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Spectrophotometric Determination of Ruthenium after Solid-Phase Extraction with 3-Hydroxy-2-methyl-1,4-naphthoquinone 4-Oxime into Microcrystalline *p*-Dichlorobenzene

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A Highly sensitive extraction method has been developed for the spectrophotometric determination of ruthenium after extraction of its 3-hydroxy-2-methyl-1,4-naphthoquinone 4-oxime (HMNQO) complex into microcrystalline *p*-dichlorobenzene. The optimum pH range for the extraction is 5.0—7.0. The solid *p*-dichlorobenzene containing the ruthenium-HMNQO complex is separated by filtration and dissolved in *N*,*N*-dimethylformamide. The absorbance is measured at 450 nm against a reagent blank. Beer's law is obeyed upto 10.1 ppm of ruthenium. The molar absorptivity and Sandell sensitivity are 2.7×10^4 dm^3 mol^{-1} cm^{-1} and 0.0037 μg cm^{-2}, respectively which is compared with the molar absorptivity and Sandell sensitivity without using solid phase extraction method (1.4×10^4 and 0.0072). The interference of various ions has been studied in detail.

A highly sensitive and selective extraction method has been developed for the metal ions which require high temperature for complex formation. Many reagents have been employed for the spectrophotometric determination of ruthenium, but all are having poor sensitivity or selectivity or both and there are objectionable interferences from other ions.[1—8] For example most sensitive known reagent for ruthenium is *N*,*N*-dimethyl-*p*-nitrosoaniline, but controlled conditions are required for full color development and also there is serious interferences by osmium and nitrate.

Present solid phase extraction method is more sensitive and simpler than *N*,*N*-dimethyl-*p*-nitrosoaniline method. The main advantages of this method are that the equilibrium distribution between the two phases is attained in a few seconds owing to the high temperature used, and the metal chelates are dissolved merely by contact with the molten phase. As the organic phase is solid at room temperature, phase separation is quantitative and can be achieved simply by filtration or decantation. The method is selective, and simple, and the complexes are stable for a long time. The sensitivity of the present method is promising and much better than other known reagents.

Experimental

Apparatus. A PC based Beckman DU-64 Spectrophotometer and an ECIL model PH5652 digital pH meter were used.

Reagents. Doubly distilled water and analytical-reagent grade chemicals were used throughout, unless stated otherwise.

Standard Ruthenium Solution. A standard solution of ruthenium(III) was prepared by dissolving ruthenium(III) chloride (Johnson Matthey, London) in doubly distilled water, containing sufficient hydrochloric acid to give a final concentration of 1 mol dm^{-3} HCl. Since these solutions have tendency to turn dark brown on keeping due to oxidation, the stock solution was obtained by refluxing for 3—5 h with HCl and ethanol. The ruthenium solution was standardised gravimetrically by precipitating ruthenium as hydrated oxide, followed by careful ignition in air and then reduction to the metal in presence of H_2 gas and cooling in an atmosphere of CO_2 gas. Subsequent dilutions were made from the stock solution according to requirements.

3-Hydroxy-2-methyl-1,4-naphthoquinone 4-Oxime (HMNQO). Preparation of HMNQO has been reported earlier by us.[9] The 1.0×10^{-2} mol dm^{-3} solution of HMNQO was prepared by dissolving 0.203 g of HMNQO in 100 cm^3 ethanol.

Sodium Acetate–Acetic Acid Buffer. 0.2 mol dm^{-3} sodium acetate solution and acetic acid were mixed in suitable proportions.

***N*,*N*-Dimethylformamide (DMF).** DMF was dried by keeping the liquid over solid potassium hydroxide for 5—6 h. The liquid was shaken frequently during this period, then filtered directly into a flask containing freshly prepared calcium oxide, refluxed for 1—2 h and distilled at atmospheric pressure under dry conditions.

***p*-Dichlorobenzene.** *p*-Dichlorobenzene was of analytical reagent grade.

General Procedure. Ruthenium(III) solution (30—290 μg) is taken in a 100 cm^3 beaker and a ten-times molar excess of the reagent solution is added. Measure the pH, adjust it, if necessary, to lie within the range 5.0—7.0 by adding sodium acetate solution or acetic acid, then add 2 cm^3 of buffer solution. Transfer the solution into a 100 cm^3 round-bottom flask and heat to 60°C in a water bath. Add 2.0 g of *p*-dichlorobenzene, stopper the flask and continue to heat until the *p*-dichlorobenzene has melted. Remove the flask from the water bath and shake it vigorously until the *p*-dichlorobenzene separates out as a solid mass. Repeat the melting and solidification procedure. Separate the *p*-dichlorobenzene from the aqueous phase by filtration through a filter paper. Dissolve the solid mass in DMF and dilute to 50 cm^3 with DMF in a calibrated flask. Dry the solution by pouring onto anhydrous sodium sulfate (2 g) in a beaker. Place a portion of this solution in a 1-cm cell and measure the absorbance at 450 nm against a reagent blank. Prepare a calibration graph under similar conditions.

Results and Discussion

Absorption Spectra. Absorption spectra of HMNQO and its ruthenium complex in *p*-dichlorobenzene–

Table 1. Comparison of Sensitivity and Molar Absorptivity with and without Using Solid-Phase Extraction Method

Molar absorptivity/$dm^{-3}\,mol^{-1}\,cm^{-1}$		Sensitivity/$\mu g\,cm^{-2}$	
Present method	In 60% ethanol (without extraction)	Present method	In60% ethanol (without extraction)
2.70×10^4	1.4×10^4	0.0037	0.0072

DMF solutions were recorded against DMF and the reagent blank, respectively. The ruthenium–HMNQO complex shows maximum absorption at 450 nm. All absorbance measurements were made at 450 nm in subsequent studies (Table 1).

Effect of pH. Extraction were carried out at different pH values, keeping the other conditions constant. The nature of the spectral curves remained constant, indicating the formation of only one species of ruthenium complex under these conditions. The extractions were quantitative in the pH range 5.0—7.0.

Effect of *p*-dichlorobenzene. The amount of *p*-dichlorobenzene was varied from 0.5 to 5.0 g. The extractions were quantitative when the amount of *p*-dichlorobenzene was in the range 1.5—5.0 g. Below 1.5 g the extraction was incomplete.

Effect of Buffer Solution. The addition of acetate buffer solution in the volume range 1.0—10.0 cm^3 caused virtually no variation in the extraction. In all the experiments, 2 cm^3 of buffer solution was used.

Effect of Shaking Time. The extraction of the complex into *p*-dichlorobenzene was found to be very rapid and no change was observed in the extent of extraction when the shaking time was varied from 1 to 15 min.

Beer's Law and Sensitivity. Beer's law is obeyed up to 10.1 ppm while the optimum concentration range for accurate determination, as determined from the Ringbom plot, is 0.6—5.8 ppm. The sensitivity of the reaction was found to be 0.0037 $\mu g\,cm^{-2}$ for log $(I_0/I)=0.001$. The corresponding molar abosrptivity is 2.7×10^4 dm^3 mol^{-1} cm^{-1}.

Effect of Foreign Ions. Synthetic solutions containing 1.01 ppm of ruthenium and various amounts of other ions were prepared and the proposed procedure for the determination of ruthenium was followed. An error of ±2% in the absorbance reading was considered to be tolerable. The amounts (in ppm) of ions that do not cause any interference are as follows: chloride, 1000; bromide, thiocyanate, thiosulfate, iodide, 500; fluoride, 800; nitrate, sulfate, sulfite, tartrate, 400; nitrite, oxalate, EDTA, 100; phosphate, 300; Ca(II), Ba(II), Hg(II), 100; Mg(II), As(III), Zn(II), Cd(II), Mn(II), 50; Al(III), 20; Cr(III), 30; Fe(II), Co(II), Ni(II), Cu(II), 20 (EDTA masking agent); Sn(II), 100 (F^- masking agent); Pd(II), Pt(IV), Ir(III), 8 ($S_2O_3{}^{2-}$ masking agent); Os(VIII), 8 (SCN^- masking agent); Ag(I), 50 (Cl^- masking agent); V(IV), 20 (F^- masking agent); U(VI), Pb(II), 20.

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