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Extraction and Separation Studies of Iridium(III) 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 iridium(III) from malonate medium with 4-(4-methoxybenzylideneimino)-5-methyl-4*H*-1,2,4-triazole-3-thiol(MBIMTT) dissolved in chloroform as an extractant. The iridium(III) from the organic phase is stripped with 2 M hydrochloric acid and determined spectrophotometrically with stannous chloride method. The method affords the binary separation and determination of iridium(III) from the alloys and synthetic mixture. The method is highly selective, simple and reproducible

Keywords: Iridium(III); Solvent extraction, Alloys.

INTRODUCTION: Iridium is a good catalyst organic transformation reaction. Owing to its corrosion resistance properties and easy alloying, iridium and its alloys are also used in chemical industry, medical devices and jewelry manufacture. The platinum group metals are scarce and have wide range of industrial applications; therefore it is of paramount importance in the development of separation method to recover these metals to meet the future demand. The determination of iridium has always been difficult. Solvent extraction has become an effective technique in the recovery and separation of iridium [1-4]. The aqueous chemistry of iridium is extremely complex. The important tendency of iridium 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 iridium in aqueous medium plays an important role in the extraction from acidic solution by an anion exchange mechanism. Other extractants reported for iridium(III) are alamine-336[5], N-n-octyaniline[6-8], tri-octylamine (TOA)[9], 4-(non-5-yl)pyridine (NP)[10]. 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 iridium(III) using 4-(4-methoxybenzylideneimino)-5-methyl-4*H*-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) and Os(VIII) [11-16].

MATERIALS AND METHODS: 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 iridium(III) was prepared by dissolving 1g of iridium chloride hydrate (S. D. Fine, India) in dilute AnalaR hydrochloric acid (1mol/dm^3) and diluting to 100 ml with distilled water and further standardizing it[17]. A working solution 100 □g ml^{-1} was prepared from it by diluting the stock solution with distilled water. The reagent MBIMTT synthesized by known literature method [11]. MBIMTT (0.1 mol/dm^3) 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 □g of iridium(III) and sufficient quantity of sodium malonate to make its concentration 1 M in total volume of 25 mL, then the pH of solution adjusted to 1.0 using 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 0.1 mol/dm^3 MBIMTT solution in chloroform for 30 second. The phase was allowed to separate and the metal from the organic phase was backstripped with two 10 ml portions of 2M hydrochloric acid solution. The extract was evaporated to moist dryness and leached with dilute hydrochloric acid to form the solution. Iridium(III) was estimated spectrophotometrically with stannous chloride method[18].

RESULTS AND DISCUSSION:

Effect of reagent concentration: The concentration of MBIMTT in chloroform was varied from the 1 × 10^{-5} – 2 M under optimum condition. It was found that 0.1 M reagent in chloroform was needed for quantitative extraction of Ir(III) from malonate medium.

Effect of equilibration time: Variation of the shaking period from 5 seconds to 5 minutes showed that a minimum 10 second equilibration time is adequate for quantitative extraction of iridium(III) from malonate media. As a general procedure, 30 second of equilibration time is recommended in order to ensure complete extraction of iridium(III) malonate medium. Prolonged shaking up to 5 minutes has no adverse effect on the efficiency of extraction.

Effect of diluents: Keeping all other variable constant, the Ir(III) was extracted with MBIMTT with various diluents. MBIMTT solution in carbon tetrachloride, chloroform, xylene, toluene and benzene provides quantitative extraction of iridium(III). The extraction of iridium(III) was found to be incomplete in isobutyl methyl ketone, isoamylalcohol, while no extraction in 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 $D_{[Ir(III)]}$ versus log $C_{[MBIMTT]}$ at sodium malonate concentration was to be found linear and having slope of 1.27. Hence the probable composition of extracted species in chloroform has been found to be 1:1, [Ir(III): MBIMTT].

Loading capacity of MBIMTT: The concentration of Iridium(III) was varied to determining the loading capacity of MBIMTT. The loading capacity of 10 mL of 0.1 M MBIMTT was found to be 6.5 mg of Iridium(III).

Effect of Diverse Ions: Various ions were used in order to assess the tolerance of these ions on the extraction of iridium(III). Iridium(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 Iridium. The results showed that in the extraction and determination 100 □g of the iridium, these ions did not interfere at the level tested. The reproducibility of iridium 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 iridium(III) Ir(III) = 100 □g; HCl; Aq/Org = 25:10; extractant = 0.1 M 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 iridium(III) from base metals: The method allowed separation and determination of iridium(III) from a binary mixture containing either iron (III), cobalt(II), nickel(II), and copper(II). The separation of iridium(III) from iron(III), cobalt(II), nickel(II), and copper(II) by its extraction with 0.1 mol/dm^3 MBIMTT in chloroform. Under these condition all the base metals remain quantitatively in the aqueous phase and these base metals determined spectrophotometrically with thiocyanate[19], 1-nitroso-2 naphthol[19], DMG[19], and pyrimidine-2-thiol [20] respectively. Iridium is stripped from the organic phase with two 10 ml portion of 2 M HCl. The extract was evaporated to moist dryness and leached with 1 mol/dm^{3}hydrochloric acid to form the solution. Iridium(III) was estimated spectrophotometrically with stannous chloride method[19]. The recovery of iridium(III) and that added ions was 99.6□ and results are reported in Table 2.

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

Composition of Metal ions, /µg	Recovery* Pd(II) %	Relative Standard Deviation(%).
Ir(III) 100; Fe(III); 15000	99.6	0.13
Ir(III), 100; Co(II) 10000	99.7	0.07
Ir(III), 100; Ni(II) 5000	99.6	0.11
Ir(III), 100; Cu(II) 5000	99.8	0.13

**-average f six determinations*

Separation of iridium(III) from multicomponent synthetic mixture: In its natural occurrence iridium is always associated with the noble and base metals; hence its separation from these metals is of great importance. Under the optimum condition for extraction of iridium(III), there is quantitative extraction of Pd(II), Pt(IV) and Rh(III). But the coextracted metal ions cannot be backstripped by 2 M hydochloric acid solution. Thus the MBIMTT reagent is made selective towards Iridium(III) by taking advantage of the strippent used. The proposed method allows the selective separation and determination of iridium from many metal ions (Table 3).

Analysis of alloys: To ascertain the selectivity of the reagent the proposed method was successfully used in the determination of iridium(III) in alloys. The real samples were not available; hence the synthetic mixtures were prepared corresponding to the composition of alloy. The results of the analysis are reported in Table 4. The average recovery of iridium(III) has been found to be 99.5□.

Table 3: Analysis of Synthetic Mixtures.

Composition (µg)	Iridium found[a] (µg)	Recovery (%)*	R.S.D. (%)
Ir, 100; Pt,500	99.7	99.4	0.05
Ir 100; Pd,500	99.4	99.8	0.07
Ir, 100; Ru,500	99.7	99.8	0.07
Ir100; Rh,500	99.6	99.6	0.05
Ir, 100; Pt,500; Ru,500	99.7	99.7	0.06
Ir, 100; Pt,500; Pd,500	99.6	99.6	0.07
Ir, 100; Pt,500; Rh,500	99.5	99.5	0.07
Ir, 100; Pt,500; Ru,500; Pd, 500	99.8	99.8	0.05
Ir, 100; Pt,500; Rh,500; Pd, 500	99.5	99.5	0.06
Ir, 100; Pt,200; Ru,200; Pd, 200	99.2	99.2	0.07

**- average six determination*

Table 4: Analysis of Alloys.

Alloys	Composition of Alloys %	Iridium (III) Taken (µg)	Iridium(III) found by proposed method* (µg)	Recovery (%)
Platinum-iridium alloy	i) Pt, 90; Ir, 10	100	99.7	99.5
	ii) Pt, 70; Ir, 30	100	99.6	99.7
Copper-iridium alloy	Cu, 8; Ir, 92	100	99.5	99.6

CONCLUSION: These results underline the potential of the proposed method for the quantitative, selective extraction of iridium(III) with MBIMTT containing low concentration of iridium. It is free from interference from the large number of diverse ions which are associated with iridium(III) 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 (30 seconds).The method is effective to determine and separate the iridium content from the catalyst. The method is applicable to the analysis of iridium(III) in synthetic mixtures and corresponding to alloys. The method is very simple, selective and reproducible.

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