

Spectrophotometric Determination of Ru(III) with Promethazine Hydrochloride

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Promethazine hydrochloride forms a red-coloured complex with Ru(III) in hydrochloric or sulphuric acid medium. The complex exhibits absorption maximum at 514-518 nm. An eleven-fold molar excess of the reagent is necessary for the full development of colour intensity. The sensitivity of the reaction is $0.016 \mu\text{g}/\text{cm}^2$ in hydrochloric acid medium and $0.024 \mu\text{g}/\text{cm}^2$ in sulphuric acid medium. Beer's law is valid over the concentration ranges 0.4-4.4 ppm and 0.5-11.6 ppm in hydrochloric and sulphuric acids respectively. The effects of acidity, time, order of addition of reagents, temperature, reagent concentration and diverse ions are reported. The composition of the complex as determined by molar ratio method is 1:2. The stability constant ($\log K$) of the complex is 10.02 ± 0.1 in 3M hydrochloric acid and 10.65 ± 0.1 in 1.5M sulphuric acid.

PROMETHAZINE hydrochloride (PH) was proposed as a new reagent for the spectrophotometric determination of Pd(II)¹. A survey of chemical literature showed that no attempt was made to study the reaction between PH and Ru(III). In the present investigation, the authors have studied the reaction between Ru(III) and PH and proposed PH as a sensitive reagent for the spectrophotometric determination of Ru(III).

A stock solution of ruthenium was prepared by dissolving 0.9850 g of Ru(III) chloride (M/s Johnson Matthey, London) in dilute Analar hydrochloric acid and diluted to 1 litre to give 1M with respect to the acid. It was standardized gravimetrically by the thionalide method². The stock solution was further diluted to give a standard solution of 20 $\mu\text{g}/\text{ml}$.

A 0.2% aqueous solution of PH (May & Baker) was prepared and stored in an amber-coloured bottle in a refrigerator.

Solutions of acids and diverse ions of suitable concentrations were prepared using analytical grade reagents.

Determination of Ru(III) — To an aliquot of the stock solution containing 10-290 μg of ruthenium were added 10 ml of 7.5M hydrochloric acid (or 7.5 ml of 5M sulphuric acid) and 4 ml of 0.2% PH solution and the volume made up to 25 ml by adding doubly distilled water. The solution was mixed well and the absorbance measured at 515 nm after standing for 15 min against a reagent blank prepared in the same way. The amount of ruthenium was then deduced from the standard calibration curve.

PH reacts with Ru(III) at room temperature in the presence of either hydrochloric or sulphuric acid to form a red-coloured complex. The rate of reaction and stability of the colour depend on the nature and concentration of the acid medium.

Nitric acid cannot be used as reaction medium because it oxidizes PH to a red-coloured radical. The absorption spectra of the ruthenium-PH complex exhibits maximum absorbance at 514-518 nm in both the acids. Reagent and ruthenium do not absorb around this wavelength. Maximum absorbance is achieved in the acid range 2.0-4.0M with respect to hydrochloric acid and 1.0-2.2M with respect to sulphuric acid. Below 2M HCl or 1M H₂SO₄ the development of red colour of the complex is slow. The reagent is slowly oxidized at acidities higher than 4.0M HCl or 2.2M H₂SO₄. An acid strength of 3.0M HCl or 1.5M H₂SO₄ was chosen for all subsequent work.

The ruthenium-PH complex is formed at room temperature and constant absorbance values are obtained 15 min after adding the reagent to ruthenium solution in HCl medium and immediately in sulphuric acid medium. The absorbance values remain constant for 45 min in HCl or 60 min in H₂SO₄. An eleven-fold molar excess of the reagent is required in order to obtain maximum absorbance. The optimum amount of the reagent is 4 ml of a 0.2% PH solution in a final volume of 25 ml in both acids. The absorbance readings are constant in the temperature range 10-40°. No change in the absorbance is observed when the order of addition of reactants was changed.

Beer's law is valid over the concentration ranges 0.4-4.4 ppm in HCl and 0.48-11.6 ppm in H₂SO₄. The optimum concentration range for the effective spectrophotometric determination evaluated by Ringbom's method^{3,4} is 1.2-4.2 ppm in HCl or 1.4-11.0 ppm in H₂SO₄. For A = 0.001, the sensitivity of the reaction is $0.016 \mu\text{g}/\text{cm}^2$ in HCl or $0.024 \mu\text{g}/\text{cm}^2$ in H₂SO₄. Molar absorptivities of 6.3×10^3 litre mole⁻¹ cm⁻¹ in HCl and 4.2×10^3 litre mole⁻¹ cm⁻¹ in H₂SO₄ are obtained for the ruthenium-PH complex. Sample solutions containing 100 μg of ruthenium, prepared by the standard procedure, gave a mean absorbance of 0.250 and 0.165 in HCl and H₂SO₄ respectively with a standard deviation of 0.014 and a relative error of $\pm 0.4\%$.

The effect of anions and cations which often accompany ruthenium were studied with 4 μg of ruthenium per ml in HCl or H₂SO₄ medium. An error of 2% in the absorbance was considered tolerable. The results presented in Table 1 show that the tolerance limit is higher in H₂SO₄ medium.

TABLE 1 — TOLERANCE LIMIT OF DIVERSE IONS IN THE DETERMINATION OF 4 PPM OF Ru(III)

Anion	Tolerance limit ppm		Cation	Tolerance limit ppm	
	HCl	H ₂ SO ₄		HCl	H ₂ SO ₄
Cl ⁻	8500	9500	Rh(III)	21	24
F ⁻	1240	1460	Pd(II)	0.2	0.4
Br ⁻	980	1035	Os(VIII)	0.6	0.8
I ⁻	0.4	0.6	Ir(III)	9	10
NO ₃ ⁻	900	5450	Pt(IV)	30	32
SO ₄ ²⁻	6000	6000	Fe(III)	1.5	2
PO ₄ ³⁻	1430	1470	Co(II)	90	96
CH ₃ COO ⁻	7865	8080	Ni(II)	1100	1140
EDTA	25	5800	Cu(II)	500	1235

Efforts to increase the tolerance limit of cations by the addition of masking agents were unsuccessful.

The continuous variation⁶ and slope ratio⁶ methods failed to reveal any definite composition for Ru(III)-PH complex owing to the masking of yellow colour of ruthenium at relatively low range of reagent concentration. However, the molar ratio method⁷ shows a sharp break at the ruthenium to reagent ratio of 1:2 in the presence of HCl or H₂SO₄. The apparent stability constant (log *K*) of the complex in 3*M* HCl and in 1.5*M* H₂SO₄ at 27° ± 1°C as evaluated by molar ratio method⁷ is 10.02 ± 0.1 and 10.65 ± 0.1 respectively.

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Spectrophotometric Determination of Ru(III) with Trifluoperazine Dihydrochloride

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A spectrophotometric method has been devised for the determination of microgram amounts of Ru(III) utilizing the reaction between trifluoperazine dihydrochloride and ruthenium(III) in strong sulphuric or hydrochloric acid. The orange-red complex has absorption maximum at 500 nm with molar absorptivity 4.285×10^3 litre mole⁻¹ cm⁻¹. The sensitivity is 0.0233 µg Ru cm⁻² for log *I*₀/*I* = 0.001. Beer's law is valid over the concentration range 1.0-8.8 µg ruthenium ml⁻¹ and the optimum range for the effective spectrophotometric determination is 2.0-8.0 µg Ru ml⁻¹. The composition of the complex is 1:1. The influence of some common ions is reported.

A WIDE variety of chromogenic reagents employed for the spectrophotometric determination of Ru(III) have been reviewed¹⁻⁵. Unfortunately, the formation of the complexes between ruthenium and the chromogenic reagents is quite slow in aqueous media at room temperature, and conditions for obtaining reproducible colour development are usually quite empirical, i.e. heating for a specific time at a specific temperature is required.

During the investigation⁶ on the spectrophotometric determination of Pd(II) with trifluoperazine dihydrochloride (TFP), the latter was found to give an orange-red colour with Ru(III) instantaneously in the presence of sulphuric or hydrochloric acid. This has now been made the basis of a spectrophotometric method for the determination of microgram amounts of Ru(III). The proposed method offers the advantages of simplicity, reasonable

sensitivity, insensitivity to temperature and rapid determination in higher acid concentration without the need for extraction or heating.

A stock solution of ruthenium was prepared by dissolving 0.9924 g of Ru(III) chloride (M/s Johnson Matthey, London) in 500 ml of 1*M* hydrochloric acid and standardized gravimetrically by precipitating ruthenium as the hydrated oxide, followed by careful ignition in air and then reducing in hydrogen and cooling in an atmosphere of carbon dioxide.

A stock solution of TFP (Smith, Kline & French) was prepared by dissolving 0.50 g of TFP in 250 ml of doubly distilled water. This was stored in an amber-coloured bottle in a refrigerator.

All other reagents were of analytical grade and were used without further purification.

Determination of Ru(III)—To a sample solution containing 25-220 µg of Ru(III) was added sulphuric acid so that the final solution was 1.5*M* in sulphuric acid. 5 ml of 0.2% TFP was added and the solution diluted to 25 ml by adding doubly distilled water. The solution was mixed thoroughly and the absorbance measured at 500 nm against a corresponding reagent blank. The Ru(III) concentration of the sample solution was then deduced from the standard calibration curve.

A detailed investigation of Ru-TFP complex has shown that TFP forms an orange-red coloured complex instantaneously in the presence of sulphuric or hydrochloric acid (*pH* 0.0-3.5). The maximum colour development takes place at room temperature and requires no heating. The sensitivity of the reaction and the stability of the orange-red complex depend on the nature and strength of the acid medium. The sensitivity in four acid media is in the order of HCl > H₂SO₄ > H₃PO₄ > AcOH. The maximum colour development takes place immediately in hydrochloric or sulphuric acid medium and after 10 min in phosphoric or acetic acid medium after mixing the reagents. The orange-red complex is stable in 1.5*M* H₂SO₄, HCl, AcOH and H₃PO₄ for 40, 15, 10 and 5 min respectively. Hence the sulphuric acid medium has been selected. Nitric acid medium cannot be used as it oxidizes TFP to a red-coloured radical.

The absorbance of the complex remains constant in 0.2-2.0*M* H₂SO₄. At higher acid concentrations (>3.0*M*) the reagent slowly undergoes oxidation to a red-coloured radical.

It was found that a nineteen-fold molar excess of the reagent was necessary in order to assure complete complexation. The orange-red complex exhibits absorption maximum at 500 nm at which point the reagent does not absorb. The absorbance values remained constant for 40 min and were insensitive to temperature in the range 5-60°C. The order of addition of reagents was not critical.

Beer's law was obeyed in the concentration range 1.0-8.8 µg Ru(III) ml⁻¹. The optimum concentration range evaluated by Ringbom method^{7,8} was 2.0-8.0 µg Ru(III) ml⁻¹. The molar absorptivity is 4.285×10^3 litre mole⁻¹ cm⁻¹ and the Sandell sensitivity index is 0.0233 µg Ru(III) cm⁻².

Composition and nature of the complex—The composition of the complex was studied by Job's method^{9,10} of continuous variation using equimolar