The phase was allowed to separate and the metal from the organic phase was backstripped with two 5-ml portions 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 [21].

RESULTS AND DISCUSSION

Effect of reagent concentration

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

Effect of equilibration time

Variation of the shaking period from 5 seconds to 5 minutes showed that a minimum 30 second equilibration time is adequate for quantitative extraction of gold(III) from malonate media. As a general procedure, 1 minute of equilibration time is recommended in order to ensure complete extraction of gold(III) malonate medium. Prolonged shaking up to 5 minutes has no adverse effect on the efficiency of extraction.

Effect of diluents

The extractions were performed from malonate medium using 0.1M MBIMTT in various solvents as diluents. It was found that 0.1M 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.

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 fixed sodium malonate concentration was found to be linear and having slope of 1.24. Hence the probable composition of extracted species in chloroform has been found to be 1:1, [Au(III): MBIMTT].

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).

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 recovery of gold. The results showed that in the extraction and determination 100 µg of the gold, these ions did not interfere at the level tested. The reproducibility of gold extraction investigated from six replicate measurement was found to be 99.00± 0.95%.

APPLICATIONS

Binary separation of gold(III)from base metals

The method allowed separation and determination of gold(III) from a binary mixture containing either iron (III), cobalt(II), nickel(II), and copper(II).

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

| Foreign ion added |
|---|
| Fluoride, Citrate, Oxalate, Acetate, EDTA, Bromide, Iodide |
| Ca(II), Ba(II), Be(II), Mg(II), Fe(III) |
| Mn(II), Fe(II), Cr(III), Co(II) |
| Mo(VI), Sr(II), Ti(IV), Ce(IV) |
| U(VI), Mn(VII), Sb(III), Zn(II), Pb(II), Hg(II), Ni(II), Sn(II), Cu(II) |
| Pt(IV), Rh(III), Pd(II), Ru(III) |
| |

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

| Composition of Metal ions, /µg | Recovery* Au(III) % | Relative Standard Deviation % |
|--------------------------------|---------------------|-------------------------------|
| Au(III), 100; Fe(III); 15000 | 99.4 | 0.11 |
| Au(III), 100; Co(II) 10000 | 99.5 | 0.12 |
| Au(III), 100; Ni(II) 5000 | 99.2 | 0.11 |
| Au(III), 100; Cu(II) 5000 | 99.5 | 0.12 |
| | c · · · · | |

*-average f six determinations

Table 3 Analysis of Synthetic Mixtures

| Gold found ^a (µg) | Recovery* (%) | R.S.D.(%) |
|---------------------------------|---|--|
| 99.4 | 99.5 | 0.05 |
| 99.6 | 99.6 | 0.08 |
| 99.6 | 99.6 | 0.06 |
| 99.8 | 99.5 | 0.08 |
| 99.3 | 99.3 | 0.07 |
| 99.5 | 99.5 | 0.09 |
| 99.6 | 99.7 | 0.08 |
| 99.7 | 99.4 | 0.06 |
| 99.4 | 99.7 | 0.05 |
| 99.2 | 99.6 | 0.08 |
| | Gold found ^a (µg) 99.4 99.6 99.6 99.8 99.3 99.5 99.6 99.6 99.7 99.4 99.2 | Gold founda Recovery* (µg) (%) 99.4 99.5 99.6 99.6 99.6 99.6 99.8 99.5 99.3 99.3 99.5 99.5 99.6 99.5 99.7 99.7 99.7 99.4 99.4 99.7 99.4 99.7 99.4 99.7 99.4 99.7 99.4 99.7 |

*- average six determination

Table 4 Analysis of Alloys

| Alloys | Composition of Alloys | Gold(III) | Gold(III) found by | Recovery | R.S.D. |
|-------------------------------|----------------------------------|----------------|--------------------|----------|--------|
| | % | found by AAS % | proposed method* % | % | % |
| Copper silver cold allow | i) Cu, 49.35; Ag, 7.25; Au, 43.4 | 43.4 | 43.2 | 99.6 | 0.12 |
| Copper-silver-gold alloy | ii) Cu, 35; Ag, 5; Au, 60 | 59.8 | 59.6 | 99.7 | 0.11 |
| Low Melting Dental Alloy | Pd, 25; Au, 10; Co,22 Ni, 34 | 9.9 | 9.6 | 99.5 | 0.08 |
| Jewellery alloy (Pd-Au alloy) | Pd, 50; Au, 50 | 49.9 | 49.7 | 99.7 | 0.07 |
| Solder Alloy | Pt, 10; Pd, 30; Au, 60 | 59.9 | 59.5 | 99.5 | 0.12 |

*- average six determination

The separation of gold(III) from iron(III), cobalt(II), nickel(II), and copper(II) by its extraction with 0.1M MBIMTT in chloroform. Under these condition all the base metals remain quantitatively in the aqueous phase and these base metals determined spectrophotometrically with thiocyanate [22], 1-nitroso-2 naphthol [22], DMG [22], and pyrimidine-2-thiol [23] respectively. Gold is stripped from the organic phase with two 5ml portion of ammonia

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Kaluram N. Vidhate

buffer solution(pH -10.1). The extract was evaporated to moist dryness and leached with 1M hydrochloric acid to form the solution. Gold(III) was estimated spectrophotometrically with stannous chloride. The recovery of gold(III) and that added ions was 99.7% and results are reported in Table 2.

Separation of gold(III) from multicomponent synthetic mixture

In its natural occurrence gold is always associated with the noble and base metal, hence its separation from these metals is of great importance. Under the optimum condition for extraction of gold(III), there is quantitative extraction of Pd(II), Pt(IV) and Rh(III). But the coextracted metal ions cannot be backstripped by ammonia buffer solution(pH-10.1). Thus the MBIMTT reagent is made selective towards 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 5 Analysis of Gold(III) |) in Ayurvedic samples |
|-------------------------------|------------------------|
|-------------------------------|------------------------|

| Name of Medicine | Name of Medicine Amount found by Amount found by | | R.S.D. |
|---|--|-----------------------|--------|
| | AAS, µg/ml | proposed method*µg/ml | % |
| Vita-Ex-Gold (Shree Baidyanath, Nagpur) | 82 | 81.3 | 0.14 |
| Suvarna Sootashekar (Ayurvedic Rasashala, Pune) | 40 | 39.4 | 0.11 |
| Makardwaja Vati (Ayurvedic Rasashala, Pune) | 38 | 37.5 | 0.15 |

^{*-} average six determination

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 sample was carried out by using literature method [5]. This brings the metals present into the proper oxidation states for the extraction of gold(III) with MBIMTT. An aliquot of the 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 99.3%.

Determination of Gold(III) from Ayurvedic Sample

The proposed method is applicable for the determination of gold content in the pharmaceutical samples. Dissolution of sample is carried out by using literature method [5]. 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(IIII) was 99.2%. The accuracy of the results was confirmed using atomic absorption spectroscopy (AAS).

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