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Liquid Anion Exchange Chromatographic Extraction And Separation Of Platinum (IV) With 4-(4-Methoxybenzylideneimino)-5-Methyl-4*H*-1,2,4-Triazole-3-Thiol In Malonate Medium

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ABSTRACT

A novel method is proposed for the extraction of microgram level concentration of platinum(IV) from malonate medium with 4-(4-methoxybenzylideneimino)-5-methyl-4H-1,2,4-triazole-3-thiol(MBIMTT) dissolved in chloroform as an extractant. The platinum (IV) from the organic phase is stripped with water and estimated spectrophotometrically with stannous chloride. The effect of acid, reagent concentration and various foreign ions has been investigated. The method affords the binary separation and determination of platinum (IV) from the alloys and synthetic mixture. The method is highly selective, simple and reproducible.

Keywords: Platinum (IV), solvent extraction, MBIMTT, Spectrophotometry.

INTRODUCTION

Platinum is a good catalyst and in petroleum and chemical process. Platinum has wide application in automotive exhaust-gas control converters and is of immense importance to the electronic industries as well as used in jewelry. The increasing application of the platinum (IV) 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 platinum metal.

Liquid-liquid extraction is one of the most efficient methods used to separate, concentrate and purify metal ions and organic compounds [1-5]. The inertness of the chlorocomplex of platinum in aqueous medium plays an important role in the extraction from acidic solution by an anion exchange mechanism. Other extractants reported to extract the platinum (IV) are triphenyl phosphine [6], trioctylamine [7] N-benzyl aniline[8], bis (2-ethylhexyl) hydrogen phosphate[9] C_{8-10} alkyl aniline hydrochloride [10], organoamono phosphate [11] N-n-octylaniline [12] n-octylaniline [13] 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 platinum (IV) using 4-(4-methoxybenzylideneimino)-5-methyl-4*H*-1, 2, 4-triazole-3-thiol(MBIMTT) dissolved in chloroform as an extractant presence of hydro chloric acid 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) [14-20].

MATERIALS AND METHODS

Equipments 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(±0.01)

A stock solution of platinum (IV) was prepared by dissolving 1g of platinum (IV) chloride hydrate in dilute AnalaR hydrochloric acid (1M) and diluting to 100mL with distilled water and further standardizing it [21]. 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 known literature method [14]. 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.

Recommended method: An aqueous solution containing 100 μg of platinum (IV) and sufficient quantity of sodium malonate to make its concentration 1 M in a total volume of 25mL 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 1 minute. The phase was allowed to separate and the metal from the organic phase was stripped with two 10 mL portions of water. The extract was evaporated to moist dryness and leached with dilute hydrochloric acid to form the solution. Platinum (IV) was estimated spectrophotometrically by stannous chloride method [22].

RESULTS AND DISCUSSION

Effect of reagent concentration: The concentration of MBIMTT in chloroform was varied from the1×10^{-5} to 0.2M under optimum condition. It was found that 0.1M reagent in chloroform was needed for the quantitative extraction of platinum(IV) from malonate acid.

Effect of equilibration time: Variation of the shaking period from 5 sec to 5 min showed that a minimum 30 sec equilibration time is adequate for quantitative extraction of platinum (IV) from malonate media. As a general procedure, 1 min of equilibration time is recommended in order to ensure complete extraction of platinum (IV) malonate medium. Prolonged shaking up to 5 min has no adverse effect on the efficiency of extraction.

Effect of diluents: Keeping all other variable constant, the platinum (IV) was extracted with MBIMTT with various diluents. The extraction was quantitative in carbon tetrachloride, chloroform, xylene, toluene and benzene. The extraction of platinum (IV) 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 $D_{[Pt(IV)]}$ 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, [Pt(IV): MBIMTT].

Loading capacity of MBIMTT: The concentration of platinum (IV) 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 platinum (IV).

Effect of Diverse Ions: Various ions were used in order to assess the tolerance of these ions on the extraction of platinum (IV). Platinum (IV) 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 platinum. The results showed that in the extraction and determination 100 μg of the platinum, these ions did not interfere at the level tested. The reproducibility of platinum extraction investigated from six replicate measurement was found to be 99.00± 0.95%.

Table 1: Effect of diverse ions on the extractive determination of platinum(IV)
Pt(IV) = 100 μg; Aq/Org = 25:10; extractant = 0.1 mol/dm^3 MBIMTT in Chloroform

Tolerance limit (mg)	Foreign ion added
100	Fluride, 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)

APPLICATIONS

Binary separation of platinum (IV) from base metals: The method allowed separation and determination of platinum (IV) from a binary mixture containing either iron (III), cobalt (II), nickel (II), and copper (II). The separation of platinum (IV) 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[23], 1-nitroso-2 naphthol [23], DMG [23], and pyrimidine-2-thiol [24] respectively. Platinum is stripped from the organic phase with two 10 mL portion of water. The extract was evaporated to moist dryness and leached with 1M hydrochloric acid to form the solution. Platinum (IV) was estimated spectrophotometrically with stannous chloride [21]. The recovery of platinum (IV) and that added ions was 99.5 % and results are reported in table 2.

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

Composition of Metal ions, /μg	Recovery* Pt (IV) %	Relative Standard Deviation %.
Pt(IV) 100; Fe(III); 15000	99.6	0.13
Pt(IV), 100; Co(II) 10000	99.7	0.07

Pt(IV), 100; Ni(II) 5000	99.6	0.11
Pt(IV), 100; Cu(II) 5000	99.8	0.13

*-average f six determinations

Separation of platinum (IV) from multi-component synthetic mixture: In its natural occurrence platinum 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 platinum (IV), there is quantitative extraction of Au (III), Pd (II) and Rh (III). But the co extracted metal ions cannot be back stripped by water. Thus the MBIMTT reagent is made selective towards platinum (IV) by taking advantage of the strippent used. The proposed method allows the selective separation and determination of platinum from many metal ions (Table 3).

Table 3. Analysis of synthetic mixture

Composition (*μg*)	**Platinum found^a(*μg*)**	**Recovery*(%)**	**R.S.D.(%)**
Pt, 100; Pd,500	99.8	99.6	0.07
Pt, 100; Au,500	99.6	99.8	0.05
Pt, 100; Ru,500	99.4	99.7	0.07
Pt, 100; Rh,500	99.6	99.8	0.05
Pt, 100; Pd,500; Ru,500	99.5	99.9	0.06
Pt, 100; Pd,500; Au,500	99.6	99.7	0.06
Pt, 100; Pd,500; Rh,500	99.5	99.8	0.07
Pt, 100; Pd,500; Ru,500; Au, 500	99.4	99.7	0.08
Pt, 100; Pt,500; Rh,500; Au, 500	99.4	99.7	0.07
Pt, 100; Pd,200; Ru,200; Au, 200; Rh(III),200;Fe,2000;Co, 2000; Ni, 2000; Cu, 2000	99.5	99.6	0.06

*- average six determination

Analysis of alloys: To ascertain the selectivity of the reagent the proposed method was successfully used in the determination of platinum (IV) in alloys. The synthetic mixtures were prepared corresponding to the composition of the alloys. The results of the analysis are reported in table 4. The average recovery of platinum (IV) has been found to be 99.5 %.

Table 4: Analysis of alloys

Alloy	Composition (%)	Platinum taken (μg)	Platinum found* (μg)	Recovery (%)	R.S.D. (%)
Solder alloy	Pt, 10; Pd, 30; Au, 60	100	99.7	99.8	0.05
Oakay alloy	Pt, 20; Pd, 10.5; Ni, 60; V, 9.5	100	99.6	99.5	0.06
Alloy for electrical contacts	Pt, 10; Pd, 35; Ag, 30; Cu, 14; Au, 10; Zn, 1.0	100	99.4	99.5	0.05

*- average six determination

CONCLUSIONS

These results underline the potential of the proposed method for the quantitative, selective extraction of platinum (IV) with MBIMTT containing low concentration of palladium. It is free from interference from the large number of diverse ions which are associated with platinum (IV) in its natural occurrence. The important features of this method are low reagent concentration is required, and the time required for the equilibrium is very short (1 min). The method is applicable to the analysis of platinum (IV) in synthetic mixtures and corresponding to alloys. The method is very simple, selective and reproducible.

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