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Spectrophotometric Determination of Ruthenium(III) and Rhodium(III) with 9,10-Phenanthrenequinone Monoxime after Extraction into Molten Naphthalene

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9,10-Phenanthrenequinone monoxime has been used as a reagent for the spectrophotometric determination of ruthenium(III) and rhodium(III) after extraction into molten naphthalene. The extracted mixture of the metal complex and naphthalene was dissolved in chloroform and ruthenium and rhodium were determined spectrophotometrically. Beer's law holds in the concentration range of 0.2—4.1 μg/cm³ for ruthenium and 0.3—5.3 μg/cm³ for rhodium in 10 cm³ of the final solution. The molar absorptivities and Sandell sensitivities are calculated to be 9.70×10^3 l mol^{-1} cm^{-1} and 0.01 μg/cm² (660 nm) for ruthenium and 1.13×10^4 l mol^{-1} cm^{-1} and 0.009 μg/cm² (410 nm) for rhodium respectively. Aliquots containing 2.0 μg of ruthenium and 4.1 μg of rhodium give mean absorbances of 0.192 and 0.451 with standard deviations of 0.0017 and 0.0039, respectively. Interference of various ions has been studied and the method has been applied to the determination of ruthenium and rhodium in various synthetic mixtures. This procedure is also applied to the simultaneous determination of ruthenium and rhodium present together in a solution.

9,10-Phenanthrenequinone monoxime has been suggested as a possible analytical reagent by Trikha and Kamil in the spectrophotometric[1-3] and gravimetric[4] determination of some metals. Since both these metals form complexes with the reagent at a high temperature, ordinary liquid-liquid extraction is not applicable. Liquid-liquid extraction no doubt is a convenient technique for the separation and determination of metal ions, but it fails in the extraction of those metal ions which form complexes with the complexing agents at a high temperature or the solubility of their complexes is low at room temperature. In such cases, the metal complex is first precipitated at a high temperature and then extracted into a suitable organic solvent after cooling to room temperature.[5] Thus the method becomes time consuming. Fujinaga and co-workers have developed a method of extraction, *i.e.* "solid-liquid separation after liquid-liquid extraction" in which all the above mentioned difficulties are overcome.[6] The advantages of this technique over the liquid-liquid extraction have already been stated in a previous communication.[7] In the present work this technique has been applied to the extraction of ruthenium and rhodium with 9,10-phenanthrenequinone monoxime into molten naphthalene and their subsequent determination by spectrophotometric method after dissolution of the solid naphthalene containing the metal complex in chloroform. Interference of various ions has been studied and this method has been applied to the determination of these metals in various synthetic mixtures. Conditions have also been developed for the simultaneous determination of these metals in synthetic mixture since these metal complexes absorb at two different wavelengths.

Experimental

Reagents. 9,10-Phenanthrenequinone monoxime (molecular weight: 223) was prepared and purified according to the method given in the literature,[3] and its 0.001 M solution (1 M=1 mol dm^{-3}) was prepared in ethanol. Solutions of ruthenium(III) chloride and rhodium(III) chloride were prepared from samples (1 g ampule) in 1 M hydrochloric acid and standardized gravimetrically.[7] Buffer solution of sodium acetate (0.2 M)–acetic acid (0.2 M) of pH 5.2 was used for pH adjustment. Naphthalene and chloroform were of analytical reagent grade and tested spectrophotometrically before use. To study the interference of various ions, 5000 μg/cm³ of anion and 100 μg/cm³ of metal ion solutions were prepared in redistilled water.

Equipment. An Elico pH meter and Sp-700/500 spectrophotometer were used for measurements.

General Procedure. To an aliquot of each of the metal solution taken separately was added 1.0 cm³ of the reagent and the pH was adjusted with 2.0 cm³ of buffer solutions (Fig. 2). These solutions were transferred to stoppered round-bottomed flasks and 2.0 g of naphthalene was added to each. Temperature was raised to about 85—90 °C to melt naphthalene and the mixture was stirred vigorously with a magnetic stirrer-hot plate arrangement for 35 min for both the metals (Fig. 3). Naphthalene containing the metal complex was separated by filtration. If was dried in the folds of a filter paper and then dissolved in 10 cm³ of chloroform. This solution was dried with anhydrous sodium sulfate (2.0 g) and the absorbance was measured in a 1-cm cell at 660 nm for ruthenium and 410 nm for rhodium against a reagent blank. The calibration curves were constructed under similar conditions.

Results and Discussion

Absorption Spectra. The absorption spectra of 9,10-phenanthrenequinone monoxime and its ruthenium and rhodium complexes were recorded in naphthalene–chloroform solution against weter and reagent blank, respectively (Fig. 1). It was observed that both the complexes have two absorption peaks, *i.e.* 520—535 nm and 660 nm for ruthenium and 400—410 nm and 470—480 nm for rhodium. The reagent absorbed only slightly at 410 nm, while it absorbed negligibly at the other wavelengths. The simultaneous determination of ruthenium and rhodium is possible because of a large difference of their λ_{max} (Fig. 1). All the measurements were made at 660 nm for ruthenium and at 410 nm for rhodium.

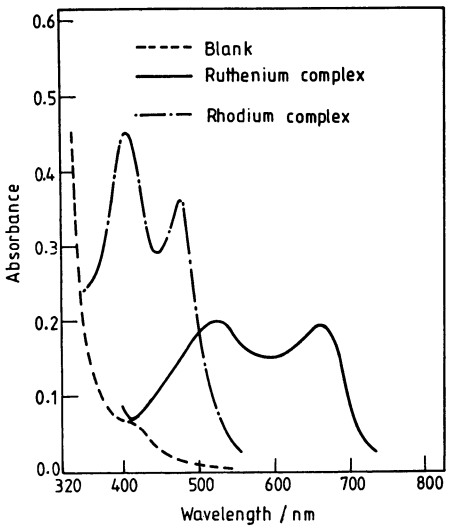

Fig. 1. Absorption spectra.
Reagent blank, 9-10 phenanthrenequinone monoxime (0.001 M): 1.0 cm³. Reference: water; Ru: 2.0 μg, pH: 5.2, Rh: 4.1 μg, pH: 5.2, reference: reagent blank. Naphthalene 2.0 g, chloroform: 10.0 cm³.

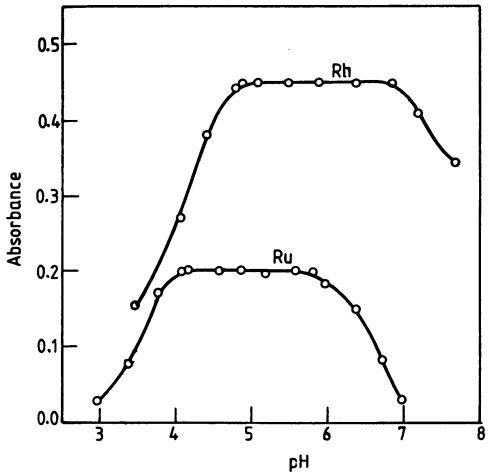

Fig. 2. Effect of pH.
Acetate concentration 1 M: 2.0 cm³. Ru: 2.0 μg, wavelength: 660 nm, Rh: 4.1 μg, wavelength: 410 nm, 9,10-phenanthrenequinone monoxime (0.001 M): 1.0 cm³, naphthalene: 2.0 g, chloroform: 10.0 cm³. Stirring time: 35 min, reference: reagent blank.

Effect of pH. Extraction behaviours of these metal-9,10-phenanthrenequinone monoximates were studied over a wide range of pH. Ruthenium was quantitatively extracted over the pH range of 4.1—5.8 and rhodium between 4.9—6.8. Extraction was incomplete beyond these pH ranges (Fig. 2).

Effect of Buffer Concentration. Extraction was carried out by varying the volume of 0.2 M sodium acetate–0.2 M acetic acid buffer (pH 5.2). It was observed that it has no effect on absorbance when the volume was varied between 1.0—5.0 cm³ per 30 cm³ of aqueous solution. Thus 2.0 cm³ of the buffer solution was used for subsequent studies.

Effect of Reagent Concentration. Extraction was carried out at optimum pH and at varying volumes of

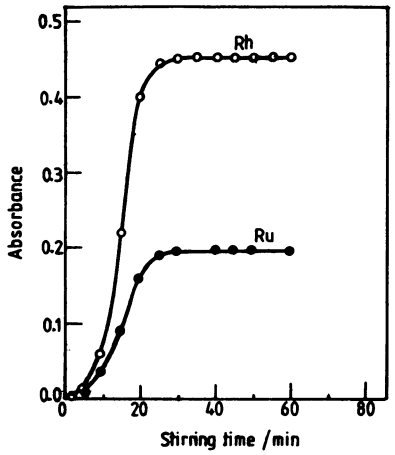

Fig. 3. Effect of stirring time.
Conditions were same as in Fig. 2.

0.001 M reagent solution. It was found to be quantitative in the volume range of 0.1—3.0 cm³ for ruthenium and 0.3—3.0 cm³ for rhodium. Thus 1.0 cm³ was used for further studies.

Effect of Amount of Naphthalene. Extraction was carried out by varying the amounts of naphthalene from 0.2—4.0 g at optimum pH and keeping other parameters constant. With both metals the absorbance remained constant when the amount of naphthalene used was in the range of 1.3—3.5 g. The extraction was not complete with less than 1.3 g while above 3.5 g of naphthalene it was difficult to dissolve it in the limited quantity of chloroform (10 cm³). Thus 2.0 g of naphthalene was selected for further work.

Effect of Aqueous Phase Volume. Since the amount of naphthalene is small (2.0 g) as compared to that of the aqueous phase the effect of the volume of the latter on extraction was studied. Extraction was quantitative when the aqueous phase did not exceed 60 cm³.

Effect of Stirring Time. Since ruthenium and rhodium form complexes with reagent at a high temperature,[7] the effect of stirring time on extraction was examined. A mixture of naphthalene and the complex was stirred at different intervals of time with a magnetic stirrer-hot plate arrangement at 85—90 °C. It was found that the extraction was complete when the mixture was stirred for more than 30 min at this temperature in each case. (Fig. 3).

Effect of Standing Time. Absorbance of the extract in naphthalene–chloroform was constant for at least 24 h for ruthenium and 48 h for rhodium.

Effect of Electrolytes. Various electrolytes such as sodium chloride, sodium acetate, potassium chloride, and sodium nitrate (0.3—3.0 cm³ of 1.0 M) caused no improvement in extraction, indicating that the extraction was complete in the presence or in the absence of these electrolytes showing the absence of salting effect.

Composition of the Complex. The nature of ruthenium and rhodium-9,10-phenanthrenequinone monoximates in naphthalene–chloroform solution was studied by Job's method of continuous variation and mole-ratio method. This suggested that $[Ru^{II}(C_{14}H_8O_2N)_2]$ and $[Rh^{III}(C_{14}H_8O_2N)_3]$ complexes were

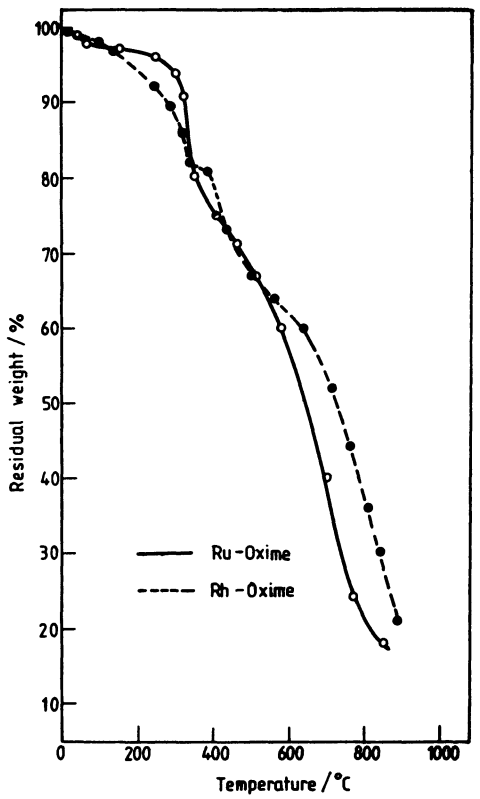

Fig. 4. Typical thermograms of the complexes. Complex (Ru or Rh): 5 mg; atmosphere: air: 20 cm³/min, heating rate: 10 °C/min.

extracted into molten naphthalene being the same as in liquid-liquid extraction.[8] It was reported by Trikha[8] that the elemental analysis of the complexes gave Ru: 18.5%, N : 5.10% corresponding to Ru : 18.54% N : 5.16% and Rh: 13.35%, N : 5.40% corresponding to Rh : 13.38%, N: 5.46 K, which also supports the above composition. Magnetic susceptibility of the isolated ruthenium and rhodium complexes have been determined by the Guoy procedure. It was found to be diamagnetic indicating it to be a spin paired square-planar ruthenium complex whereas the rhodium complex was found to be diamagnetic and thus a spin-paired octahedral complex. The infrared shows C=O and C=N stretching frequencies at 1600 and 1525 cm^{-1} in the free ligand. In the metal chelates these modes were observed at 1585 and 1520 cm^{-1} for ruthenium and 1580 and 1520 cm^{-1} for rhodium respectively. This further corroborates the composition stated above.

Thermal Stability of the Complex. The thermal stability of the complexes was determined by thermogravimetric analysis (TGA) by plotting the percentage residual weight against temperature (Fig. 4). The decomposition curve showed some plateaus which were indicative of constant weight representing stable phase over the particular temperature range (Experiment was performed on a Stanton Red-Croft TG-750 thermobalance in a air atmosphere at a heating rate of 10 °C/min). Successive plateaus probably correspond to the decomposition of water (100 °C), metal complex followed by the metal oxide. From the plot it was found that ruthenium and rhodium complexes indeed are thermally stable but the former decomposes at 270 °C while the latter at 360 °C.

Beer's Law and Sensitivity. Under the optimum conditions described above, calibration curves were constructed at 660 nm for ruthenium and 410 nm for rhodium. Beer's law was obeyed in the concentration range of 0.2—4.1 μg of ruthenium and 0.3—5.3 μg of rhodium in 10 cm³ of the chloroform solution. The

Table 1. Effect of diverse anions
Ru: 2.0 μg, Rh: 4.1 μg

Alkali salt added	Anion added (μg/cm³)	Absorbance λ/nm Ru 660 nm	Rh 410 nm
—	—	0.192	0.450
Sodium fluoride	5000	0.195	0.451
Sodium chloride	5000	0.195	0.450
Potassium bromide	5000	0.195	0.448
	3000	0.192	0.451
Potassium iodide	5000	0.200	0.456
	3000	0.193	0.450
Sodium acetate	5000	0.192	0.450
Potassium thiocyanate	5000	0.150	0.438
	2000	0.180	0.445
	1000	0.191	0.450
Sodium citrate	5000	0.145	0.440
	3000	0.184	0.450
	2000	0.192	0.450
Potassium sodium tartrate	5000	0.185	0.440
	3000	0.190	0.446
	1000	0.192	0.450
Sodium nitrite	5000	0.160	0.420
	3000	0.181	0.448
	2000	0.190	0.446
	1000	0.192	0.450
Sodium nitrate	5000	0.191	0.440
	3000	0.193	0.451
Sodium sulfate	5000	0.191	0.445
	3000	0.193	0.450
Sodium oxalate	5000	0.140	0.400
	3000	0.165	0.434
	2000	0.182	0.440
	1000	0.190	0.449
Sodium orthophosphate	5000	0.150	0.380
	3000	0.165	0.410
	2000	0.178	0.435
	1000	0.191	0.448
EDTA(disodium)	5000	0.100	0.148
	3000	0.120	0.185
	2000	0.125	0.190
	1000	0.138	0.318
	200	0.158	0.438
	100	0.191	0.448

Table 2. Effect of diverse cations

Ru: 2.0 μg, Rh: 4.1 μg

Metal salt added	Metal ion added (μg/cm³)	Absorbance λ/nm		Remarks
		Ru 660 nm	Rh 410 nm	
—	—	0.192	0.450	—
Ammonium vanadate	100	0.194	0.462	—
	50	0.193	0.453	—
Chromium(III) chloride	100	0.192	0.510	—
	50	0.192	0.454	—
Iron(III) chloride	100	0.193	0.452	Removed by pre-extraction at room temperature
Cobalt(II) chloride	100	0.193	0.454	Removed by pre-extraction at room temperature
Nickel(II) chloride	100	0.194	0.452	Removed by pre-extraction at room temperature
Copper(II) acetate	100	0.193	0.453	Removed by pre-extraction at room temperature
Ammonium molybdate	100	0.191	0.454	—
Ruthenium(III) chloride	100	—	0.480	—
	50	—	0.460	—
	30	—	0.454	—
Rhodium(III) chloride	100	0.210	—	—
	50	0.200	—	—
	30	0.193	—	—
Palladium(II) nitrate	100	0.192	0.451	Removed by pre-extraction at room temperature
Silver(I) nitrate	100	0.192	0.472	—
	50	0.193	0.454	—
Osmium(III) oxide	100	0.193	0.452	Removed by pre-extraction at room temperature
Iridium(III) chloride	100	0.194	0.650	Masked with 100 μg of EDTA
	50	0.193	0.466	Masked with 100 μg of EDTA
	30	0.192	0.452	Masked with 100 μg of EDTA
Platinum(IV) chloride	100	0.194	0.455	—
	50	0.192	0.450	—
Gold(III) chloride	100	0.194	0.460	—
	50	0.192	0.450	—
Mercury(II) nitrate	100	0.194	0.454	—
	50	0.192	0.450	—
Lead(II) nitrate	100	0.194	0.451	—
Bismuth(III) nitrate	100	0.191	0.448	—
Uranyl acetate	100	0.192	0.452	—

Table 3. Determination of ruthenium in synthetic mixture

Composition of the synthetic mixture (μg)	Ruthenium taken (μg)	Ruthenium found (μg)	Average (μg)	Error/%
Ru^{III}: 10, Ir^{III}: 45, Os^{VIII}: 45	2.5	2.4, 2.5, 2.5, 2.6, 2.4	2.48	+0.80
Ru^{III}: 5, Ir^{III}: 40, Os^{VIII}: 45, Au^{III}: 10	3.5	3.5, 3.5, 3.4, 3.5, 3.4	3.46	+1.10

Table 4. Determination of rhodium in synthetic mixture

Composition of the synthetic mixture (μg)	Rhodium taken (μg)	Rhodium found (μg)	Average (μg)	Error/%
Rh^{III}: 5, Pt^{IV}: 95	2.5	2.5, 2.6, 2.5, 2.5, 2.5	2.52	−0.80
Rh^{III}: 30, Au^{III}: 50, Pt^{IV}: 20	3.5	3.4, 3.5, 3.5, 3.5, 3.5	3.48	+0.57

Table 5. Simultaneous determination of ruthenium and rhodium in synthetic mixture

Composition of the synthetic mixture (μg)	Ru and Rh taken (μg)	Ru and Rh found (μg)	Average (μg)	Error/%
Ru^{III}: 2.5, Rh^{III}: 5.0	Ru: 2.5	2.5, 2.5, 2.4, 2.5, 2.6	2.50	+0.0
Os^{VIII}: 30, Pd^{II}: 10, Au^{III}: 20, Pt^{IV}: 30.5	Rh: 5.0	5.0, 5.0, 5.0, 4.9, 5.0	4.98	+0.4

molar absorptivities and Sandell sensitivities were calculated to be 9.70×10^3 l mol^{-1} cm^{-1} and 0.01 μg/cm^2 for ruthenium and 1.13×10^4 l mol^{-1} cm^{-1} and 0.009 μg/cm^2 for rhodium. Solutions containing 2.0 μg of ruthenium and 4.1 μg of rhodium gave mean absorbances of 0.192 and 0.451 with standard deviations of 0.0017 and 0.0039 respectively.

Effect of Diverse Ions. Various ions were added individually to a solution containing 2.0 μg of ruthenium and 4.1 μg of rhodium and the general procedure was applied. Among the anions (Table 1), thiocyanate, citrate, tartrate, nitrite, oxalate, orthophosphate, and EDTA interfered with the determination of these metals but relatively low amounts could be tolerated. Of the meal ions (Table 3), interference of Fe^{III}, Co^{II}, Ni^{II} Cu^{II}, Pd^{II}, and Os^{VIII} has been eliminated by preextraction at room temperature in each case. For rhodium the interference of Ir^{III} was removed by masking with EDTA.

Determination of Ruthenium(III) and Rhodium(III) in Synthetic Mixtures. Synthetic mixtures were prepared containing both ruthenium and rhodium and aliquot of synthetic mixture was taken in a beaker, 1.0 cm^3 of ethanolic solution of the 9,10-phenanthrenequinone monoxime was added, the pH adjusted to 5.2 with acetate buffer solution and determined by the general procedure already described. The results are recorded in Tables 3 and 4.

On the basis of the absorption maximum of the complexes, these metals have been separated from each other (Fig. 1) and determined when present together. The results are summarized in Table 5.

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