

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.

References

1. SANKE GOWDA, H. & KESHAVAN, B., *Indian J. Chem.*, **14** (1976), 293.
2. BEAMISH, F. E., *The analytical chemistry of the noble metals* (Pergamon Press, London), 1966, 250.
3. RINGBOM, A., *Z. analyt. Chem.*, **115** (1938), 332.
4. AYRES, G. H., *Analyt. Chem.*, **21** (1949), 652.
5. JOB, P., *Ann. Chim.*, **9** (1928), 113.
6. HARVEY, A. E. & MANNING, D. L., *J. Am. chem. Soc.*, **72** (1950), 4488.
7. YOE, J. H. & JONES, A. L., *Ind. Engng Chem.*, **16** (1944), 111.

Spectrophotometric Determination of Ru(III) with Trifluoperazine Dihydrochloride

H. SANKE GOWDA & P. G. RAMAPPA

Postgraduate Department of Chemistry, University of Mysore
Mysore

Received 6 October 1975; accepted 11 December 1975

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

TABLE 1 — DETERMINATION OF RUTHENIUM IN SYNTHETIC MIXTURES CORRESPONDING TO URANIUM ALLOY (FUEL)

Ru(III) present ppm	U ppm	Mo ppm	Zr ppm	Pd ppm	Rh ppm	Ru(III) found ppm
0.40	19	0.5	0.02	0.01	0.01	0.40
0.80	38	1.0	0.04	0.02	0.02	0.80
1.20	57	1.5	0.06	0.03	0.03	1.19
1.60	76	2.0	0.08	0.04	0.04	1.54
2.00	95	2.5	0.10	0.05	0.05	1.89

TABLE 2 — DETERMINATION OF RUTHENIUM IN Zn-Mg ALLOY

(Av. of 5 determinations)

Zinc added mg	Magnesium added mg	Ru(III) (μg)	
		Added	Found
30	—	4.00	4.00
—	30	4.00	4.00
15	15	4.00	3.99
15	15	2.00	2.00

solutions and mole ratio method¹¹. Both the methods indicate the formation of 1:1 complex between the metal and the reagent. The orange-red solution of Ru-TFP was passed through Dowex 50W-X8 cation exchange resin and Dowex 1-X8 anion exchange resin. The orange-red solution passed through the anion exchange resin but the orange-red colour was retained on the cation exchange resin. This indicated that the complex was cationic.

Effect of diverse ions — The following amounts ($\mu\text{g ml}^{-1}$) of foreign ions were found to give less than 3% error in the determination of 4 μg of Ru ml^{-1} : $\text{UO}_2(\text{II})$ 800; Ni(II) 1600; Cu(II) 300; Co(II) 100; Fe(III) 8; Pt(IV) 6; Rh(III) 6; Os(VIII) 4; Zn(II) 1000; Mg(II) 1000; Zr(IV) 100; Mo(VI) 50; chloride 2000; fluoride 2000; bromide 2000; iodide 25; sulphate 2000; acetate 2000; nitrate 800; EDTA 1200. Thiosulphate, thiourea, Pd(II), Au(III), Ag(I), V(V) and Ce(IV) were found to interfere at all concentrations.

Analysis of synthetic samples — Fuel for the initial core loading of the Experimental Breeder Reactor-II (EBR-II) is an alloy of 95% uranium, 2.5% molybdenum, 2.0% ruthenium and smaller amounts of zirconium, palladium and rhodium. In one phase of the processing system devised for EBR-II, molten zinc and zinc-magnesium alloy are used as solvents in the separation of uranium from ruthenium and other fission products. Hence the analysis of uranium fuel and zinc-magnesium alloy is of great importance. Synthetic mixtures containing the metals corresponding to (1) the uranium alloy (fuel) and (2) zinc-magnesium alloy were prepared and ruthenium content was determined. The results of analyses of synthetic mixtures are given in Tables 1 and 2.

References

1. BEAMISH, F. E. & VAN LOON, J. C., *Recent advances in the analytical chemistry of the noble metals* (Pergamon Press, Oxford), 1972, 306.

2. BEAMISH, F. E., *Analytical chemistry of the noble metals* (Pergamon Press, Oxford), 1966, 366.
3. BOLTZ, D. F. & MELLON, M. G., *Analyt. Chem.*, **46** (1974), 234R; **44** (1972), 300R; **42** (1970), 152R; **40** (1968), 255R; **38** (1966), 317R.
4. BEAMISH, F. E. & MCBRYDE, W. A. E., *Analyt. chim. Acta*, **9** (1953), 349; **18** (1958), 551.
5. BEAMISH, F. E., *Talanta*, **12** (1965), 789.
6. SANKE GOWDA, H. & RAMAPPA, P. G., *J. Indian chem. Soc.*, **52** (1975), 1123.
7. RINGBOM, A., *Z. analyt. Chem.*, **115** (1938), 332.
8. AYRES, G. H., *Analyt. Chem.*, **21** (1949), 652.
9. JOB, P., *Ann. Chim.*, **9** (1928), 113.
10. IRVING, H. & PIERCE, T. B., *J. chem. Soc.*, (1959), 2565.
11. YOE, J. H. & JONES, A. L., *Ind. Engng Chem.*, **16** (1944), 111.

N-Substituted Phenothiazines as Reagents for the Spectrophotometric Determination of Traces of Au(III)

H. SANKE GOWDA & K. N. THIMMAIAH

Postgraduate Department of Chemistry, University of Mysore
Mysore

Received 5 November 1975; accepted 26 December 1975

Triflupromazine hydrochloride, promethazine hydrochloride and mepazine hydrochloride form coloured compounds with gold(III) in hydrochloric acid medium. Absorption maxima and molar absorptivities of these coloured compounds are: for triflupromazine hydrochloride 503 nm, 1.303×10^4 ; for promethazine hydrochloride 517 nm, 1.609×10^4 ; and for mepazine hydrochloride 514 nm, 2.184×10^4 litre mole⁻¹ cm⁻¹. The first two N-substituted phenothiazines give full development of colour intensity in hydrochloric acid media ranging from 2.0-4.0M and 2.5-4.0M respectively and the third one in an aqueous solution in the pH range 1.8-2.1. Beer's law is valid over the concentration range 0.32-14.22 ppm of Au for triflupromazine hydrochloride, 0.20-11.90 ppm of Au for promethazine hydrochloride and 0.24-12.64 ppm of Au for mepazine hydrochloride.

SANKE GOWDA *et al.*¹ proposed promethazine hydrochloride (PH) as redox indicator for vanadometry. Cavatorta² used the reaction of PH with palladous chloride for the colorimetric determination of PH. The present paper describes triflupromazine hydrochloride (TPH), PH and mepazine hydrochloride (MH) as new sensitive reagents for the spectrophotometric determination of Au(III).

A stock solution of gold was prepared from Au(III) chloride (Baird & Tatlock, London) in doubly distilled water and standardized gravimetrically³.

Aqueous 0.2% solutions of TPH, PH and MH were prepared and stored in amber-coloured bottles in a refrigerator.

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

Procedure for the determination of Au(III): With TPH — To an aliquot of gold solution containing 8.0-35.0 μg were added 7.5 ml of 10M hydrochloric acid and 3 ml of 0.2% TPH. The solution was diluted to 25 ml with doubly distilled water, mixed thoroughly and the absorbance measured at 503 nm against a corresponding reagent blank prepared