April, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 59, 1223—1227 (1986)*

Spectrophotometric Determination of Micro-Amounts of Ruthenium(III) and Platinum(IV) with Acenaphthenequinone Mono(thiosemicarbazone)

Shailendra Kumar Singh, Rakesh Kumar Sharma, and Sharwan Kumar Sindhwani*
Department of Chemistry, University of Delhi, Delhi-110007, India

(Received February 19, 1985)

Ruthenium(III) and platinum(IV) form 1:2 (metal:ligand) complexes with acenaphthenequinone mono(thiosemicarbazone) (AQTS). The complexes are soluble in 70% *N,N*-dimethylformamide (DMF). The reagent has been used for the spectrophotometric determination of Ru(III) and Pt(IV). The optimum ranges of concentration for the determination of Ru(III) and Pt(IV) are 2.02—7.09 and 2.83—11.6 ppm over the pH range 5.3—6.8 and 1.9—4.1, respectively. The Sandell sensitivities for the determination of Ru(III) and Pt(IV) are 0.01 and 0.016 μg cm^{-2}, respectively. The determination has also been carried out in the presence of foreign ions.

When the solution of acenaphthenequinone mono (thiosemicarbazone) was added to Ru(III) or Pt(IV) solution, a yellowish green or yellowish orange colored complex was formed. The present study was undertaken to investigate the possibility of the use of AQTS as a reagent for spectrophotometric determination of ruthenium or platinum. Optimum conditions for maximum color development, composition of the complex and possibility of determination of ruthenium(III) or platinum(IV) alone or in the presence of diverse ions have also been investigated. Further, attempts to increase the selectivity by the use of masking agents have been made. To ascertain the selectivity of the reagent the method was successfully used for the determination in alloys.

Experimental

Reagents and Apparatus. Preparation of acenaphthenequinone mono(thiosemicarbazone) (AQTS) has been reported earlier.[1] The 3.2×10^{-3}M (1M=1 mol dm^{-3}) solution of AQTS was prepared in *N, N*-dimethylformamide.

In the pH range 3.42—5.89, walpole buffers[2] prepared by mixing 0.2 M acetic acid and 0.2 M sodium acetate in various proportions, were used. Below and above these pH values, dilute solutions of acetic acid, hydrochloric acid, or sodium hydroxide were added for pH variations.

Standard Ruthenium(III) Solution. A required amount of ruthenium(III) chloride (Johnson Matthey, London) was dissolved in doubly distilled water, containing sufficient hydrochloric acid to give the final concentration of 1M HCl. Since the ruthenium(III) has a tendency to burn dark brown on keeping due to oxidation, the stock solution was obtained by refluxing for 3—5 h with hydrochloric acid and ethanol. The ruthenium content was determined gravimetrically by precipitating ruthenium as the hydrated oxide, followed by careful ignition in the air. The oxide was reduced to the metal in the presence of hydrogen and by cooling in an atmosphere of carbon dioxide. Subsequent dilutions were made from the stock solution according to requirements. In no case, the solutions older than 10 d were used.

Standard Platinum(IV) Solution. One gram of grade I platinum thermocouple wire (99.99%) was dissolved in aqua regia. The resultant solution was evaporated almost to dryness and a small amount of hydrochloric acid was added. The solution was again evaporated to dryness. This treatment was repeated 3 or 4 times in order to distroy any nitroso complexes. After the final evaporation, 5 cm^3 of hydrochloric acid was added and the solution was made upto 100 cm^3 with doubly distilled water. More dilute solutions, as required, were prepared by diluting the stock solution. Two standard platinum solutions prepared by exactly the same procedure were found to give the same spectrophotometric readings.

Reagent grade chemicals were used in the study of interferences. Doubly distilled water was used throughout the work. A Unicam, SP 600, spectrophotometer, with a tungsten filament lamp and matched glass cells of 10-mm light path, were used for absorbance measurements. An ECIL expanded scale pH-meter, PH821A, was used for pH adjustment.

Absorption Spectra and Effect of pH. Both ruthenium and platinum show maximum absorption at 655 and 515 nm, respectively (Figs. 1 and 2). Subsequent studies have carried out at these wavelengths. A plot of absorbance vs. pH shows that the absrobances remain constant in the pH range 5.3—6.8 and 1.9—4.1 for Ru(III) and Pt(IV), respectively. Further studies have been carried out at pH 6.1 and 2.8 for ruthenium and platinum, respectively.

Rate of Color Development and Stability of the Complexes. The rate of reaction between metal and AQTS is slow at room temperature. The color intensity was found to increase when the solutions containing a fixed amount of Ru(III) or Pt(IV) and excess of reagents were heated on a water bath for various intervals of time and absorbance was measured at 655 or 515 nm for Ru or Pt, respectively. Results of this study show that complete complex formation takes place on heating the contents for about 2.5 h and 40 min for ruthenium and platinum, respectively.

Effect of DMF Concentration. The complexes were found to be soluble in *N, N*-dimethylformamide. Increasing volumes of DMF added it was observed that complete dissolution of precipitate takes place in 70% DMF medium. Higher percentage of DMF had no effect on the absorbance. In subsequent work, the percentage of DMF was maintained at 70.

Effect of Reagent Concentration. A plot of absorbance vs. moles of ligand shows that at least five and seven times molar excess of the reagent is required for maximum complex formation for ruthenium and platinum, respectively (Figs. 3 and 4). In further studies ten times molar excess of the reagent was used for both metals.

Adherence to Beer's Law, Optimum Range and Sensitivity. Beer's law is obeyed upto 9.39 and 13.58 ppm (1 ppm=

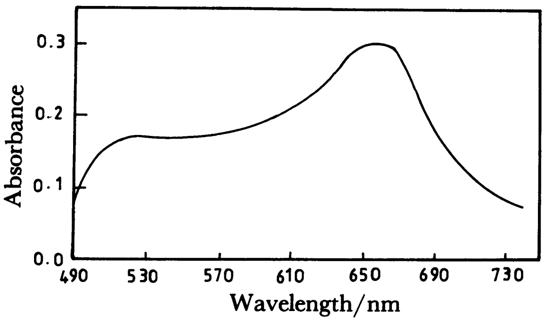

Fig. 1. Absorption spectra of ruthenium(III) complex vs. reagent.
Ru(III): 3.2X10^{-5} M, AQTS: 3.2X10^{-4} M, pH: 5.9.

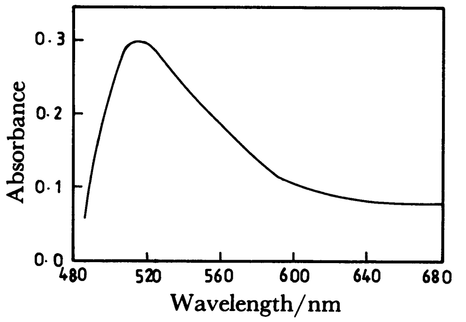

Fig. 2. Absorption spectra of platinum(IV) complex vs. reagent.
Pt(IV): 2.5X10^{-5} M, AQTS: 2.5X10^{-4} M, pH: 2.7.

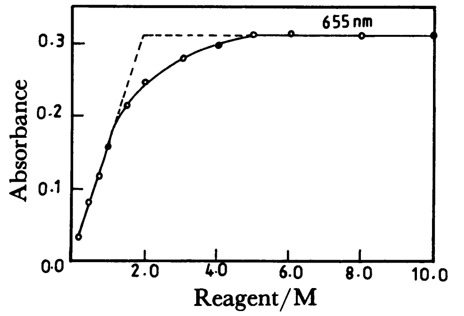

Fig. 3. Effect of reagent concentration.
Ru(III): 3.2X10^{-5} M.

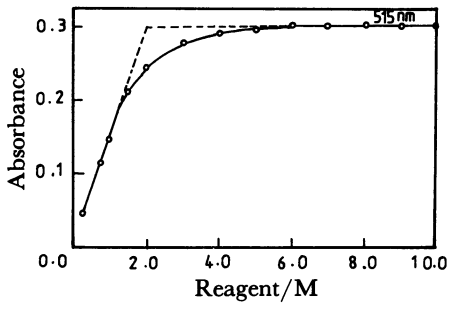

Fig. 4. Effect of reagent concentration.
Pt(IV): 2.5X10^{-5} M.

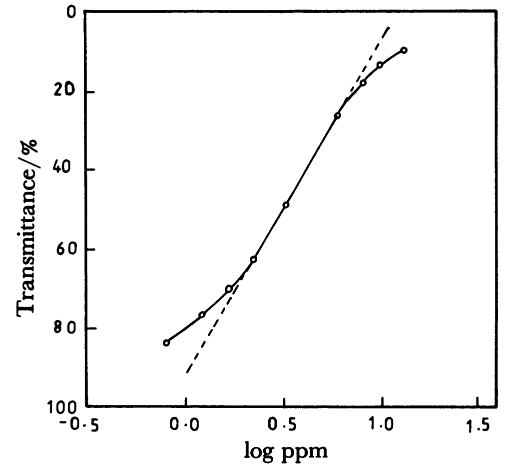

Fig. 5. Ringbom plot for Ru(III)-AQTS complex.

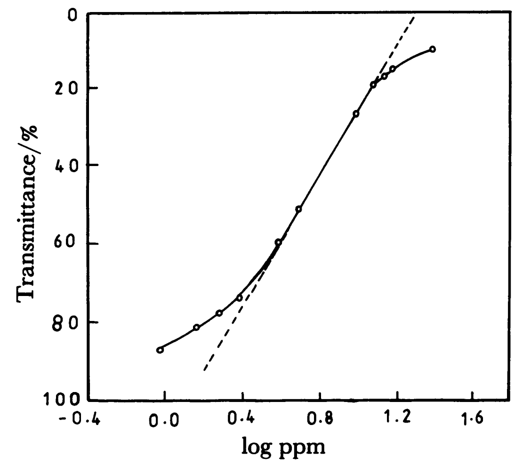

Fig. 6. Ringbom plot for Pt(IV)-AQTS complex.

1 μg cm^{-1}) while the optimum concentration ranges for accurate determination, as deduced from Ringbom plot (Figs. 5 and 6), are 2.01—7.09 ppm and 2.83—11.6 ppm for ruthenium and platinum, respectively. The sensitivity in terms of Sandell's definition is 0.01 μg Ru/cm^2 and 0.01 μg Pt/cm^2 for log I_0/I=0.001 with molar absorptivity 9843.9 and 12000 mol^{-1} cm^2, respectively.

Recommended Procedure. To a suitable aliquot containing 50.25—177.25 μg of Ru(III) or 70.8—290 μg of Pt(IV) is added to ten times molar excess of reagent. The pH is adjusted between 5.3—6.8 for ruthenium and 1.9—4.1 for platinum with acetate buffer and dilute solution of sodium hydroxide. The mixture is heated on a boiling water-bath for 2.5 h and 40 min respectively for ruthenium and platinum, and it is cooled to room temperature (30±0.5 °C). The total volume is raised to 25 cm^3 with doubly distilled water, keeping 70% *N,N*-dimethylformamide concentration. The absorbance of the solution is measured at 655 nm for ruthenium and 515 nm for platinum against reagent blank prepared under similar conditions. The amount of ruthenium and platinum is deduced from the calibration curve.

Molar Composition of the Complexes. The composition of the complexes were determined by Job's method of continuous variations[3,4] (Figs. 7 and 8) and mole ratio method[5] (Figs. 3 and 4). Both of these methods show that the stoichiometric ratio of metal to AQTS in the (Ru: AQTS) and (Pt: AQTS) complex is 1:2.

Absorbance Deviations. The precision of the procedure was checked by measuring absorbance of eight samples, each

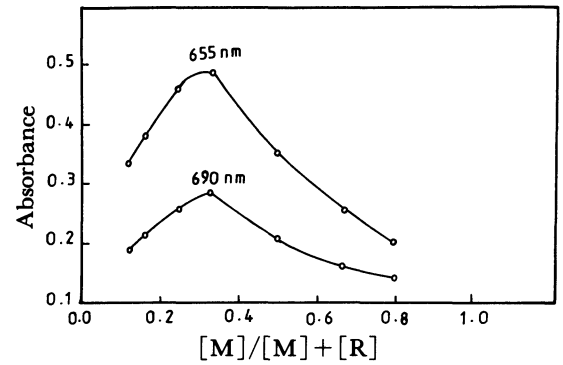

Fig. 7. Composition of Ru(III)-AQTS complex by Job's method.
Total molarity: 2.4×10^{-4} M.

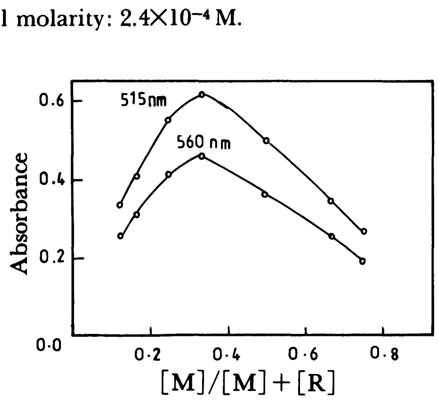

Fig. 8. Composition of Pt(IV)-AQTS complex by Job's method.
Total molarity: 3.2×10^{-4} M.

containing 3.37 ppm of ruthenium. The average relative deviation was found to be 0.33% with standard deviation of 3.6×10^{-3}. In case of platinum eight samples each containing 4.89 ppm of platinum gave average relative deviation 0.53% with standard deviation of 4.18×10^{-3}.

Effect of Diverse Ions. The effect of diverse ions was studied in the determination of ruthenium and platinum following the recommended procedure. The amounts (in ppm) of ions which do not cause any interference with 3.37 ppm of ruthenium(III) are summarized in Table 1. However nitrite, copper(II) and rhodium(III) interfere seriously.

Platinum(IV) has been determined in synthetic solution, each containing 4.89 ppm of platinum and varying amounts of foreign ions. The amounts of different ions tolerated are shown in Table 2. Among anions, iodide and thiourea interfere seriously and among cations copper(II), rhodium(III) and palladium(II) could not be masked. Masking agents were used wherever necessary.

Table 1. Effect of Diverse Ions in the Determination of Ruthenium(III)
Ruthenium Taken=3.37 ppm

Diverse ion added	Amount tolerated (in ppm)	Diverse ion added	Amount tolerated (in ppm)
Chloride	550	Calcium(II)	65
Bromide	350	Barium(II)	65
Nitrate	350	Magnesium(II)	65
Sulfate	350	Iron(II)[a]	15
Iodide	250	Cobalt(II)[b]	2
Oxalate	250	Nickel(II)[b]	4
Fluoride	40	Silver(I)[c]	15
Tartrate	40	Zinc(II)[b]	2
Cyanide	40	Cadmium(II)[b]	2
Borate	150	Osmium(VIII)[b]	5
Phosphate	80	Iridium(III)[d]	10
Thiocyanate	300	Platinum(IV)[e]	4
EDTA	30	Manganese(II)	15
Thiosulfate	25	Uranyl(II)	65
		Aluminium(III)	5
		Vanadium(V)	5
		Lead(II)[e]	5

a) Masked with phosphate. b) Masked with cyanide. c) Masked with chloride. d) Masked with thiocyanate. e) Masked with iodide.

Table 2. Effect of Diverse Ions in the Determination of Platinum(IV)
Platinum Taken=4.89 ppm

Diverse ion added	Amount tolerated (in ppm)	Diverse ion added	Amount tolerated (in ppm)
Chloride	700	Magnesium(II)	100
Bromide	700	Calcium(II)	100
Fluoride	700	Strontium(II)	100
Nitrate	600	Barium(II)	100
Nitrite	40	Iron(II)	20
Borate	55	Cobalt(II)	5
Thiosulfate	50	Mercury(II)	20
Tartrate	250	Nickel(II)	20
Phosphate	250	Silver(I)[a]	50
EDTA	100	Zinc(II)	40
Thiocyanate	40	Cadmium(II)	40
Citrate	175	Tungsten(IV)	80
Oxalate	30	Ruthenium(III)	6
Sulfite	200	Osmium(VIII)[b]	2
		Iridium(III)[c]	5
		Tin(II)	20
		Vanadium(V)	50
		Manganese(II)	20
		Uranyl(II)	80
		Aluminium(III)	60

a) Masked with chloride. b) Masked with cyanide. c) Masked with thiocyanate.

Discussion

Many organic reagents have been employed for the spectrophotometric determination of ruthenium(III) and platinum(IV), but most of them lack in selectivity or sensitivity or both, and there are objectionable interferences from many of the bases and noble metals. The most sensitive method yet reported is a catalytic method,[6] but this method is lengthy and offers no special advantage over others except for its sensitivity. Thiocyanate,[7] 2,4,6-tri(2-pyridyl)-1,3,5-triazine,[8] and 2,3-diaminopyridine[9] have been suggested for the determination of ruthenium, but they require controlled parameters and the selectivity of these methods is not very high. Thiocyanate method has the disadvantage that the determination of ruthenium

Table 3. Comparison of the Sensitivities of Reagents for Ru and Pt Determination

Reagent	Sensitivity µg Ru/cm^2	Reagent	Sensitivity µg Pt/cm^2
Anthranilic acid	0.024/620 nm	*N*,*N*-Dimethyl-*p*-nitrosoaniline	0.0029/525 nm
4-Hydroxy-2*H*-1-benzopyran-2-one oxime	0.014/520 nm	Anthranilic acid	0.068/500 nm
		Tin(II) chloride	0.024/405 nm
Dithiooxamide	0.020/630 nm 0.010/650 nm	Thiotropolone	0.012/600 nm
N,*N*-Dimethyl-*p*-nitrosoaniline	0.0028/610 nm	4-Hydroxy-2*H*-1-benzopyran-2-one oxime	0.138/490 nm
2,3-Diaminopyridine	0.0084/572 nm	Acenaphthenequinone monoxime	0.021/390 nm
		Benzil α-monoxime	0.29/440 nm
Thiocyanate/CCl$_4$	0.0071/590 nm	Acenaphthenequinone mono(thiosemicarbazone) (Present method)	0.016/515 nm
Acetylacetone	2.5/505 nm		
1,4-Diphenylthiosemicarbazide	0.010/565 nm		
Acenaphthenequinone mono(thiosemicarbazone) (Present method)	0.01/655 nm		

Table 4. Determination of Pt(IV) in Synthetic Solutions

Mixture	Pt taken	Metal ion added/ppm		Pt found	Error/%
	ppm	Ni	W	ppm	
Pt–Ni alloy	(I) 6.0	4.0		5.97	−0.50
	(II) 4.5	5.5		4.48	−0.44
	(III) 3.0	2.0		3.01	+0.33
Pt–W alloy	(I) 2.0		0.09	2.00	0.00
	(II) 3.0		0.14	3.00	0.00
	(III) 5.0		0.23	5.02	+0.40

has to be carried out after the extraction of its tetraoxide in carbon tetrachloride. Oxidation of ruthenium to tetraoxide is a critical step in this method. 4-Hydroxy-2*H*-1-benzopyran-2-one oxime[10] has low sensitivity. 4-Hydroxyimino-4-phenyl-2-butanone[11] has low sensitivity (0.018 µg cm^{-2}/470 nm) and iron, platinum, and palladium interfere. 4-Hydroxyimino-2-pentanone,[12] phenothiazine,[13] and 2-thiophenecarbaldehyde oxime[14] methods have low sensitivity. As for the 3-(4-dimethylaminophenyl)-3-hydroxy-1-phenyltriazene[15] method, pH range is narrow (7.7—7.8). Tin(II) chloride[16] method is not selective, Pd(II), Rh(III), Ir(IV), Fe(III), Cu(II), Co(II), and SO_4^{2-}, NO_3^-, PO_4^{3-} interfere seriously. In furil α-dioxime[17] method other platinum metals and iron interfere.

For the determination of platinum with *N*,*N*-dimethyl-*p*-nitrosoaniline,[18] time of heating, pH changes and amount of buffer used are critical factors. Most of the associated metals interfere. Potassium iodide[18] is a useful reagent for platinum but it is less selective. Anthranilic acid[19] is not sensitive and large amount of reagent result in decrease of absorbance. In *o*-phenylenediamine[18] associated base metals and platinum metals interfere and also the complex is stable only for 1 h. In case of 4-hydroxy-2*H*-1-benzopyran-2-one oxime,[20] sensitivity is poor. Os, Pd, and Ru must be removed initially in 3,4-diaminobenzoic acid.[21]

The present method, using acenaphthenequinone mono(thiosemicarbazone) involves simple technique. The method is quite sensitive and the complexes formed are stable for many hours. Other factors such as heating time, pH, effect of buffer, and amount of reagent do not have any effect on the absorbance. Most of the associated metals do not interfere. The sensitivity is comparable (Table 3) with other methods known for the purpose.

Determination of Platinum in Synthetic Mixtures. To ascertain the selectivity of the reagent the method was successfully used for the determination of platinum in alloys. Analyzed sample of platinum–nickel and platinum–tungsten alloy were not available. Synthetic solutions similar to these alloys of platinum were prepared and the amount of platinum was determined following the recommended procedure. The results are summarised in Table 4.

One of the authors (S. K. Singh) thanks the University Grants Commission, New Delhi, for financial assistance.

References

1) P. T. Sah Peter and T. C. Daniels, *Rec. Trav. Chim. Pays-Bas*, **69**, 1545 (1950).

2) H. T. S. Briton, "Hydrogen Ions," Chapman and Hall Ltd., London (1955), Vol. 1, p. 357.

3) P. Job, *Ann. Chim.*, **9**, 113 (1928).

4) H. Irving and T. B. Pierce, *J. Chem. Soc.*, **1959**, 2565.

5) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Anal. Ed.*, **16**, 111 (1944).

6) C. Surasiti and E. B. Sandell, *Anal. Chim. Acta*, **22**, 261 (1960).

7) F. E. Beamish, "Analytical Chemistry of Platinum

Metals," Pergamon, London (1966), p. 366.

8) W. A. Embry and G. H. Ayres, *Anal. Chem.*, **40**, 1499 (1968).

9) G. H. Ayres and D. T. Eastes, *Anal. Chim. Acta*, **44**, 67 (1969).

10) G. S. Manku, A. N. Bhat, and B. D. Jain, *Talanta*, **14**, 1229 (1967).

11) B. J. Desai and V. M. Shinde, *Z. Anal. Chem.*, **295**, 412 (1979).

12) V. V. Yeole and V. M. Shinde, *Z. Anal. Chem.*, **286**, 251 (1977).

13) B. Keshavan and H. Sanke Gowda, *Indian J. Chem.*, **17**, 315 (1979).

14) N. M. Pradhan and D. N. Patkar, *Natl. Acad. Sci. Lett.*, **3**, 83 (1980).

15) D. N. Purohit, Nizamuddin, and J. S. Noriega Rodriguez, *Z. Anal. Chem.*, **298**, 160 (1979).

16) E. Halmos and A. Vizi, *Mogy. Kem. Foly.*, **88**, 238 (1982).

17) V. I. Lazareva and A. I. Lazarev, *Zavod. Lab.*, **49**, 11 (1983).

18) F. E. Beamish, *Talanta*, **12**, 743 (1965).

19) A. K. Majumdar and J. G. Sengupta, *Z. Anal. Chem.*, **177**, 265 (1960).

20) G. S. Manku, A. N. Bhat, and B. D. Jain, *Talanta*, **16**, 1421 (1969).

21) C. D. Johnson and G. H. Ayres, *Anal. Chem.*, **38**, 1218 (1966).