

## Separation of gold (III) from ayurvedic medicines and alloys by extraction chromatography

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A new method is proposed for the extractive chromatographic separation of gold(III). Gold(III) is extracted from 0.5 mol/L of hydrochloric acid by a silica gel column coated with N-n-octylaniline (liquid anion exchanger), eluted with 0.25 mol/L ammonia and determined by spectrophotometrically as its complex with stannous chloride. The various influencing parameters such as acid concentrations, effect of flow rate of mobile phase and reagent concentration was studied. The method was free from large number of interferences from cations and anions. Proposed method has been applied for analysis of gold(III) from the ayurvedic medicine and synthetic mixtures corresponding to alloys. The reliability of analytical data was verified by statically. The nature of extracted species is  $[RR'NH_2^+ AuCl_4]_{org}$ .

Key words: gold(III), separation, Ayurvedic medicine, alloys

### INTRODUCTION

Gold is one of the precious metal. It has wide range of applications as a catalyst in hydrogenation of some organic compounds. The beauty and rarity of gold has led to its use in jewellery, in coinage, as a monetary standard, in jewellery and dentistry. The infrared reflectivity of gold leads to its use in the aeronautics and space industries. The economy of nation depends to a significant extent on the size of its gold reserves. Since many decades every human is having great desire of suvarna i.e. gold. By nourishing the brain cells it improves memory, increases the strength and immunity of the body and improves the pronunciation. It increases blood corpuscles, haemoglobin and improves cardiac functions as well. Gold has low abundance, high prices and wide range of applications hence it is essential to develop an innovative method for its separation is an analytical merits. Reversed phase extraction chromatography (RPEC) is an extremely versatile technique and has been applied successfully for the separation of various metals [1-5]. Literature survey revealed that gold was quantitatively extracted with Bis(2-ethylhexyl) phosphate (HDEHP) [6] from 7-8 mol/L hydrochloric acid and is eluted with 2.0 mol/L hydrochloric acid. Tributylphosphate [7] used as stationary phase towards the column and gold was separated from binary and multicomponent mixtures. The extraction of gold(III) from hydrochloric and hydrobromic acid with 5% tri-iso-

octylamine (TIOA) solution in carbon tetrachloride has been studied [8]. The method suffers from interferences of anions like thiocyanate, cyanide, sulphide, sulphite, thiosulphate, EDTA, bromide, nitrite, iodide and silver(I). Separation of gold (III), palladium(II) and platinum(IV) in chromites was achieved by anion exchange chromatography using inductively coupled plasma-atomic emission spectrometry (ICP-AES) [9]. This method suffers from the drawback viz. it requires more elution time and palladium(II) can't be determined. Solid phase extraction of gold(III), platinum(IV) and palladium(II) was carried out using polystyrene-divinylbenzene porous resin (XAD-4) [10]. Platinum(II), palladium(II) and gold(III) were separated by Amberlite XAD-7 resin [11] column gave the recovery of elements greater than 95%. Study was made for the sorption of negative charged sulphate complexes of platinum, palladium, iridium and gold on poly-aniline [12].

Gold has been separated with N-n-octylaniline [13, 14] using solvent extraction method but this method requires large amount of solvents. The use of n-octylaniline in the extraction of noble metals has been described in the literature [15, 16]. The comparison can be made on the merits of N-n-octylaniline relative to n-octylaniline as an extractant of noble metal. The extraction depends upon method of preparation of the reagent. Some of the drawbacks of the method are emulsion formation, requirement of more elution time (30 min), higher reagent concentration and need of multiple extractions.

N-n-octylaniline has been used in this laboratory for reversed phase extraction chromatographic

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separation of some platinum group metals [17-20] and coinage metals [21]. The use of this reagent is found to be advantageous as it can be synthesized at low cost, with high yield and of best purity. The present investigation describes its use in quantitative extraction of gold (III) and the development of a rapid and selective method for the separation of gold (III) from Ayurvedic medicine and synthetic mixtures corresponding to alloys.

## EXPERIMENTAL

### Apparatus

An Elico spectrophotometer model SL-159 with 10 mm path length quartz cell was used for absorbance measurements.

### Reagents

The stock solution of gold (III) was prepared by dissolving 1.0 g chloroauric acid ( $\text{HAuCl}_4$ ) (Loba Chemie Pvt. Ltd. Mumbai, India) in 1.0 mol/L hydrochloric acid using distilled water, diluted to 250 mL and standardized gravimetrically [22]. A working solution containing 50  $\mu\text{g}$  gold (III) was prepared by further dilution.

Hydrochloric acid was of analytical grade provided by Qualigene fine chemical Pvt. Ltd. (Mumbai, India). Other standard solutions of different metals used for study of effect of foreign ions (Table 1) were prepared by dissolving their salt in dilute hydrochloric acid. The solutions of anions were prepared by dissolving respective sodium salts in distilled water. The stock solution of *N-n*-octylaniline was prepared using method reported by Gardlund [23].

### Preparation of anion exchange material

Silica gel (60–120 mesh) obtained from British Drug House India Ltd., dried at 120 °C for 2-3 h and stored in desiccators. It was packed in a U tube through which a stream of nitrogen was bubbled through a small Durand bottle containing 20.0 mL dimethyldichlorosilane (DMCS) (Acros Organics, New Jersey, USA). DMCS vapour was continued for 4 h. The silica gel was washed with anhydrous methanol, then dried. A portion of 5.0 g silanated silica gel was soaked with 0.087 mol/L *N-n*-octylaniline which was previously equilibrated with hydrochloric acid (0.5 mol/L) for 10 min, and then solvent was evaporated to get nearly dried gel. Slurry of coated silica gel in distilled water was prepared by centrifugation at 2000 r/min and was packed into chromatographic column which made from borosilicate glass tube, having bore 8 mm, length 30 cm, fitted with glass-wool plug at the

bottom, to give a bed height 6.0 cm. The bed was then covered with a glass wool plug.

### General procedure

An aliquot solution containing 50  $\mu\text{g}$  gold (III) was made up to 25.0 mL by adjusting the concentration of hydrochloric acid to 0.5 mol/L. It was passed through the column containing 0.087 mol/L *N-n*-octylaniline coated with silica gel at a flow rate of 1.0 mL/min. After extraction, gold (III) was eluted with 25.0 mL, 0.25 mol/L ammonia solution. The eluents were evaporated to moist dryness. The residue was dissolved in 5 mL aqua regia and evaporated to moist dryness. Then 2 mL of 2% sodium chloride solution, concentrated hydrochloric acid solutions were added and mother liquor was evaporated again. The procedure of evaporation was repeated to remove the oxides of nitrogen. The residue was dissolve in 0.05 mol/L hydrochloric acid and gold (III) was determined spectrophotometrically by stannous chloride method [24].

## RESULTS AND DISCUSSION

### Effect of hydrochloric acid concentration on extraction

The effect of hydrochloric acid concentration on the percentage extraction of gold (III) was studied in the range 0.125 to 1.5 mol/L on the column coated with 0.087 mol/L *N-n*-octylaniline as the stationary phase on hydrophobic silica gel. The extraction of gold (III) was found to be quantitative at 0.5 mol/L hydrochloric acid. Hence, all the extractions were carried out at this concentrations Fig. 1.

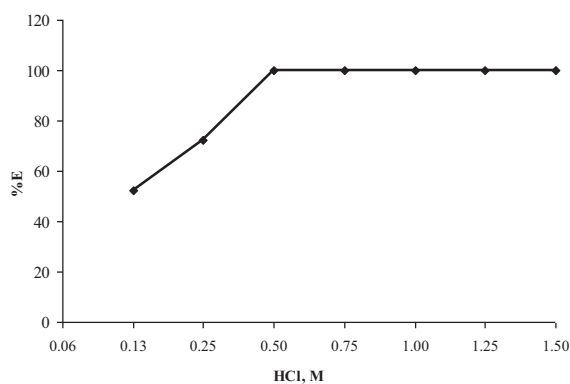


Fig. 1 Extraction of gold (III) as a function of hydrochloric acid concentration

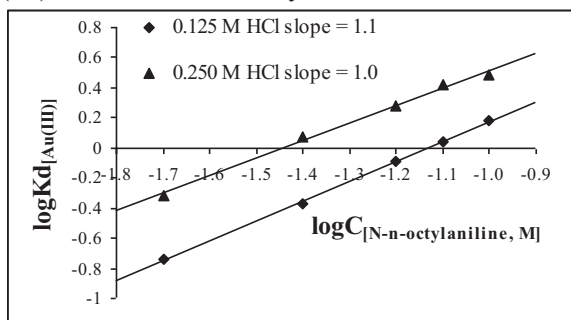
### Effect of flow rate

The effect of flow rate on percentage extraction of gold (III) was studied from 0.5 to 3.0 mL/min. It

was observed that the percentage extraction decreases with increase the flow rate. Therefore the flow rate was kept at 1.0 mL/min for further extraction studies.

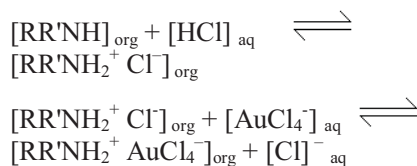
*Effect of N-n-octylaniline concentration*

The concentration of *N-n*-octylaniline was varied from 0.022 to 0.110 mol/L while the concentration of hydrochloric acid ranges from 0.125 to 1.25 mol/L for gold (III). It was found that, for quantitative extraction of gold (III), 0.087 mol/L *N-n*-octylaniline was sufficient

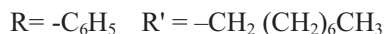


**Fig 2.** Log-log plot of distribution coefficient versus *N-n*-octylaniline concentration in hydrochloric acid media. The percentage extraction of gold (III) increases when the concentration of *N-n*-octylaniline increases. Log-*n*-octylaniline concentration at 0.125 and 0.25 mol/L hydrochloric acid

log plot of *N-n*-octylaniline concentration versus distribution coefficient at 0.125 and 0.25 mol/L hydrochloric acid gives slope 1.1 and 1.0 respectively (Fig. 2). The probable composition of extracted species was calculated 1:1 (metal to amine) ratio. The extraction mechanism can be explained as follows



where



*Effect of foreign ions*

Various amounts of foreign ions were added to a fixed amount of gold (III) (50 µg) to study the effect of interference according to the recommended procedure. The tolerance limit was set at the amount required to cause ± 1.5% error in the recovery of gold (III), Table 1. It was observed that the method was free from interference from a

**Table 1.** Effect of foreign ions

| Foreign ion | Added  | Tolerance limit/µg | Foreign ion                   | Added  | Tolerance limit/µg |
|-------------|--|--------------------|-------------------------------|--|--------------------|
| Mn(II)      | MnCl <sub>2</sub> .6H <sub>2</sub> O   | 250                | Pd(II)                        | PdCl <sub>2</sub> .xH <sub>2</sub> O         | 100                |
| V(V)        | V <sub>2</sub> O <sub>5</sub>  | 400                | Pt(IV)                        | PtCl <sub>6</sub> .xH <sub>2</sub> O         | 200                |
| U(VI)       | UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O                 | 300                | Te(IV)                        | Na <sub>2</sub> TeO <sub>3</sub>             | 200                |
| Tl(III)     | TlNO <sub>3</sub>  | 400                | Ni(II)                        | NiCl <sub>2</sub> .6H <sub>2</sub> O         | 300                |
| Zn(II)      | ZnSO <sub>4</sub> .7H <sub>2</sub> O   | 400                | Ir(III)                       | IrCl <sub>3</sub> .xH <sub>2</sub> O         | 200                |
| Cd(II)      | 3CdSO <sub>4</sub> .8H <sub>2</sub> O  | 400                | Fe(II)                        | FeSO <sub>4</sub> .7H <sub>2</sub> O         | 400                |
| Bi(III)     | Bi(NO <sub>3</sub> ) <sub>3</sub> .5H <sub>2</sub> O                               | 300                | Pb(II)                        | Pb(NO <sub>3</sub> ) <sub>2</sub>            | 250                |
| Ce(IV)      | Ce(SO <sub>4</sub> ) <sub>2</sub>  | 400                | Os(VIII)                      | OSO <sub>4</sub>                             | 200                |
| Mo(VI)      | (NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> .2H <sub>2</sub> O | 400                | Rh(III)                       | RhCl <sub>3</sub> .xH <sub>2</sub> O         | 200                |
| Ag(I)       | AgNO <sub>3</sub>  | 300                | Ru(III)                       | RuCl <sub>3</sub> .xH <sub>2</sub> O         | 200                |
| Sr(II)      | Sr(NO <sub>3</sub> ) <sub>2</sub>  | 300                | EDTA                          | EDTA(disodium salt)                          | 1000               |
| Sb(III)     | Sb <sub>2</sub> O <sub>3</sub>   | 300                | Tartrate                      | C <sub>6</sub> H <sub>6</sub> O <sub>6</sub> | 1000               |
| Mg(II)      | MgCl <sub>2</sub> .6H <sub>2</sub> O   | 250                | Malonate                      | CH <sub>2</sub> (COONa) <sub>2</sub>         | 1000               |
| Fe(III)     | FeCl <sub>3</sub>  | 300                | Oxalate                       | (COOH) <sub>2</sub> .2H <sub>2</sub> O       | 1000               |
| Co(II)      | CoCl <sub>2</sub> .6H <sub>2</sub> O   | 300                | Fluoride                      | NaF  | 1000               |
| Be(II)      | BeSO <sub>4</sub> .4H <sub>2</sub> O   | 300                | Bromide                       | KBr  | 1000               |
| Ca(II)      | CoCl <sub>2</sub> .6H <sub>2</sub> O   | 250                | H <sub>2</sub> O <sub>2</sub> | H <sub>2</sub> O <sub>2</sub>                | 2.0 ml             |
| Ba(II)      | BaCl <sub>2</sub> .H <sub>2</sub> O  | 250                | Iodide                        | KI   | 1000               |
| Cu(II)      | CuCl <sub>2</sub> .H <sub>2</sub> O  | 250                | Persulfate                    | K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> | 1000               |

**Table 2.** Separation of gold(III) from synthetic mixtures and alloys. *N-n*-octylaniline: 0.087 mol/L; eluent: 25 mL 0.25 mol/L ammonia; hydrochloric acid 0.5 mol/L; Flow rate 1.0 mL/min.

| Sample Compositions /µg | Au (III) Certified /µg | Au (III) Found /µg  | Mean (n=3) | Recovery % (n=3) | RSD % (n=3) |
|-------------------------|------------------------|---------------------|------------|------------------|-------------|
| Cu 49.35; Ag 7.25       | 43.40                  | 43.35, 43.20, 43.25 | 43.27      | 99.7             | 0.30        |
| Cu 35.00; Ag 5.00       | 60.0                   | 59.90, 59.95, 59.80 | 59.88      | 99.8             | 0.20        |

**Table 3.** Separation of gold(III) from pharmaceutical formulations. *N-n*-octylaniline: 0.087 mol/L; eluent: 25 mL 0.25 mol/L ammonia; Hydrochloric acid 0.5 mol/L; Flow rate 1.0 mL/min.

| Sample (Source)                                    | Au(III)<br>Certified value, % | Found/% |
|--|-------------------------------|---------|
| Bruhatwat Chintamani (Koral Pharma, Nashik)        | 0.18                          | 0.15    |
| Vasant Kusumkar (Koral Pharma, Nashik)             | 0.15                          | 0.13    |
| Suvarna Malini Vasant (Koral Pharma, Nashik)       | 0.55                          | 0.53    |
| Suvarna Sutshekhar (Koral Pharma, Nashik)          | 2.13                          | 2.00    |
| Shwas Kas Chintamani (Koral Pharma, Nashik)        | 1.18                          | 1.15    |
| Suvarna Bhasma (Shree Dhootapapeshwar Ltd, Mumbai) | 7.60                          | 7.50    |

(Average of three determinations)

**Table 4.** Statistical treatment of the analytical data ( $n=6$ ). Au(III): 50  $\mu$ g; *N-n*-octylaniline: 0.087 mol/L; eluent: 25 mL 0.25 mol/L ammonia; hydrochloric acid 0.5 mol/L; Flow rate 1.0 mL/min.

| Mean (M) | Median (m) | Average deviation (d) | Mean average deviation (D) | Standard deviation (s) | Mean of standard deviation (S) | Coefficient variation (C.V.) |
|----------|------------|-----------------------|----------------------------|------------------------|--------------------------------|------------------------------|
| 99.3     | 99.9       | 0.0004                | 0.0002                     | 0.095                  | 0.036                          | 0.10%                        |

large number of cations and anions. The only cations showing interference in the method are chromium (VI) and manganese (II) which are strong oxidizing agents. Thiosulphate, thiourea and thiocyanate form very strong complexes with gold (III) because precious metals such as gold, silver, platinum group metals (PGMs) are belong to the soft metals which possess a strong affinity to ligands containing donor type sulphur atom which acts as soft bases.

#### *Analysis of synthetic mixture corresponding to alloys*

The proposed method was successfully applied for the analysis of synthetic mixtures corresponding to alloys containing gold (III) i.e. copper-silver-gold alloy. The results of analysis matched with certified values [25], Table 2.

#### *Analysis of gold (III) from ayurvedic samples*

Ayurvedic samples containing gold are useful for various chronic disorders, general debility, diseases which deplete immunity, anaemia, mental disorders, respiratory tract disorders etc. The proposed method was successfully applied for the separation of gold (III) from bruhatwat chintamani, vasant kusumkar, suvarna malini vasant, suvarna sutshekhar, shwas kas chintamani and suvarna bhasma. The samples are brought into solution form by wet-oxidation method. Gold (III) was extracted by the proposed method and determined by the standard procedure. The results are in good agreement with certified value calculated by standard calibration curve method Table 3.

#### *Statistical treatment of the analytical data*

The evaluation and interpretation of an analytical data is verified by statically. It is measure of performance for analytical procedure. The various criteria used to evaluate the analytical data. The important values obtained were reported in Table 4.

### CONCLUSIONS

Proposed method is very simple, selective and reproducible. It is free from the interferences from large number of foreign ions, which are in their states of nature. Low reagent and acid concentration is required for quantitative recovery of gold (III). It is applied for the separation of gold from ayurvedic samples and alloys. Reliability of method verified by statistical treatment analytical data.

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## РАЗДЕЛЯНЕ НА ЗЛАТО (III) ОТ АЮРВЕДИЧНИ ЛЕКАРСТВА И СПЛАВИ ЧРЕЗ ЕКСТРАКЦИОННА ХРОМАТОГРАФИЯ

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(Резюме)

Предложен е нов метод за екстракционно хроматографско разделяне на злато (III). Злато (III) се екстрахира от разтвор на 0,5 мол/л солна киселина в колона със силикагел, покрит с N-н-октиланилин (течен анионообменник), елюира се с 0,25 мол/л разтвор на амоняк и се определя спектрофотометрично като комплекс с калаен хлорид. Изучени са различни параметри като концентрация на киселината, ефекта на скоростта на потока на подвижната фаза и концентрацията на реагентите. Методът не се влияе от голям брой аниони и катиони. Предложеният метод е бил приложен за анализ на злато (III) от аюрведическата медицина и синтетични смеси, съответстващи на сплави. Надеждността на аналитичните данни беше проверена статистически. Екстрахираното съединение е  $[\text{RR}'\text{NH}_2^+ \text{AuCl}_4]_{\text{org}}$ .