
CHAPTER - VI

SPECTROPHOTOMETRIC SIMULTANEOUS DETERMINATIONS OF RUTHENIUM (III) AND OSMIUM (VIII)

6.1 INTRODUCTION

The molecular absorption spectroscopy for the simultaneous determinations in binary or ternary systems has been used mainly because of the absorption bands in visible region are broad and hence overlapping. The problems of analyses of binary and ternary systems such as alloys and mixed oxides are attaining increasing importance in analytical chemistry. Therefore, it is interesting to investigate the systems where there will be perfect additivity of spectral properties to develop methods of simultaneous determinations.

The author has investigated the possibility of 2-benzoyl pyridine guanylhydrazone (BPG) as a reagent for the spectrophotometric simultaneous determinations of Ruthenium(III) and Osmium(VIII).

Separate estimation of ruthenium and osmium is well developed and various reagents have been used for the photometric determination of individual element. But very little work appears to have been done on the simultaneous determination of these elements.

Systematic studies of the complexes of ruthenium and osmium¹ in chloride, nitrate, sulphate and perchlorate media have been carried out. Sensitive flotation spectrophotometric methods for the determination of both ruthenium and osmium metals were presented by Balserzak².

This chapter describes a spectrophotometric method for simultaneous determinations of Ru(III) and Os(VIII) by using the reagent BPG.

6.2 EXPERIMENTAL

6.2.1 Standard Solutions :

Standard ruthenium(III) solution :

As described in chapter four.

Standard osmium(VIII) solution :

As described in chapter five.

Reagent (BPG) solution :

0.6 mg/ml in distilled ethyl alcohol ($2.5 \times 10^{-3} \text{M}$).

Buffer solution :

Buffer solution of pH 4.0 was prepared by dissolving appropriate amounts of citric acid and disodium hydrogen phosphate.

Potassium thiocyanate solution :

4.0 % KCNS in distilled water.

6.2.2 Recommended Procedure :

An aliquot of the solution containing upto 200 μg of ruthenium(III) and 137 μg of osmium(VIII) was taken in 10 ml volumetric flask. To this, 3.8 ml of $2.5 \times 10^{-3} \text{M}$ reagent (BPG) and 1.9 ml of 4.0 % potassium thiocyanate solution were added. The pH of the solution was adjusted to 4.0. The solution was then diluted to the mark with distilled water. The absorbances of Ru(III) and Os(VIII) complexes were measured at 520 nm and 435 nm respectively and were substituted in the simultaneous equations developed on the basis of spectral measurements.

6.3 RESULTS AND DISCUSSION

6.3.1 Spectral Characteristics :

Figure 6.1 shows the absorption spectra of Ru(III)-BPG complex, Os(III)-BPG complex and the mixture of Ru(III)-BPG and Os(III)-BPG

complexes. The reagent does not absorb in the visible region. The observations are given in table 6.1.

Table 6.1 : Absorption spectra of Ru(III)-BPG complex, Os (III)-BPG complex and the mixture of Ru(III)-BPG and Os (III)-BPG complexes.

Wavelength, λ , nm	Absorbances		
	Ru(III)-BPG complex 2.0×10^{-4} M	Os (III)-BPG complex 7.2×10^{-5} M	Mixture of Ru(III)-BPG and Os (III)-BPG complexes
400	0.340	0.380	0.720
410	0.360	0.400	0.760
420	0.390	0.455	0.840
430	0.410	0.512	0.920
435	0.420	0.537	0.957
440	0.430	0.525	0.960
450	0.440	0.475	0.910
460	0.445	0.450	0.895
470	0.460	0.437	0.897
480	0.480	0.412	0.892
490	0.500	0.375	0.875
500	0.520	0.330	0.850
510	0.525	0.287	0.812
520	0.530	0.250	0.780
530	0.510	0.215	0.725
540	0.490	0.175	0.665
550	0.460	0.150	0.610
560	0.410	0.125	0.535
580	0.330	0.070	0.400
600	0.260	0.025	0.285
620	0.195	0.015	0.210
640	0.150	0.010	0.160
660	0.130	0.005	0.135
680	0.120	0.003	0.123
700	0.090	0.002	0.092

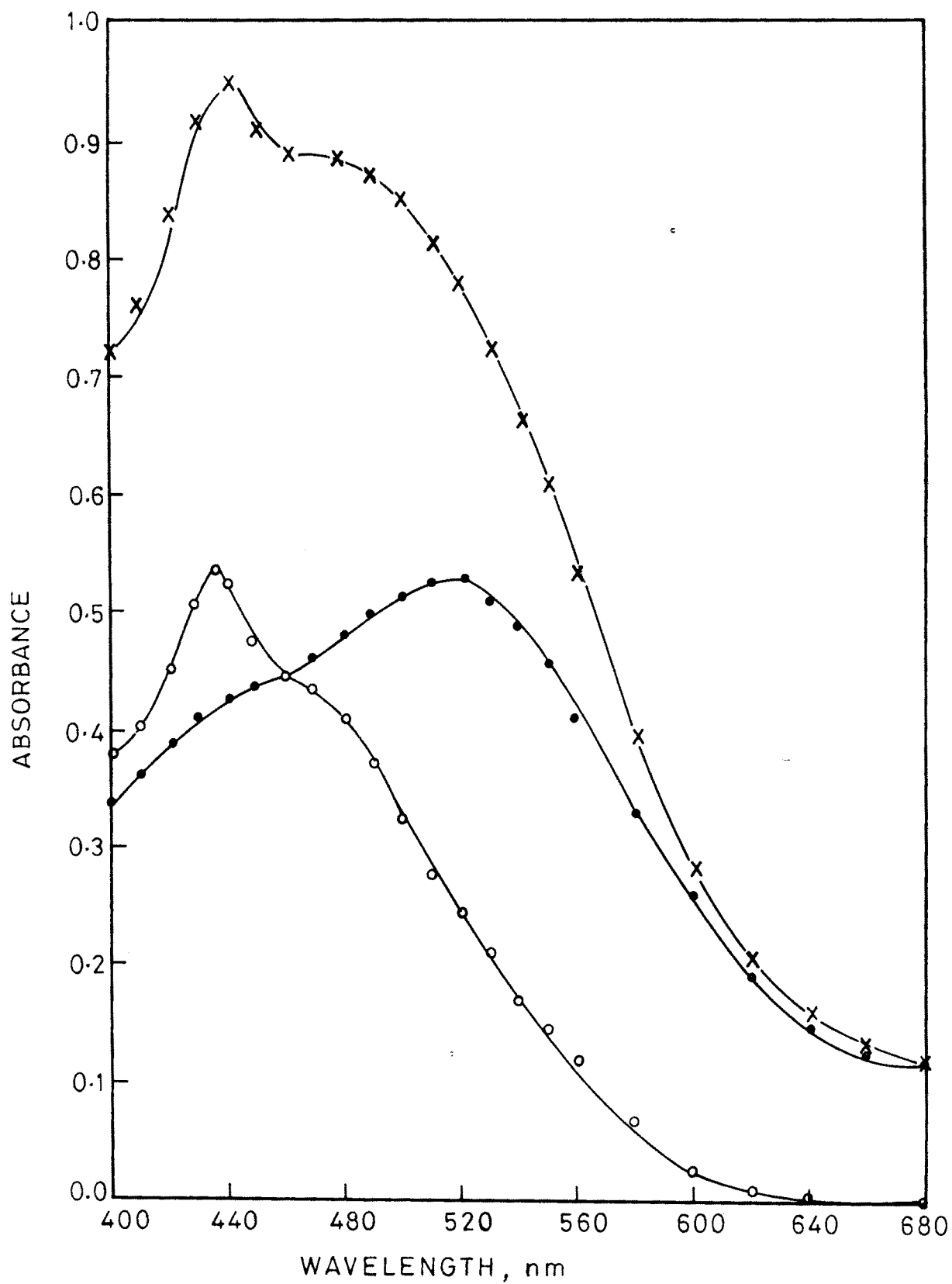


FIG.6.1 — ABSORPTION SPECTRA OF

- OSMIUM (III) — BPG COMPLEX (7.2×10^{-4} M).
- RUTHENIUM (III) — BPG COMPLEX (2.0×10^{-3} M).
- x—x MIXTURE OF OSMIUM (III) — BPG AND RUTHENIUM (III) — BPG COMPLEXES.

The method for the simultaneous determination is developed on the basis of -

- 1) well separated absorption maxima of the complexes,
- 2) sufficiently high values of extinction coefficients of the complexes,
- 3) no absorption by the reagent in the visible region,
- 4) stability of the complexes of the two metals at pH 4.0 and
- 5) additivities of the absorbances of the complexes.

Table 6.2 summarises the spectral characteristics of Ru(III) and Os (III) complexes of BPG.

Table 6.2 : Spectral characteristics of the complexes

Complex	λ_{\max} , nm	Molar extinction coefficient, ϵ		Colour
		520 nm	435 nm	
Ru(III)	520	0.265×10^4 $1 \text{ mole}^{-1} \text{cm}^{-1}$	0.210×10^4 $1 \text{ mole}^{-1} \text{cm}^{-1}$	Reddish violet
Os (III)	435	0.1388×10^4 $1 \text{ mole}^{-1} \text{cm}^{-1}$	0.2986×10^4 $1 \text{ mole}^{-1} \text{cm}^{-1}$	Yellowish orange

Equations (1) and (2) are used to develop the equations (3) and (4).

$$(1) \quad A_{520} = \epsilon_{520}^{\text{Ru}} \times [\text{Ru}] + \epsilon_{520}^{\text{Os}} \times [\text{Os}]$$

$$(2) \quad A_{435} = \epsilon_{435}^{\text{Ru}} \times [\text{Ru}] + \epsilon_{435}^{\text{Os}} \times [\text{Os}]$$

$$(3) \quad A_{520} = 0.2650 \times 10^4 [\text{Ru}] + 0.1388 \times 10^4 [\text{Os}]$$

$$(4) \quad A_{435} = 0.2100 \times 10^4 [\text{Ru}] + 0.2986 \times 10^4 [\text{Os}]$$

Equations (3) and (4) are used to develop the equations (5) and (6) which are used for the simultaneous determinations of the two constituent elements.

$$(5) \quad [\text{Ru}] \times 10^4 = 5.974 A_{520} - 2.777 A_{435}$$

$$(6) \quad [\text{Os}] \times 10^4 = 5.302 A_{435} - 4.201 A_{520}$$

where

A_{520} - Absorbance of the mixture at 520 nm.

A_{435} - Absorbance of the mixture at 435 nm.

$[\text{Ru}]$ - Molar concentration of ruthenium.

$[\text{Os}]$ - Molar concentration of osmium.

6.4 APPLICATIONS

6.4.1 Determination of Ruthenium(III) and Osmium(VIII) in Alloys :

Solutions of alloys containing ruthenium and osmium were prepared. Suitable aliquots were taken and analysed as per recommended procedure. The results are summarised in table 6.3.

Table 6.3 : Analyses of Ru + Os alloys

Sample	Composition of the alloy	Weight of the sample in mg	Expected, mg		Found, mg	
			Ru(III)	Os(VIII)	Ru(III)	Os(VIII)
A	75% Ru 25% Os	16.0	12.0	4.0	11.98	4.03
B	60% Ru 40% Os	10.0	6.0	4.0	6.03	3.96
C	50% Ru 50% Os	8.0	4.0	4.0	4.04	3.98

6.4.2 Determination of Ruthenium(III) and Osmium(VIII) in SyntheticMixtures :

Several synthetic mixtures were prepared and analysed in triplicate. The results of analyses are summarised in table 6.4.

Table 6.4 : Simultaneous determination of Ruthenium(III) and Osmium(VIII) in synthetic mixtures.

Sample	Ru(III)/Os(VIII) ratio	Amount taken, ppm		Amount found, ppm	
		Ru(III)	Os(VIII)	Ru(III)	Os(VIII)
1	0.25	1.00	4.00	0.98	4.03
2	0.50	2.00	4.00	2.02	3.98
3	0.75	3.00	4.00	3.04	4.02
4	1.00	4.00	4.00	3.97	4.01

6.5 REFERENCES

1. Balcerzak, M.; P.R. Nauk. Politech. Warsz, Chem., 55, 3 (1991).
2. Balcerzak, M.; Analis ; 20(6), 295 (1992).