Extraction and separation studies of iridium(III) with 4-(4-methoxy benzylideneimino)-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 iridium(III) from hydrochloric acid medium with 4-(4-methoxybenzylideneimino)-5-methyl-4H-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.
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INTRODUCTION

The abundance of iridium in the earth's crust is 0.001 ppm. Iridium is a good catalyst organic transformation reactions. 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 high molecular weight amines[5], alamine-336[6-7], N-n-octyaniline[8-9], tri-octylamine (TOA)[10], 4-(non-5-yl)pyridine (NP) [11], , 4-octylamino- pyridine[12]. 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.
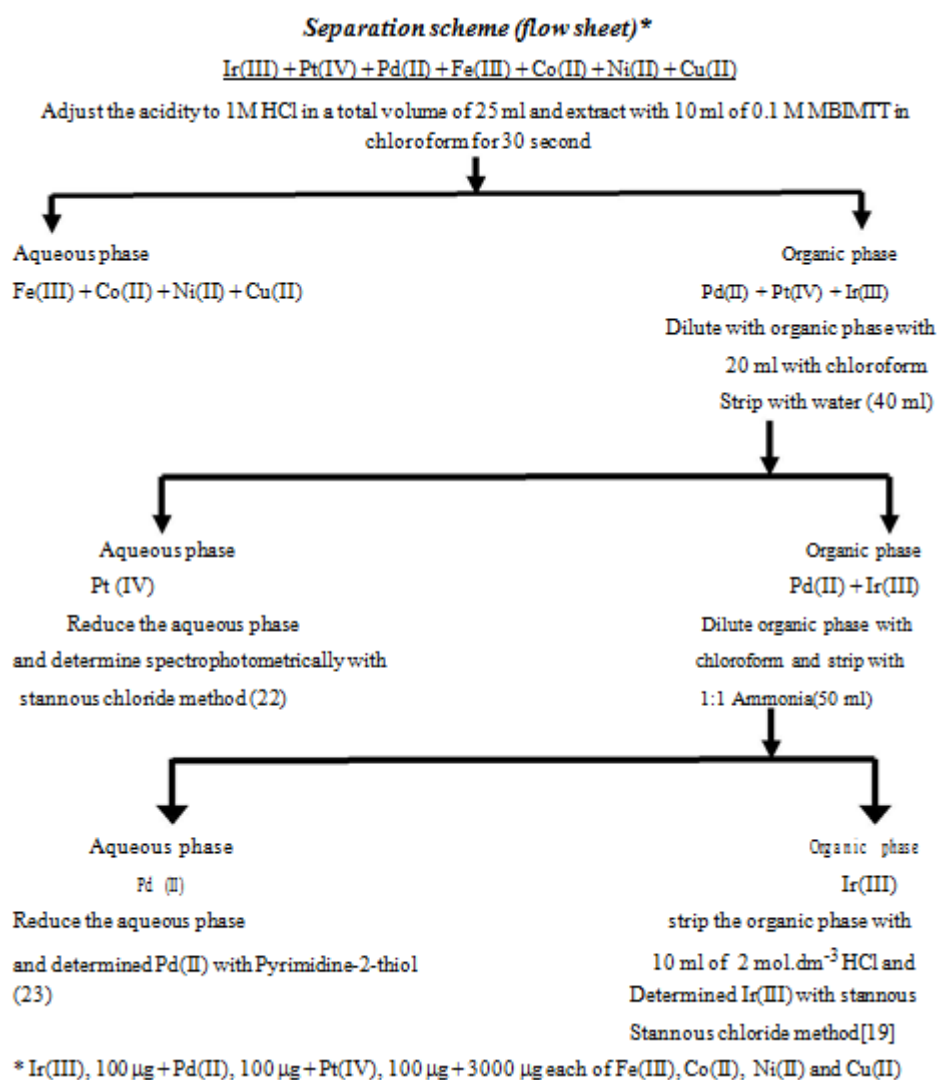
In present investigations, extraction behavior of iridium(III) using 4-(4-methoxybenzylideneimino)-5-methyl-4*H*-1,2,4-triazole-3-thiol(MBIMTT) dissolved in chloroform as an extractant presence of hydrochloric acid media. MBIMTT has been employed successfully in this laboratory for the extraction of Rh(III), Ru (III) and Au(III), Pd(II) and Pt(IV) [13-17].

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)

Separation scheme (flow sheet)*

Ir(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) + Ir(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 (22)

Organic phase
Pd(II) + Ir(III)
Dilute organic phase with
chloroform and strip with
1:1 Ammonia(50 ml)

Aqueous phase
Pd (II)
Reduce the aqueous phase
and determined Pd(II) with Pyrimidine-2-thiol
(23)

Organic phase
Ir(III)
strip the organic phase with
10 ml of 2 mol.dm^{-3} HCl and
Determined Ir(III) with stannous
Stannous chloride method[19]

* Ir(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)

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[18]. A working solution 100 µg ml^{-1} was prepared from it by diluting the stock solution with distilled water. The reagent MBIMTT synthesized by known literature method [13]. 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 µg of iridium(III) and enough hydrochloric acid and water were added to give final concentration of 1 mol/dm^3 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 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[19].

RESULTS AND DISCUSSION

Extraction of iridium(III) as a function of acid concentration

The extraction of 100 μg iridium(III) was carried out from different acid medium with 0.1 mol/dm^3 MBIMTT in chloroform keeping the aqueous to organic volume ratio 2.5:1. The extraction was found to be complete from hydrochloric acid. Iridium(III) was extracted over the 0.2- 10 mol/dm^3 acidity range with hydrochloric acid with 0.1 mol/dm^3 MBIMTT in chloroform. It was observed that extraction increased in the acidity of the aqueous solution and became quantitative at 1 mol/dm^3 hydrochloric acid. It was incomplete in sulphuric acid due to emulsion formation. The extraction was quantitative in nitric acid medium in the 6-7 mol/dm^3 range, but third-phase formation took place above this range of acidity. Hence, the hydrochloric acid system was used for further studies.

Effect of reagent concentration

Iridium(III) was extracted over the 0.5-3 mol/dm^3 acidity range with hydrochloric acid with varying concentrations of MBIMTT. The reagent concentration was varied from $1 \times 10^{-5} – 2$ mol/dm^3 . It was observed that extraction increased in the acidity of the aqueous solution and became quantitative at 1 mol/dm^3 hydrochloric acid. It was found that 0.1 mol/dm^3 reagent in chloroform was needed for quantitative extraction of Ir(III) from 1 mol/dm^3 hydrochloric acid.

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 hydrochloric acid media. As a general procedure, 30 second of equilibration time is recommended in order to ensure complete extraction of iridium(III) hydrochloric acid medium. Prolonged shaking up to 5 minutes has no adverse effect on the efficiency of extraction.

Effect of diluents

The extractions were performed from 1 mol/dm^3 hydrochloric acid medium using 0.1 mol/dm^3 MBIMTT in various solvents as diluents. It was found that 0.1 mol/dm^3

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 (60 %), isoamylalcohol (40 %), 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 4 mol/dm^3 hydrochloric acid was found to be linear and having slope of 1.28. Hence the probable composition of extracted species in chloroform has been found to be 1:1, [Ir(III): MBIMTT].

Loading capacity of MBIMTT

The loading capacity of the extractant was determined by the repeated contact of organic phase with a fresh feed solution of the metal of some concentration. For a 10 ml of 0.1 solution of MBIMTT in chloroform at 1 hydrochloric acid medium and a Aq/Org phase ratio of 2.5:1, the maximum loading capacity for iridium(III) was found to be 4.5 mg.

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 μg 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%.

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 at 1 mol/dm^3 hydrochloric acid. Under these condition all the base metals remain quantitatively in the aqueous phase and these base metals determined spectrophotometrically with thiocyanate[20], 1-nitroso-2 naphthol[20], DMG[20], and pyrimidine-2-thiol [21] respectively. Iridium is stripped from the organic

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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: 1 Effect of diverse ions on the extractive determination of iridium(III)
Ir(III) = 100 μg; aqueous phase = 1 mol/dm^3 HCl; 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)

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

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
Ir,100; 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; Fe,2000; Co,2000;Ni, 2000; Cu, 2000	99.2	99.2	0.07

*- average six determination

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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

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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 4 Analysis of Alloys

Alloys	Composition of Alloys %	Iridium(III) taken (μg)	Iridium(III) found by proposed method* (μg)	Recovery (%)	R.S.D.
Platinum-iridium alloy	i) Pt, 90; Ir, 10	100	99.7	99.5	0.05
Copper-iridium alloy	ii) Pt, 70; Ir, 30 Cu, 8; Ir, 92	100 100	99.6 99.5	99.7 99.6	0.07 0.05

- average six determination

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

It is possible to extract and separate iridium(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 iridium(III), palladium(II), platinum(IV) and base metals, corresponding to the various alloy are given in the Table 3. Iridium(III) was estimated spectrophotometrically by the standard stannous chloride method.

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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