

SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM USING PHENANTHRAQUINONE MONOTHIOSEMICARBAZONE

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Abstract—Phenanthraquinone monothiosemicarbazone forms a brown colored insoluble chelate with rhodium (iii) on heating on water bath in the pH range 4.4-6.1. The chelate is soluble in DMF and has maximum absorbance at 510 nm. The system obeys Beer's law up to 12.88ppm of rhodium. The optimum concentration range for the determination of rhodium is 2.4-10.0 ppm. Sensitivity of the reaction is $1.3 \times 10^{-2} \mu\text{g Rh/cm}^2$. The method has few advantages over other known methods.

Index Terms— SPECTROPHOTOMETRIC,
PHENANTHRAQUINONE.

I. INTRODUCTION

Several methods for the determination of trace amounts of rhodium have been summarized (1,2). The well known reagents for the purpose are p-nitrosodimethylaniline, tin (II) chloride, bromide and iodide, thiosalicylamide, oximidobenzotetronic acid, allyl ether of thio oxine, 1-Phenyl-3- (2-pyridyl) thiourea, N, N'-bis (3-dimethylaminopropyl) dithio- oxamide, tropolone, chrome azurole S, xylenol orange, 8- quinoline, nitoso- R- salt, 8- quinolinol, thoron, thiocyanate, alizarin red S, 4- (2 pyridylazo)- resorcinol, acenaphthenequinonemonoxime, benzoin- α - oxime, 1- phenyl-3- (2 pyridyl)- thiourea and 4,4'-hydroxybenzophenone thiosemicarbazone.

The present study was made to investigate the use of phenanthraquinone monothiosemicarbazone (PTS) for the spectrophotometric determination of rhodium. Optimum conditions for the determination , molar composition of the complex and selectivity of the method have been investigated.

II. EXPERIMENTAL

Preparation of PTS: PTS was prepared by oxidation of phenanthrene (Fluka, AG) to phenanthraquinone by the method of Schultz and was purified. Then equimolar amounts of phenanthraquinone and thiosemicarbazide (E.Merck GR) were dissolved separately in minimum amounts of methanol and then mixed. After mixing, the solution was refluxed for three hours on a boiling water bath. The hot solution was filtered under suction and cooled. Red crystals of PTS were obtained which were recrystallised from methanol (m.p, 191-192). The purity of the ligand has been checked by elemental analysis and thin layer chromatography. The wavelength of

maximum absorption of PTS is at pH 0.7 , 6.5 and 11.9 is at 250, 254 and 207 nm respectively. PTS solution was prepared by dissolving it in dimethyl formamide (DMF) because its greater solubility in this solvent. The solution is stable for two days

Standard rhodium (III) solution : A standard rhodium (III) solution was prepared by dissolving rhodium trichloride in 1M hydrochloric acid. The solution was

standardized gravimetrically by precipitating rhodium as the sulphide, followed by its

ignition to the oxide and then reduction to the metal in a current of hydrogen and cooling in carbon dioxide. Subsequent dilutions were made from this stock solution according to requirement.

Preliminary investigation : Rhodium (III) forms a brown colored insoluble chelate with PTS on heating on the water bath. The chelate is fairly soluble in DMF. It has been observed that 80% aqueous DMF is required to dissolve the complex, but with higher percentage of DMF, there is no change in absorbance. In further studies 80% of DMF (v/v) was maintained in the solutions.

Absorption Spectra : The absorption spectra of the chelate against a reagent blank prepared under identical condition was observed. The maximum absorbance was found at 510 nm and therefore subsequent studies were carried out at this absorbance.

Heating time and stability of the complex: It was found that color formation is slow at room temperature, but is accelerated on heating on a boiling water bath. Solutions containing 25 ml of 5×10^{-4} M rhodium (III) and 2.5×10^{-3} M reagent were heated for various interval of time. Measurement of absorbance show that 90 minutes are required for maximum color development and absorbance remain constant for about twenty hours after which it decreases. Therefore in all studies, the chelate was heated for 90 minutes.

Effect of pH : 25 ml of 5×10^{-4} M rhodium (III) and 2.5×10^{-3} M reagent solution in DMF were mixed and apparent pH was adjusted by the use of 0.2M potassium hydrogen phthalate. For higher and lower pH , dilute solutions of sodium hydroxide and hydrochloric acid were used. The contents were heated on boiling water bath for about 90 minutes. cooled and total volume was raised to 25 ml, keeping 80% DMF concentration. The pH of this solution was taken to be the final pH of the solution. The constant absorbance was

observed between the pH range 4.4 – 6.1. Subsequent studies were carried out at pH 5.0 ± 0.1 .

Effect of excess of reagent : Increasing amounts of reagent solution were added to fixed amount of rhodium (128.76 μg) at pH 5.0. The chelate was dissolved in usual manner and absorbances were measured at 510 nm against the reagent blank prepared under similar conditions. It was found that seven times reagent is required for maximum color development. Therefore ten fold molar excess of the reagent was used in subsequent studies.

Beers Law and sensitivity of the reaction : A series of solutions were prepared containing increasing amounts of rhodium (III) and constant amount of reagent. The pH in each case was adjusted to 5.0 ± 0.1 . Absorbances were measured at 510 nm. It has been found that the system obeys Beers law up to 12.88 ppm of rhodium. The sensitivity of the reaction from Beers law plot, is $1.3 \times 10^{-2} \mu\text{g Rh/cm}^2$ at 510 nm for log I₀/I 0.001, with molar absorptivity of 7900 l mole⁻¹ cm⁻¹. The optimum concentration range for determination of rhodium, as evaluated from Ringbom plot, is 2.4-10.0 ppm of rhodium

Recommended procedure : 60.0 – 250.0 μg rhodium (III) is taken and tenfold of reagent solution is added. The pH of the solution is adjusted in the range of 4.4 – 6.1 and the solution is heated on a water bath for about 90 minutes. After cooling, the total volume is made to 25.0 ml, keeping 80% DMF medium. Absorbance of the solution is recorded at 510 nm against blank prepared under identical conditions. Knowing the absorbance , rhodium content is obtained from the calibration curve.

Stoichiometry of the complex : The stoichiometry of the complex has been ascertained by Jobs method. Absorbances of the complex were measured at 510 and 530 nm, which were plotted against mole fraction of rhodium. The complex shows maximum absorbance at 0.33 mole fraction of the metal ,which corresponds to 1: 2 ratio of the metal to ligand in the complex.

Precision of the method : Absorbance deviations were measured under optimum conditions for eight samples, each containing 5.15 ppm of rhodium. Average relative percentage error was 0.30 and maximum relative percentage error was 0.78. The standard deviation comes out to be 3.26×10^{-3} .

Effect of diverse ions : Effect of diverse ions in the solution containing 5.1 ppm of rhodium (III) solution at pH 5.0 was studied by measuring absorbance at 510 nm.. The amounts of diverse ions (in ppm) which did not alter the absorbance by more than ± 2.0 % are given below in parentheses, with masking agents, if any

Chloride (700), bromide (400), iodide (300), fluoride (80), nitrate (800), borate (100), sulphate (600), nitrite and thiosulphate (50 each), oxalate (100), phosphate (250),cyanide (40), EDTA (20), iron (II) (20, PO₄-3), cobalt (II) (3, CN-1), nickel (ii) (4, CN-1), calcium (II) and barium (II) (100 each), magnesium (II) (250), silver (I) (20,Cl-1), zinc (II) and cadmium (II) (5 each, CN-1), osmium (VIII) (1,SCN-1), iridium (III) (3, tart.), platinum (IV) (5, I-1),manganese (II) (10), titanium (IV) (10).

Ruthenium (III), palladium (II) and copper (II) could not be masked. Tartrate and citrate have been found to interfere.

III. DISCUSSION AND CONCLUSION

Only few satisfactory chromogenic reagents have been reported for the determination of rhodium. The most sensitive one is p- nitrosodimethylaniline. Though the complete complexation takes place in 10 minutes on heating but the absorbance starts decreasing after 20 minutes and volume of the buffer solution used affects the absorbance. Rhodium (III) forms complex with tin bromide but complex is stable for 3 hours and its composition is unknown. Tin (II) chloride forms red color with rhodium in 2M HCl, which changes to yellow on dilution. Yellow form is more stable than red. Both the methods are unselective.

N,N' – bis (3- dimethylaminopropyl) dithio-oxamide has been used for the determination of rhodium at 7.5 M HCl. Sensitivity of the method is low and other platinum metals interfere. Acenaphthenequinonemonoxime is a sensitive reagent but thiosulphate, EDTA, iron, copper, platinum, iridium interfere seriously. 1- Phenyl-3-(2-pyridyl)thiourea is very sensitive reagent for rhodium but the absorption maximum lies in uv region.

In the present study, PTS has been successfully used for the determination of small quantities of rhodium. The method is sensitive and the advantage of the method is that the volume of buffer solution, excess of reagent and heating time are not a critical factor as in the case of other reagents. Extraction is not required as in many methods.

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