

Solvent extraction separation of Rhodium(III) with 4-(4-ethoxybenzylidene amino)-5-methyl-4H-1, 2, 4-triazole-3-thiol (EBIMTT) as an extractant

Uzma parveen K. Shaikh, Machhindra K. lande and Balasaheb R. Arbad*

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, M.S, India

ABSTRACT

Investigation was made on the extraction and spectrophotometric determination of microgram level of Rhodium (III) with a newly synthesized extractant 4-(4-ethoxybenzylideneamino)-5-methyl-4H-1, 2, 4-triazole-3-thiol (EBIMTT) in chloroform from sodium malonate medium. The optimum conditions have been determined by making a critical study of acid, metal ion and extractant concentration, period of equilibration, pH, various diluents and stripping agents. The effect of diverse ions on the quantitative extraction of Rhodium(III) has also been studied. The method is simple, rapid, reproducible, and free from interference of almost all metal ions tested. The proposed method is applicable for the analysis of binary mixtures, synthetic mixtures, alloys and real samples. The molar absorptivity and Sandell's sensitivity of Rhodium (III)-EBIMTT complex are ($1.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and ($0.054 \mu\text{g cm}^{-2}$), respectively which indicates the applicability of the method.

Keywords: Rhodium (III), EBIMTT, Solvent extraction, Spectrophotometry.

INTRODUCTION

At present there is growing demand of platinum group metals, the name platinum group metals include the six elements: Ruthenium, Rhodium, Platinum, Palladium, Osmium, and Iridium. In the past few decades these metals have found new applications outside the jewellery and decorative industries due to its excellent physical and chemical properties and are used extensively for electronic devices, catalysis in the chemical and petroleum refining industries, glass industries, pharmaceutical industries etc. Rhodium is one of the most expensive platinum group metal and is indispensable for automotive catalytic converters. However, given that natural deposits of noble metals are limited, it is essential to recover PGMs from secondary sources (e.g. electronic scrap, petrochemical catalysts, and automotive catalysts).

Though several sophisticated techniques are in use for the determination of trace and ultra trace quantities of Rhodium, spectrometric technique still has the advantage in respect to simplicity and low operating costs but suffers due to matrix effects. Hence separation and preconcentration of trace level quantities of Rhodium is necessary prior to actual quantitative analysis. Several extraction procedures are available for this purpose however most of these are time consuming and costly, however liquid-liquid extraction technique is one of the most suitable, selective, efficient, and powerful technique for the separation and purification of platinum group metals[1].

A variety of extractants like, tributyl phosphite[2], bis-(2-ethylhexyl) phosphoric acid[3], Alamine336[4], BMPT[5], HMAINH[6] have been tested for liquid-liquid extraction of platinum group metals. In comparison to these Nitrogen-sulphur containing Schiff bases showed promising effects in the field of analytical chemistry for the separation and estimation of platinum group metals[7]. Rhodium being a soft acid, can be selectively extracted with soft donor base extractants containing 'N' or 'S' atoms. Based upon this presumption, several extractants, namely, N,N-Dialkyl-N'-benzoylthioureas[8], Kelex 100[9], dioctyl sulphides[10], trialkylphosphinesulphide[11], have been studied or used for the extraction of Rhodium (III). We have synthesised a new ligand of the class Schiff bases, namely, 4-(4-ethoxybenzylideneamino)-5-methyl-4H-1,2,4-triazole-3-thiol (EBIMTT) and studied for its extraction behavior for Rhodium (III) in real samples, synthetic mixtures and alloys.

Thus, the objective of the present article is to extract the trace amount of Rhodium (III) with a newly synthesized ligand from sodium malonate media. Efforts have been made to recover Rhodium (III) from real samples, synthetic mixtures and alloys. Moreover, the effect of acid concentration, reagent concentration, effect of time (shaking period), diluents, stripping agent and divers ions on Rhodium (III) extraction has also been studied.

MATERIALS AND METHODS

Instruments and Chemicals

A Jasco V-530 UV-Vis spectrophotometer with 1 cm quartz cells was used for absorbance measurement and pH measurements were carried out with an Elico digital pH meter model LI-120 (± 0.01). All the chemicals used were of analytical grade. Double distilled water was invariably used throughout the measurements. A stock solution of Rhodium (III) was prepared by dissolving 1g of Rhodium chloride hydrate in dilute analytical reagent grade hydrochloric acid (1M) diluted to 100 ml with distilled water and standardized gravimetrically (Furman, 1963). A working solution of $200 \mu\text{g ml}^{-1}$ of Rhodium (III) was prepared by diluting the stock solution with distilled water. 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. EBIMTT was synthesized by taking the equimolar concentration of 3-ethyl-4-amino-5-mercapto-1, 2, 4-triazole[12,13] and 0.02 mole of ethoxybenzaldehyde in 50 ml alcohol containing 3 drops of glacial acetic acid and was refluxed for 3-4 h. The product obtained was separated and recrystallized from hot ethanol as pale yellow shiny needles (m.p. 171°C). The purity of compound was monitored using ^1H NMR, FT-IR and Mass spectra. ^1H NMR (CDCl_3) δ : 2.12 (5H,s,- C_2H_5), 6.8 (2H,d,J 8 Hz, aromatic protons), 7.5 (2H,d,J 8 Hz, aromatic protons), 8.1(1H,s,-CH), 3.08 (1H, s, -SH). IR (cm^{-1}): 2885(CH), 1600(γ

C=N) and 754 for (γ C=S). Mass m/e: 262.09 (100.0%) (M^+), and its solution (0.1M) was prepared in chloroform.

Recommended method

An aqueous solution containing 200 μ g Rhodium(III) mixed with a sufficient quantity of sodium malonate (0.2 g) to make its concentration 0.03 M in a total volume of 25 ml of the solution. Then the pH of the solution was adjusted to 1.0 using dilute hydrochloric acid and sodium hydroxide. The solution was transferred into a 125 ml separating funnel and shaken with 10 ml of 0.1M EBIMTT in chloroform for just 30 seconds. After equilibration, the mixture was allowed to separate and the metal was stripped from the organic phase with two 10 ml portions of 1M hydrochloric acid solution. The extracts were evaporated to moist dryness. The residue was dissolved in minimum amount of 1M hydrochloric acid and rhodium was determined spectrophotometrically by stannous chloride method.[14]

RESULTS AND DISCUSSION

Effect of acidity

The extraction of Rh(III) was carried out from different organic acids such as sodium salts of malonic acid, salicylic acid, tartaric acid, acetic acid. Quantitative results were obtained in the sodium malonate medium (0.03M) at the pH 1.0. While in tartaric acid, salicylic acid and acetic acid very less extraction was found. Hence the sodium salt of malonic acid is used for further studies.

Effect of diluents

The extractions were performed from malonate medium using 0.1M EBIMTT in various solvents as diluents. It was found that 0.1M EBIMTT solution in carbon tetrachloride, chloroform, xylene, toluene and benzene provides quantitative extraction of rhodium(III). The extraction of rhodium(III) was found to be incomplete in isobutyl methyl ketone, isoamylalcohol and n-butanol. Chloroform is recommended for further extraction procedure because it offers better phase separation, and doesn't form emulsion at the time of extraction.

Effect of concentration of extractant (EBIMTT)

In order to optimise the conditions for extraction of Rhodium (III), chloroform solutions of EBIMTT with varying concentration (0.01- 0.20 M) were employed. It was found that 10 ml of 0.06 M EBIMTT was sufficient for quantitative extraction of 200 μ g Rhodium (III) from malonate media, but in recommended procedure 0.1 M EBIMTT in chloroform was used to ensure the complete extraction of metal ion. There was no adverse effect if one can use excess of extractant. However, a decrease in concentration of extractant resulted in lower distribution ratio, D values for Rhodium (III) that is less extraction. (Fig: 1)

Effect of Time on Extraction

The effect of time was observed on the system for a period of 5s to 30min (hand shaking) the extraction was found quantitative over the periods longer than 10 seconds. But to ensure the complete extraction of Rhodium (III) 1 min equilibration time was recommended. However, a prolonged shaking period doesn't have any adverse effect on the extraction.

Effect of Stripping Agents

Stripping is the reverse of extraction, so it should be promoted by those factors that affect extraction negatively, such as acidic and salt media. Alkalies were unsuccessful because the anion complex adhered in the organic medium under these conditions. The stripping percentage was calculated relative to the initial amount of rhodium (III) in the loaded organic solutions. Rhodium (III) was stripped with different stripping agents such as mineral acids, bases, and salts after its extraction. The stripping of Rhodium (III) was quantitative with 1M hydrochloric acid. The stripping was found to be incomplete with nitric acid (60%), sulphuric acid (40%), and with sodium chloride (20%), whereas Rhodium (III) was not stripped with ammonia, sodium hydroxide and water.

Effect of divers ions

Rhodium (III) was extracted in the presence of a large number of foreign cations and anions (Table1). The tolerance was set at the amount of the foreign ion that could be present to give an error less than $\pm 2\%$ in the recovery of Rhodium (III). The results showed that in the extraction and determination $200\mu\text{g ml}^{-1}$ of the Rhodium (III), these ions has no significant effect. The reproducibility of Rhodium (III) extraction investigated from six replicate measurements.

APPLICATION**Binary separation of Rhodium (III) from iron (III), cobalt (II), nickel (II) and copper (II)**

The method allowed separation and determination of Rhodium (III) from a binary mixture containing either iron (III), cobalt (II), nickel (II) and copper (II). In a typical experiment, solution containing $200\mu\text{g}$ of Rhodium (III) was taken and known amounts of other metals were added. Rhodium (III) was estimated spectrophotometrically by stannous chloride method. The recovery of Rhodium (III) and that added ions was 99.5% and results are reported in (Table 2).

Analysis of synthetic mixtures

The separation of Rhodium (III) from other platinum group metals that is platinum, palladium and gold was carried out by taking advantage of differences in their optimum extraction and stripping conditions. The proposed method was successfully used in the determination of Rhodium (III) from different synthetic mixtures (Table: 3). A solution containing $200\mu\text{g}$ of Rhodium (III) was taken and known amount of other metals were added. Under the optimum extraction conditions of Rhodium (III), there is a quantitative extraction of Pd (II), Pt(IV), Ru (III) and Au(III) but the co-extracted metal ions cannot be back-stripped by 1M hydrochloric acid solution. Thus, the reagent (EBIMTT) is made selective towards Rhodium (III) by taking an advantage of the stripant used.

Analysis of alloys

To ascertain the selectivity of the reagent, the proposed method was successfully used in the determination of Rhodium (III) in alloys. 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 Rhodium (III) was 99.5%.

Table: 1 Effect of various diverse ions on percentage extraction of 200µg of Rh(III) from hydrochloric acid with 0.1M EBIMTT in chloroform.

Diverse ions added	Amount tolerated (mg)
Pd ^{II}	0.5
Au ^{III} Pt ^{IV}	1
Zn ^{II} Mo ^V Cd ^{II} Hg ^{II} Pb ^{II} Ni ^{II} Sn ^{II} Cu ^{IIa} Sb ^{III}	5
Mn ^{II} Sr ^{II}	10
Fe ^{III} Bi ^{III} Ca ^{II} Mg ^{II} Be ^{II} Ba ^{II}	20
Acetate, Bromid, Iodide, EDTA	100

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

Composition of metal ions, (µg)	Recovery Rh(III) (%)	Relative standard deviation (%)	Recovery added metal ions* (%)	Relative standard deviation (%)
Rh(II),100, Fe(III); 15000	99.4	0.15	99.7	0.07
Rh(II),100, Co(II); 10000	99.5	0.19	99.6	0.13
Rh (II),100,Cu(II); 5000	99.6	0.25	99.5	0.16
Rh (II),100,Ni(II); 5000	99.5	0.17	99.6	0.19

*Average of six determination.

Table: 3 Analysis of synthetic mixture

Composition	Rhodium found(µg)	Recovery* (%)	Relative standard deviation (%)
Rh(100)+Pd(500)	99.8	99.6	0.07
Rh(100)+Au(500)	99.6	99.8	0.05
Rh(100)+Pt(500)	99.4	99.7	0.07
Rh(100)+Ru(500)	99.6	99.8	0.05
Rh(100)+Pd(500)+Ru(200)	99.5	99.9	0.06
Rh(100)+Pd(500)+Au(200)	99.4	99.7	0.07
Rh(100)+Pt(500)+Au(200)	99.4	99.7	0.07
Rh(100)+Pt(500)+Pd(200)+Au(200)	99.5	99.6	0.06
Rh(100)+Pt(200)+Pd(200)+Ru(200)+Au(200)+Co(200)	99.4	99.7	0.07

*Average of six determination.

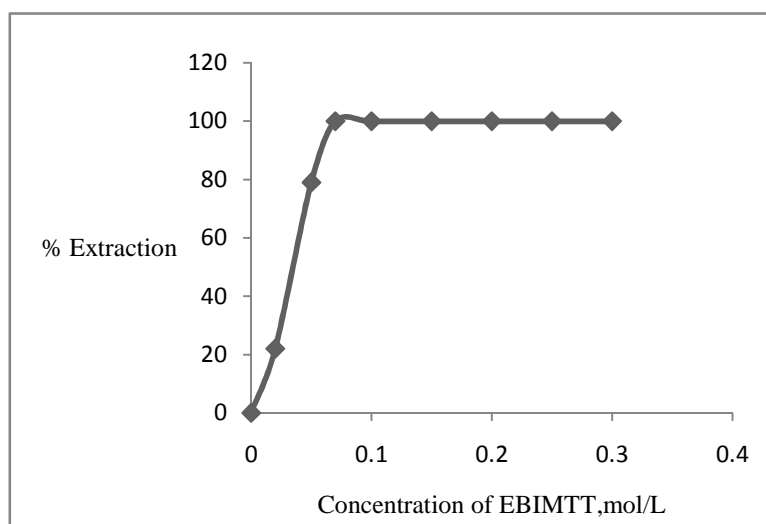
**Fig1.** Extraction of Rhodium (III) as a function of EBIMTT concentration

Table: 4 Analysis of alloys

Alloy	Composition	Amount of Rhodium (III) was found by proposed method	R.S.D (%)
Platinum-Rhodium for thermocouple wire	Pt,87: Rh,13	12.9%	0.76
Palladium-Rhodium alloy	Pd,90: Rh,10	9.78%	0.88

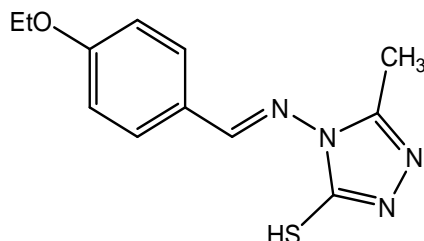


Fig 2. Structure of 4-(4-ethoxybenzylideneamino)-5-methyl -4H - 1,2,4-triazole -3-thiol(EBIMTT).

CONCLUSION

The present work points out that the synthesized extractant (EBIMTT) shows a good potential for the extraction of Rhodium (III) from sodium malonate media. The extraction time is short just 30 seconds and the extractant presents a good loading capacity and reusable. The proposed method is used for rapid and selective separation of Rhodium (III) from associated ions in their binary mixtures, synthetic mixtures and alloys.

Acknowledgment

The authors thank Professor C. H. Gill, Head Department of Chemistry, for his inspiration in the research work.

REFERENCES

- [1] N.H. Furman "Standard of Chemical Analysis", D. Van Nostrand Company, inc., princeton, New Jersey, **1963**, 902.
- [2] Wilson R.B., W.D. Jacobs, *Anal. Chem.*, **1961** 33, 1650–1652.
- [3] G. Yan and J. Alstad, *J. Radioanal. Nucl. Chem.*, **1995**, 196, 287
- [4] E. Goralska, M.T. Coll, A. Fortuny, C.S. Kedari, and A.M. Sastre, *Solv. Extr. Ion Exch.*, **2007**, 25, 65–77.
- [5] G. B. Pethe, S. G. Bhadange¹, M. D. Joshi and A. S. Aswar, *Advances in Applied Science Research*, **2010**, 1 (2): 58-64
- [6] B. Mathew, V. Mini and A. Vinnifred, *Advances in Applied Science Research*, **2010**, 1 (3) 7-14
- [7] Vest, M. Schuster, K. H. König, *Fresenius Zeitschrift für Analytische Chemie*, **1989**, 335, 759.
- [8] K.H. König, M. Schuster, B. Steinbrech, G. Schneeweis, R. Schlodder, *Fresenius' Zeitschrift für Analytische Chemie*, **1985**, 321, 457-460.
- [9] E. Benguerel, G. Cote, Demopoulos and D. Bauer, *J. Chem. Technol. Biotechnol.*, **1995**, 62, 380.
- [10] S.J. Al-Bazi, H. Freiser, *Solv. Extr. Ion Exch.*, **1987**, 5, 265.

- [11] G.H. Rizvi, J.N. Mathur, M.S. Murali, R.H. Iyer, *Sep. Sci. Tech.*, **1996**, 31, 1805.
- [12] U. P. Shaikh, S. S. Katkar, K. N. Vidhate, M. K. Lande and B. R. Arbad *J. Indian Chem. Soc.* **2011**, 88 1-4
- [13] K.S. Dhakha, J. Mohan, V.K. Chanda, and H.K. Pujari *Ind. J. Chem.*, **1974**, 12, 288.
- [14] E.B. Sandell, 'Colorimetric Determination of Traces of Metals', 3rd Ed. Interscience, New York, **1965** pp 503, 519, 702, 774, 781