

Extraction & Spectrophotometric Determination of Rhodium & Iridium with 1-Phenyl-3-thiobenzoyl Thiocarbamide

R. M. UTTARWAR & A. P. JOSHI

Department of Chemistry, Nagpur University
Nagpur 440010

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1-Phenyl-3-thiobenzoyl thiocarbamide reacts with rhodium and iridium to form orange-red coloured complexes which are extractable in chloroform. Complexation takes place at pH 5.5 on heating the reactants to 90°. The wavelengths of maximum absorbance are 435 and 425 nm for rhodium and iridium systems respectively. Optimum conditions for the determination of both the metals have been established. The methods are simple and sensitive. It is also possible to effect the separation of these two metals from platinum using the same reagent.

REAGENTS used for the spectrophotometric determination of rhodium and iridium have been reviewed recently^{1,2}. Various thio organic compounds have been used with considerable success in the determination of rhodium but these seem to have a limited application as far as determination of iridium is concerned. 2-Mercaptobenzothiazole has been used recently for the determination of iridium³. Some of the thio organic compounds used recently for rhodium determination are 1-(2-pyridylazo)-2-phenanthrol⁴, monobenzoyl thiourea⁵, phenyl tetrazoline-5-thione⁶, phthalimide-8-dithiosemicarbazone⁷ and thiotropolane TT⁸.

A new thio compound, 1-phenyl-3-thiobenzoyl thiocarbamide (PTT) has been used in the present work for the extraction and photometric determination of rhodium and iridium. Its use for the spectrophotometric determination of platinum has already been reported⁹. In the present study it is found that PTT reacts with Rh(III) and Ir(III) at pH 5.5, on heating to 90°. The orange-red coloured complexes formed are extractable in chloroform and show λ_{\max} at 435 and 425 nm respectively. Effects of various parameters have been investigated and a procedure has been developed for the quantitative determination of Ir(III) and Rh(III).

A Beckman model DU-2 spectrophotometer was used for absorbance measurements. Optically matched quartz cells with 10 mm path length were used in the studies.

The reagent was prepared and crystallized as reported¹⁰.

Stock solutions of Rh(III) and Ir(III) were prepared by dissolving metal chlorides in dil. hydrochloric acid. The solutions were standardized by the usual methods¹¹. Working solutions of suitable concentration were obtained by diluting the stock solutions.

All the other reagents used were of the reagent grade.

Sodium acetate-acetic acid buffer was used to maintain the pH of the system.

Procedure used — To a suitable aliquot of metal ion solution [10 to 70 μg of Rh(III), 50 to 125 μg of Ir(III)], 10 ml of acetate buffer of pH 5.5 were added. The volume was made up to 20 ml with distilled water. PTT solution in acetone (10 ml, 0.05%) was added and contents heated on a boiling water-bath (30 min for rhodium system and one hr for iridium system). Contents were cooled and volume of the aqueous phase made up to 20 ml with distilled water. The orange-red coloured complex solution was transferred to a separating funnel and solution equilibrated with 10 ml chloroform for one min. The organic layer was separated and absorbance measured against reagent blank at 435 and 425 nm for rhodium and iridium systems respectively. The quantity of rhodium and iridium in an unknown solution was estimated from the calibration curves drawn under identical conditions.

Extraction behaviour — The extraction behaviour of Rh-PTT and Ir-PTT complexes as a function of pH was studied and it was found that the extraction is quantitative between pH 5.2 and 5.5. Sodium acetate-acetic acid buffer is most suitable to maintain the pH at 5.5. Use of other buffers or acids does not prove to be satisfactory. The complexation in rhodium system occurs on heating the contents for 30 min. In iridium system, complexation occurs in cold also, but the rate of reaction is very slow. The rate increases on heating and Ir-PTT reaction is complete in one hr. Chloroform is found to be the best solvent for extraction. When other solvents such as carbon tetrachloride, benzene, toluene and ethyl acetate are used, absorbance is found to be less. The complexes are very stable as is evident from absorbance studies. Absorbance remains constant even after four hr of standing.

Physicochemical characteristics of the complexes — The complexes are orange-red in colour and show constant absorbance in the pH range 5.2-5.5. The values of sensitivity (Sandell's) and molar absorptivity (litre mole⁻¹ cm⁻¹) for Rh-PTT system ($\lambda_{\max} = 435$ nm) are 0.0072 $\mu\text{g}/\text{cm}^2$ and 1.42×10^4 respectively while for Ir-PTT system ($\lambda_{\max} = 425$ nm) the corresponding values are 0.017 $\mu\text{g}/\text{cm}^2$ and 1.11×10^4 respectively. Optimum reagent concentration for both the complexes is 10 ml of 0.05% solution of PTT in acetone. For Rh system, Beer's law is followed in the range of 0.5-7.0 $\mu\text{g}/\text{ml}$ and the optimum range for accurate determination as determined by Ringbom plot is 1.26-6.31 $\mu\text{g}/\text{ml}$. For Ir system, these values are 2.5-12.5 $\mu\text{g}/\text{ml}$ and 5.01-12.5 $\mu\text{g}/\text{ml}$ respectively.

Effect of diverse ions — The effect of various anions and cations was investigated in detail. Sulphate, EDTA, Co(II), Ni(II), Cu(II) and Fe(II) interfere seriously. Rhodium, however, can be estimated in the presence of Co(II), Ni(II) and Cu(II). Other platinum metals also interfere in the determination. The results obtained for other ions are given in Table 1.

Determination of rhodium in the presence of Co(II), Ni(II) and Cu(II) — To a solution containing 50 μg of rhodium and 100 μg each of the above metal ions, an excess of PTT solution in acetone (50 molar excess) was added. pH was adjusted to 5.5

TABLE 1 — TOLERANCE LIMITS OF DIVERSE IONS*

Cl ⁻ (9000, 9000)	Br ⁻ (2500, 3000)	I ⁻ (1000, 1500)
NO ₂ ⁻ (2000, 1500)	NO ₃ ⁻ (10000, 10000)	F ⁻ (5000, 4500)
SCN ⁻ (1500, 2000)	SO ₃ ²⁻ (3500, 3000)	S ²⁻ (1500, 1500)
CO ₃ ²⁻ (2000, 1500)	S ₂ O ₃ ²⁻ (1000, 1000)	Oxalate ²⁻ (1500, 800)
Citrate ³⁻ (900, none)	Malonate ²⁻ (2500, 2500)	Tartrate ³⁻ (3000, 2500)
Ca ²⁺ (1500, 1000)	Mn ²⁺ (150, 50)	Zn ²⁺ (200, 150)
Sr ²⁺ (none, 1500)	Sn ²⁺ (500, 100)	Ba ²⁺ (3000, 2500)
Ga ³⁺ (1000, 850)	Y ³⁺ (1500, 2000)	In ³⁺ (200, 150)
La ³⁺ (3000, 2500)	Ti ³⁺ (500, 700)	As ³⁺ (400, 150)
Sb ³⁺ (500, 200)	Th ⁴⁺ (1500, none)	

*Values are in μg , first value in the parentheses refers to rhodium and the second to iridium.

with acetate buffer and the mixture allowed to stand for 45 min (to allow for complete complexation of Ni(II) and Co(II) with PTT). Cu(II) under these conditions forms a red coloured solid complex with PTT which is separated by filtration. To the resulting solution, 10 ml of chloroform was added and Ni(II) and Co(II) complexes were completely extracted while rhodium remained in aqueous phase. To this phase 10 ml of PTT (0.05%) in acetone was added and the mixture heated on a boiling water-bath for about 30-40 min. After cooling to room temperature, Rh(III) complex was extracted in 10 ml chloroform. The absorbance of the organic extract was measured at 435 nm and rhodium content was deduced from the calibration curve.

Using this procedure, 2 ppm of rhodium could be satisfactorily determined in the presence of 10 ppm each of Cu(II), Ni(II) and Co(II).

Separation and estimation of rhodium and platinum, and iridium and platinum — Platinum reacts with PTT in 0.5M HCl medium on heating to 90° for 10 min. The complex formed is extractable in chloroform and shows λ_{max} at 430 nm. Rhodium or iridium under this condition does not react with PTT. The use of this fact was made in the separation and estimation of iridium and rhodium from platinum. Mixtures containing Rh+Pt and Ir+Pt in various proportions were taken (Rh = 20-40 μg , Ir = 50-90 μg and Pt = 30-55 μg). To the sample prepared thus, 20 ml of 0.5M HCl and 5 ml of 0.05% PTT in acetone were added. The mixture was heated on a boiling water-bath for 10 min and after cooling, the orange-red coloured Pt-PTT complex was extracted in 10 ml chloroform. Its absorbance was measured at 430 nm against a reagent blank and concentration of platinum was calculated from the calibration curve. The aqueous phase left was evaporated almost to dryness. 10 ml of acetate buffer ($\text{pH} = 5.5$), 10 ml of distilled water and 10 ml of 0.05% PTT solution in acetone were added and the contents heated on a boiling water-bath for appropriate time. The Rh-PTT and Ir-PTT complexes formed were extracted in chloroform and absorbance measured at 435 and 425 nm respectively. The concentrations of metal ions present were calculated from

the calibration curves. The accuracy of measurement for the three metals is $\pm 0.7\%$.

PTT is one of the most sensitive reagents for rhodium and iridium. Rhodium can be determined in presence of other common metal ions which react with PTT in cold and can be separated by extraction or filtration. The added advantage of the reagent is the separation and estimation of rhodium and platinum and iridium and platinum in a mixture.

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TLC Separation of Some Inorganic Ions Using Nitrilotriacetic Acid-impregnated Plates

S. P. SRIVASTAVA, V. K. DUA & V. K. GUPTA

Department of Chemistry, University of Roorkee, Roorkee

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A scheme for the TLC separation of Pb(II), Zr(IV), Sn(IV), Ti(IV), Zn(II), Al(III), Tl(I), Ag(I), Cu(II), Cd(II), Hg(II) and Be(II) on silica gel G plates impregnated with NTA (nitrilotriacetic acid) has been worked out using solvent systems consisting of mixtures of 5% aq. ammonia-ethanol-acetone-acetic acid and 0.5% dithizone (in chloroform) as the visualization reagent.

A SURVEY of literature¹ shows that very little work has been done on the TLC separation of metal ions using chelate forming reagents for impregnating the plates. Recently Srivastava and Dua^{2,3} reported the separation of some inorganic ions using EDTA-impregnated plates. In the present note, a suitable scheme is described for the TLC separation of 12 metal ions using NTA (nitrilotriacetic acid)-impregnated plates.