

Extractive Photometric Determination of Rhodium(III) with Cyanex 301[†]

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AJC-11758

A method is proposed for direct spectrophotometric determination of Rh(III) from HCl medium in presence of SnCl₂ using cyanex 301 in chloroform. Cyanex 301 is [*bis*-(2,4,4 trimethylpentyl) dithiophosphonic acid]. A coloured Rh-cyanex 301 complex in organic phase exhibits maximum absorption at 450 nm where absorption of reagent was found to be negligible. The effect of various parameters affecting extraction equilibrium of Rh(III) such as acid concentration, SnCl₂ concentration, equilibration time, cyanex 301 concentration, effect of diluents and diverse ions have been studied. The probable composition of the species has been deduced from the extraction data. The method is simple, rapid and sensitive and permits separation of Rh(II) from the other metal ions like Cu²⁺, Co²⁺, Mn²⁺.

Key Words: Extraction, Rhodium (III), Cyanex 301, Binary separation.

INTRODUCTION

Rhodium is one of important platinum group element having many applications in auto industry as an auto-catalyst. Rhodium with other platinum group metals, notably Pt and Pd are invaluable for the reduction of nitric oxide in vehicle emission. Rhodium remains bright in all atmospheric conditions and has uniform reflectivity (75-80 %) for its uses in Jewelry, as a reflector for search lights and for electrical contact. In view of this fact, a simple and accurate method for determination of rhodium is desirable. The most widely used extractive photometric methods for determination of rhodium have been revived¹. Berg and Senn² pointed out that percentage of Rh(III) extracted by tributyl phosphate is very low. Chen *et al.*³ obtained the same results. The extraction of Rh(III) with tributyl phosphate after adding SnCl₂ is studied by Zou *et al.*⁴. Fedorenko and Ivanova⁵ and Khatak and Magee⁶ obtained about 75-80 % extraction from 0.1 M HCl solution by tri-*n*-octylamine. Rhodium was determined spectrophotometrically at 430-435 nm as the amber to red complex of Rh(II) with 4,5-dimethyl-2-mercapto-thiazole in 3-9 M HCl after reduction from Rh(III) by SnCl₂⁷. The organo phosphorous extractant like Cyanex 923⁸ was used for separation of rhodium from the other platinum group elements. The methods involve back stripping of rhodium with nitric acid followed by determination by stannous chloride method at 525 nm. Mhasake and Dhadake⁹ used Cyanex 925 for separation of Rh(III) from other

platinum group elements. Cyanex-301 [*bis*-(2, 4, 4 trimethyl-pentyl) dithiophosphonic acid] marketed by Cytec Inc. Canada has been used as an extractant for some metal ions¹⁰⁻¹⁸. However there has been no detailed study on the use of this reagent for the direct extractive photometric determination of rhodium. Hence the attempt has been made to establish a method for the determination of rhodium using Cyanex 301 as an extractant.

EXPERIMENTAL

A 'spectronic Genesis 8' UV-visible spectrophotometer was used for absorbance measurements.

A stock solution of Rh(III) was prepared by dissolving 0.2558 g of rhodium chloride in a 100 mL measuring flask with double distilled water containing about 5 mL conc. HCl. It was standardized gravimetrically by standard method¹⁹. The working standard solutions were prepared by suitable dilution of stock solution.

Cyanex 301[*bis*-(2, 4, 4 trimethyl pentyl) dithiophosphonic acid] reagent obtained from Cytech Inc. Canada was used as such. A 0.08 mol dm⁻³ stock solution of the reagent was prepared by dissolving the reagent in chloroform. Stannous chloride, hydrochloric acid, solvents used of analytical grade from Merck.

To an aliquot of the aqueous solution containing rhodium (III) was added 1.8 mL of 0.1 mol dm⁻³ SnCl₂ to which was added hydrochloric acid to make it 4 mol dm⁻³ in a total volume

[†]Presented at International Conference on Global Trends in Pure and Applied Chemical Sciences, 3-4 March, 2012; Udaipur, India

of 15 mL. The solution was transferred into a 125 mL separating funnel and shaken for 60 sec. with 15 mL of 0.08 mol dm^{-3} Cyanex 301 solution in chloroform. After allowing the two phases to separate, the organic phase was collected in a 25 mL standard measuring flask and diluted upto the mark with chloroform. A small quantity of anhydrous sodium sulphate was added to all the 25 mL flasks to absorb the moisture. The absorbance of the extract was measured at 450 nm against the reagent blank prepared analogously.

RESULTS AND DISCUSSION

The absorption of rhodium- cyanex complex was studied over a wavelength range of 200-550 nm. The dark yellow coloured complex exhibited absorption maxima at 450 nm (Fig. 1). At this wavelength the absorption of the reagent was negligible. Therefore, the wavelength of 450 nm was chosen for all further measurements.

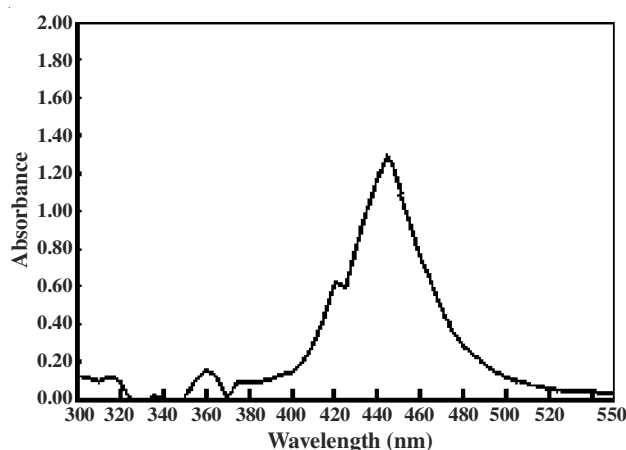


Fig. 1. Absorption spectrum of Rh-Cyanex complex

Effect of reagent concentration: The optimum concentration of Cyanex 301 for quantitative extraction of Rh(III) was ascertained by extraction with varying concentrations of Cyanex 301 from 0.01 - 0.30 mol dm^{-3} in chloroform. The extraction was quantitative with 0.08 mol dm^{-3} Cyanex 301 (Fig. 2). Hence 15mL of 0.08 mol dm^{-3} Cyanex 301 in chloroform was used throughout the study.

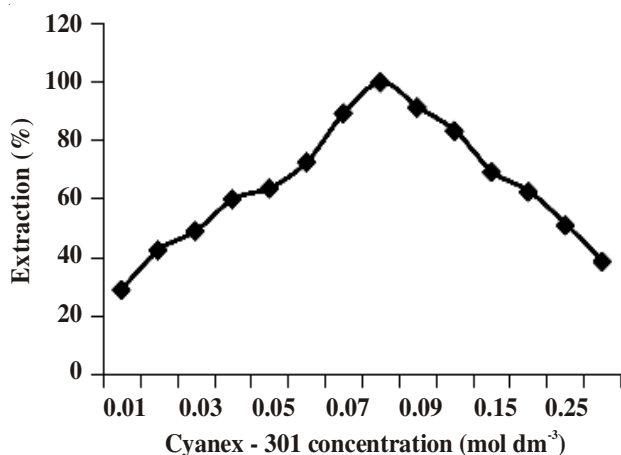


Fig. 2.

Effect of hydrochloric acid concentration: The effect of the molarity of hydrochloric acid on the absorbance of the extract was studied using the recommended procedure. By varying concentration of HCl between 0.5 to 8.0 mol dm^{-3} . The absorbance of extract was maximum for 4.0 mol dm^{-3} . Thus 4.0 mol dm^{-3} HCl concentration was used for subsequent studies.

Effect of stannous chloride concentration: Rhodium was extracted in the presence of SnCl_2 which was used as a labilizing agent. When tin was added to the solution, rhodium gets activated. This may be due to the reduction of Rh(III) to Rh(I) with SnCl_2 and thus making the complex easily extractable into Cyanex 301. In the absence of SnCl_2 , rhodium does not get extracted into Cyanex 301 using the recommended procedure. The effect of the molarity of SnCl_2 in the range of 0.05 - 0.20 mol dm^{-3} on the absorbance of the extract was studied using the recommended procedure at 450 nm with a sample containing $100 \mu\text{g}$ of rhodium(III) and 4.0 mol dm^{-3} HCl. The extraction was done using 15 mL of 0.08 mol dm^{-3} Cyanex 301 in chloroform. The absorbance was maximum for 0.12 mol dm^{-3} SnCl_2 . Hence, all the extractions were carried out using 1.8 mL of 0.1 mol dm^{-3} (0.12 mol dm^{-3}) SnCl_2 concentration.

Effect of various diluents: To find out the effect of diluents on extraction, the reagent 0.08 mol dm^{-3} of cyanex 301 was prepared in different diluents and was used for extraction from aqueous phase containing 100 mg of rhodium in 4 mol dm^{-3} HCl, 0.18 mol dm^{-3} SnCl_2 of the diluents study the absorbance and % extraction of rhodium decreased in the order: chloroform (99.8 %), toluene (81.3 %), carbon tetrachloride (80.1 %), benzene (76.2 %), xylene (64.86 %), cyclohexane (43.2 %).

Effect of equilibration period: The absorbance of the extract obtained by shaking the aqueous phase containing $100 \mu\text{g}$ rhodium (III) + 1.8 mL of 0.1 M SnCl_2 diluted to 15 mL with 4.0 M hydrochloric acid, with an organic phase containing 0.08 M Cyanex 301 in chloroform was measured, for varying time periods from 15 sec to 120 sec. It was observed that the extraction was quantitative after 60 sec of equilibration. Hence, optimum period chosen for equilibration was 60 sec.

Optimum conditions for extraction of rhodium

Parameter	Optimum condition
Rhodium(III)	$100 \mu\text{g/mL}$
Hydrochloric acid concentration	4.0 mol dm^{-3}
SnCl_2 concentration	0.12 mol dm^{-3}
Cyanex 301 concentration	0.08 mol dm^{-3}
Shaking time	60 sec
Diluent	Chloroform

Nature of extracted species: An attempt was made to find out the probable composition of the extracted species from a plot of $\log D$ vs. $\log C$ (Cyanex 301) at fixed acid and SnCl_2 concentration. The slope of this plot was found to be $0.97 \approx 1$ indicating the complex to be 1:1 with respect to Cyanex 301, thus confirming the oxidation state of Rhodium as +1 in the extracted species (Fig. 3).

Validity Beer's law: A calibration graph (Fig. 4) for determination of rhodium was prepared under optimum experimental condition (0.18 mol dm^{-3} SnCl_2 , 4 mol dm^{-3} HCl

TABLE-1
EFFECT OF FOREIGN IONS

Cations/anions	Source	Tolerance limit (μg)	Cations/anions	Source	Tolerance limit (μg)
Cu^{+2}	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Non-interfers	Li	LiCl	1500
Co^{+2}	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	Non-interfers	K^+	KCl	Non-interfers
Cd^{+2}	$\text{CdCl}_2 \cdot \text{H}_2\text{O}$	500	Na^+	NaCl	Non-interfers
Zn^{+2}	ZnCl_2	1800	Mn^{+2}	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	2500
Ba^{+2}	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	2500	Bi^{+3}	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	1200
Ni^{+2}	$\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$	1200	Sb^{+3}	SbCl_3	Non-interfers
Hg^{+2}	HgCl_2	1000	Th^{+4}	ThCl_4	2000
La^{+3}	$\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$	2000	F ⁻	NaF	2600
Ca^{+2}	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	2500	SCN^-	KSCN	2000
Sr^{+2}	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	2000	CO_3^{2-}	CaCO_3	Non-interfers
Zr^{+4}	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	2000	NO_3^-	NaNO_3	2500
Mo^{+6}	$(\text{NH}_4)_6\text{MO}_7 \cdot \text{O}_{24} \cdot 4\text{H}_2\text{O}$	1800	Br^-	KBr	2300
Fe^{+3}	$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	2700	Oxalate	$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	Non-interfers
Ti^{+4}	$\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	Non-interfers	SO_3^{2-}	Na_2SO_3	Non-interfers
Te^{+2}	$\text{Na}_2\text{TeO} \cdot 2\text{H}_2\text{O}$	2400	NH_4^+	NH_4Cl	2800
Pb^{+2}	$\text{Pb}(\text{NO}_3)_2$	700	SO_4^{2-}	Na_2SO_4	Non-interfers

TABLE-2
BINARY SEPARATION OF RHODIUM

Composition (μg)	Recovery of Rh(III)* (%)	Coefficient of variation (%)	Recovery of the added ion* (%)	Coefficient of variation (%)	Estimation procedure for the added ion and its reference
Rh(III) : Cu(II) 50 : 50	99.99	0.52	97.58	0.39	Diethyldithiocarbamate method. ²⁰
Rh(III) : Co(II) 50 : 50	99.99	0.67	98.65	0.17	Colourimetrically with Nitroso-R-salt ²⁰
Rh(III) : Ti(IV) 50 : 50	99.99	0.46	96.54	0.28	Hydrogenperoxide method ²⁰
Rh(III) : Al(III) 50 : 50	99.99	0.56	94.32	0.38	Eriochrome Cyanine R method ²⁰

*Mean of five determinations

and 0.08 mol dm⁻³ Cyanex in chloroform). Beer's law obeys with range of 10 to 150 mg of rhodium at 450 nm. The molar absorptivity of complex calculated was found to be 2.5×10^4 dm³mol⁻¹ cm⁻¹. At 450 nm Sandell's sensitivity calculated on the basis of total rhodium present is 0.0386 mg cm⁻².

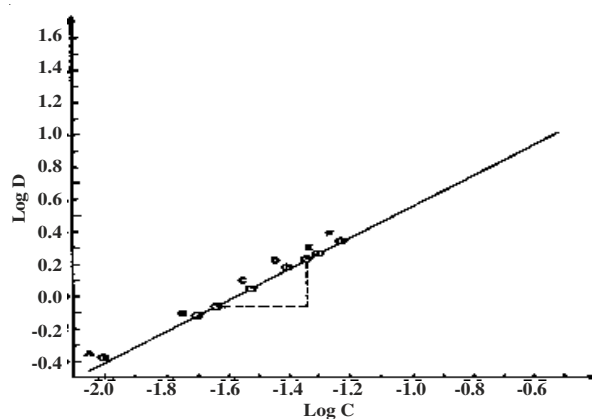


Fig. 3 Log D vs. Log [Cyanex 301] plot

Spectrophotometric data for the determination of rhodium after extraction with Cyanex 301: Rh(III) = 100 μg ; 1.8 mL of 0.1 M SnCl_2 ; $[\text{HCl}] = 4.0$ M; extracting solution = 15 mL of 0.08 M Cyanex 301 in chloroform.

Molar absorptivity	2.587×10^4 mol ⁻¹ cm ⁻¹ dm ³
Sandell's sensitivity	3.8610×10^{-3} μg cm ⁻²
Mean absorbance of 6 determinations	1.036
Beer's law range	10-150 $\mu\text{g}/\text{mL}$
Standard deviation	1.3416×10^{-3}
Coefficient of variation	0.12 %

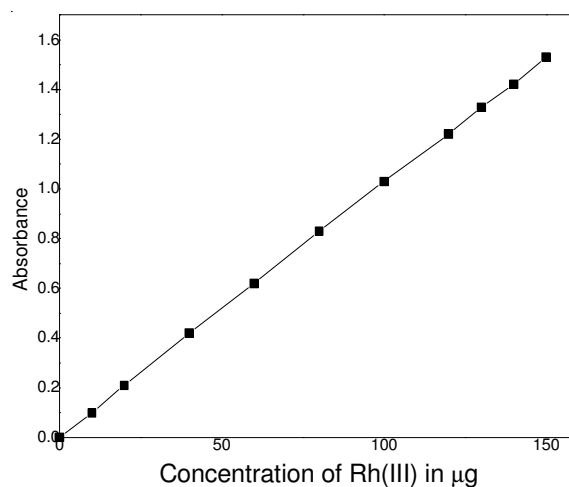


Fig. 4. Beer's law plot

Effect of diverse ions: The extraction of rhodium(III) was carried out according to the recommended procedure to examine the effect of interference from various foreign ions. The tolerance limit was set at an amount to cause an error of ± 2 % in the recovery of the metal ion. It was observed that, a large number of cations and anions were tolerated (Table-1).

Binary separations of rhodium(III): Ions such as as Cu(II), Co(II), Ti(IV), Al(III), Sb(III) do not get extracted into Cyanex 301 under optimum extraction conditions for rhodium(III) up to a certain concentration. Hence, it is possible to separate them from their binary mixtures. The unextracted Cu(II), Co(II), Ti(IV), Al(III), Sb(III) was determined spectrophotometrically by known methods (Table-2).

Conclusion

The present investigation have result in offering a convenient direct extractive photometric determination of rhodium in hydrochloric acid medium in presence of stannous chloride using Cyanex 301 in chloroform. The proposed method has number of advantages such as ease, phase separation, less equilibration time and single extraction is sufficient for quantitative extraction of rhodium. The method is also useful for extraction of rhodium from other metal ions such as Cu^{2+} , Co^{2+} , Mn^{2+} , Sb^{3+} , Al^{3+} , Ti^{4+} . The method is rapid, selective and highly precise with good reproducibility.

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