



## Liquid-Liquid Extraction and Separation of Osmium(VIII) with 4-(4-Methoxybenzylideneimino)-5-methyl-4H-1,2,4-triazole-3-thiol in Organic Acid Medium

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### ABSTRACT

*A novel method is proposed for the extraction of microgram level concentration of osmium (VIII) from malonate medium with 4-(4-Methoxybenzylideneimino)-5-methyl-4H-1,2,4-triazole-3-thiol (MBIMTT) dissolved in chloroform as an extractant. The osmium (VIII) from the organic phase is stripped with mixture of thiourea and 2M hydrochloric acid and determined by spectrophotometric method. The method affords the binary separation and determination of osmium (VIII) from synthetic mixture. The method is successfully applied for the separation and determination of osmium from the alloys. The method is highly selective, simple and reproducible. The corrosive acids are not used in extraction of Os(VIII) in this method due to this it has green approach.*

**Keywords:** Osmium (VIII), Solvent extraction, Alloys.

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### INTRODUCTION

0.001mg L<sup>-1</sup> is the abundance of osmium in the earth crust. Osmium has wide range of applications as catalyst, hardening agent in alloys, polymer staining, buckminster fullerene adducts. Osmium has electronic, industrial and environmental importance. Hence it has paramount importance in the development of separation method to recover osmium to meet the future demands. Solvent extraction has become an effective technique in the recovery and separation of osmium [1-4]. The important tendency of osmium is to form chloro complex in chloride medium. Liquid- liquid 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 osmium in aqueous medium plays an important role in the extraction from acidic solution by an anion exchange mechanism. Other extractants reported for osmium (VIII) are trioctyl phosphine oxide [5], trioctylamine [6], bis- 2-ethylhexyl phosphoric acid [7], cynex 925 [8], n-octylaniline [9-10]. The methods reported are not so reliable for routine application because these methods suffer from 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 investigation, extraction behavior of osmium (VIII) using 4-(4-methoxybenzylidene imino)-5-methyl-4H-1,2,4-triazole-3-thiol(MBIMTT) dissolved in chloroform as an extractant presence of malonate medium. MBIMTT has been employed successfully in this laboratory for the extraction of Rh(III), Ru(III) and Au(III), Pd(II) and Pt(IV), Ir(III) and Os(VIII) [11-19].

## MATERIALS AND METHODS

A Shimadzu UV-Visible spectrophotometer (UV-1701) 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 osmium (VIII) was prepared by dissolving 1g of osmium tetroxide (S. D. Fine, India) in dilute Analytical grade hydrochloric acid ( $1 \text{ mol dm}^{-3}$ ) and diluting to 100 mL with distilled water and further standardizing it [19]. A working solution  $100 \mu\text{g mL}^{-1}$  was prepared from it by diluting the stock solution with distilled water. The reagent MBIMTT is synthesized by known literature method [11]. MBIMTT ( $0.1 \text{ mol dm}^{-3}$ ) 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  $\mu\text{g}$  of osmium(VIII) 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  $0.1 \text{ mol/dm}^3$  MBIMTT solution in chloroform for 30 second. The phase was allowed to separate and the metal from the organic phase was back-stripped with mixture of 1ml 10% thiourea and 9 mL 2M hydrochloric acid solution. The extract was evaporated to moist dryness and leached with dilute hydrochloric acid to form the solution. Osmium(VIII) was estimated by spectrophotometric method [20].

## RESULTS AND DISCUSSION

The concentration of MBIMTT in chloroform was varied from the  $1 \times 10^{-5} - 2 \text{ M}$  under optimum condition. It was found that 0.1 M reagent in chloroform was needed for quantitative extraction of Os(VIII) from malonate medium.

**Effect of equilibration time:** Variation of the shaking period from 5 seconds to 5 min showed that a minimum 10 second equilibration time is adequate for quantitative extraction of osmium(VIII) from malonate media. As a general procedure, 30 second of equilibration time is recommended in order to ensure complete extraction of Os(VIII) 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 Os(VIII) was extracted with MBIMTT with various diluents. MBIMTT solution in carbon tetrachloride, chloroform, xylene, toluene and benzene provides quantitative extraction of Os(VIII). The extraction of Os(VIII) 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  $\log D_{[\text{Os(VIII)}]}$  versus  $\log C_{[\text{MBIMTT}]}$  at sodium malonate concentration was to be found linear and having slope of 1.25. Hence the probable composition of extracted species in chloroform has been

found to be 1:1, [Os(VIII): MBIMTT].

**Loading capacity of MBIMTT:** The concentration of Os(VIII) was varied to determining the loading capacity of MBIMTT. The loading capacity of 10 mL of 0.1 M MBIMTT was found to be 7 mg of Os(VIII).

**Effect of diverse ions:** Various ions were used in order to assess the tolerance of these ions on the extraction of osmium (VIII). Osmium(VIII) was extracted in the presence of different diverse ions (Table 1). The tolerance limit was set as the amount of foreign ions cause  $\pm 2\%$  errors in recovery of osmium. The results showed that in the extraction and determination 100  $\mu\text{g}$  of the osmium, these ions did not interfere at the level tested. The reproducibility of osmium extraction investigated from six replicate measurement was found to be  $99.00 \pm 0.95\%$ .

Table 1. Effect of diverse ions on the extractive determination of Os(VIII)

| Tolerance limit (mg) | Foreign ion added   |
|----------------------|---|
| 100                  | Fluoride, 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) |

**Binary separation of osmium(VIII) from base metals:** The method allowed separation and determination of osmium(VIII) from a binary mixture containing either iron(III), cobalt(II), nickel(II), and copper(II).

The separation of osmium(VIII) from iron(III), cobalt(II), nickel(II), and copper(II) by its extraction with  $0.1 \text{ mol dm}^{-3}$  MBIMTT in chloroform. Under these conditions all the base metals remain quantitatively in the aqueous phase and these base metals determined spectrophotometrically with thiocyanate, 1-nitroso-2 naphthol, DMG [21], and pyrimidine-2-thiol [22] respectively. Osmium is stripped from the organic phase with mixtures of 1 mL 10% thiourea and 9 mL of 2 M HCl. The extract was evaporated to moist dryness and leached with  $1 \text{ mol dm}^{-3}$  hydrochloric acid to form the solution. Osmium(VIII) was estimated by spectrophotometric method [20]. The recovery of osmium(VIII) and that added ions was 99.5% and results are reported in table 2.

Table 2. Binary separation of Os(VIII) from Fe(III), Co(II), Ni(II) and Cu(II)

| Composition of Metal ions $\mu\text{g}^{-1}$ | Recovery* Os(VIII) % | Relative Standard Deviation % |
|--|----------------------|-------------------------------|
| Os(VIII), 100; Fe(III); 15000                | 99.5                 | 0.12                          |
| Os(VIII), 100; Co(II) 10000                  | 99.5                 | 0.08                          |
| Os(VIII), 100; Ni(II) 5000                   | 99.7                 | 0.13                          |
| Os(VIII), 100; Cu(II) 5000                   | 99.7                 | 0.14                          |

\*-average six determinations

**Separation of Osmium(VIII) from multi component synthetic mixture:** In its natural occurrence osmium 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 osmium(VIII), there is quantitative extraction of Pd(II), Pt(IV) and Rh(III). But the coextracted metal ions cannot be back stripped by mixture of thiourea and 2M hydrochloric acid solution. Thus the MBIMTT reagent is made selective towards osmium(VIII) by taking advantage of the stripment used. The proposed method allows the selective separation and determination of osmium 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 osmium(VIII) 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 osmium(VIII) has been found to be 99.4%.

**Table 3.** Analysis of Synthetic Mixtures

| Composition( $\mu\text{g}$ )  | Iridium found( $\mu\text{g}$ ) | Recovery (%)* | R.S.D.(%) |
|---|--------------------------------|---------------|-----------|
| Os, 100; Pt,500   | 99.5                           | 99.7          | 0.06      |
| Os, 100; Pd,500   | 99.5                           | 99.7          | 0.07      |
| Os, 100; Ru,500   | 99.6                           | 99.8          | 0.07      |
| Os, 100; Rh,500   | 99.4                           | 99.6          | 0.07      |
| Os, 100; Pt,500; Ru,500   | 99.7                           | 99.8          | 0.06      |
| Os, 100; Pt,500; Pd,500   | 99.7                           | 99.6          | 0.07      |
| Os, 100; Pt,500; Rh,500   | 99.6                           | 99.4          | 0.05      |
| Os, 100; Pt,500; Ru,500; Pd, 500  | 99.5                           | 99.7          | 0.05      |
| Os, 100; Pt,500; Rh,500; Pd, 500  | 99.7                           | 99.6          | 0.06      |
| Os, 100; Pt,200; Ru,200; Pd, 200;<br>Fe,2000; Co,2000; Ni, 2000; Cu, 2000 | 99.3                           | 99.3          | 0.06      |

\*- average six determination

**Table 4.** Analysis of Alloys

| Alloys        | Composition of Alloys% | Osmium(VIII) taken ( $\mu\text{g}$ ) | Osmium(VIII) found by proposed method* ( $\mu\text{g}$ ) | Recovery (%)* | R.S.D. |
|---------------|------------------------|--------------------------------------|--|---------------|--------|
| Siserkite     | Os, 80; Ir, 20         | 100                                  | 99.6   | 99.7          | 0.06   |
| Irodosmine    | Os, 25; Ir, 75         | 100                                  | 99.6   | 99.5          | 0.06   |
| Aurosmiridium | Os, 25; Au, 25; Ir, 50 | 100                                  | 99.5   | 99.7          | 0.05   |

\* average six determination

## APPLICATION

It is used for binary separation of osmium(VIII) from base metals, Separation of Osmium(VIII) from synthetic mixtures and analysis of Alloys.

## CONCLUSION

These results underline the potential of the proposed method for the quantitative, selective extraction of osmium(VIII) with MBIMTT containing low concentration of iridium. It is free from interference from the large number of diverse ions which are associated with osmium(VIII) 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 osmium content from the alloys. The method is applicable to the analysis of osmium (VIII) in synthetic mixtures. The method is very simple, selective and reproducible.

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