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Extraction-Spectrophotometric Determination of Osmium Using 4-(2-Pyridylazo)resorcinol

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An extraction-spectrophotometric method for the determination of trace amounts of osmium(VIII) is described. Osmium is quantitatively extracted from aqueous solutions at pH 3.0—3.5 into a 10:1 chloroform–methyl isobutyl ketone mixture with tetrabutylammonium bromide, followed by spectrophotometric determination, using 4-(2-pyridylazo)resorcinol as a metallochromic indicator. The orange-red mixed complex of osmium absorbs light at λ_{max}=530 nm with a molar absorptivity of 2.5×10^4 dm^3 mol^{-1} cm^{-1}. Beer's law is obeyed over the range 0.5—18 μg cm^{-3}. The method has a wide range and is sensitive and free from interferences from many anions and cations, including some platinum metals.

Because of the increasing use of osmium oxides as popular oxidizing agents in organic chemistry, and as effective catalysts for a wide variety of chemical reactions,[1—5] the separation and determination of osmium in trace levels are of special interest. Thiocyanate,[6,7] Bismuthiol II,[8] 9,10-phenanthrenequinone monoxime,[9] 1-(2-pyridylazo)-2-phenanthrol(II),[10] and 7-amino-1-hydroxynaphthalene-3,6-disulfonic acid[11] are among the spectrophotometric reagents used for the extraction and determination of osmium. However, there are some difficulties associated with the presence of interfering ions, especially platinum metals, which cannot be eliminated uisng the direct methods. On the other hand, although the catalytic methods seem to be more sensitive than extraction-spectrophotometric procedures, there is a need for rigid control of temperature, acidity, reagent, impurities, etc.[12,13]

4-(2-Pyridylazo)resorcinol (PAR) has also been used for the determination of osmium, but it suffers from the poor selectivity for osmium over the several commonly associated interfering ions.[14] In this paper we report a sensitive method for the selective extraction of Os(VIII) with tetrabutylammonium bromide (TBAB) from acidic aqueous solutions into a 10:1 chloroform–methyl isobutyl ketone mixture, which is followed by spectrophotometric determination of osmium in organic phase using PAR as a chromogenic indicator.

Experimental

Reagents. All of the chemicals used were of the highest purity available and were used without further purification.

Tetrabutylammonium bromide (TBAB, Merck) solution, 1.5% w/v. Prepared with triply distilled water.

Organic Phase. Prepared by mixing appropriate amounts of methyl isobutyl ketone (MIBK, Merck) and chloroform (Merck) to form a 1 to 10 v/v mixture.

Osmium Stock Solution. A 1 g sealed ampul of osmium tetraoxide (Fluka) dissolved in about 100 cm^3 of 0.20 M (1 M=1 mol dm^{-3}) sodium hydroxide solution and then diluted to 1 dm^3 with triply distilled water.[15] The solution was then standardized by the Klobbie's method[16] as follows: 15 cm^3 of 6 M sulfuric acid and 2 g of potassium iodide were added to 25 cm^3 of the solution and the liberated iodine was titrated against a 0.250 normal solution of sodium thiosulfate. The end-point was determined using starch paper externally as indicator. Working solutions were prepared by suitable dilution of the stock solution.

4-(2-Pyridylazo)resorcinol (PAR, Merck) solution, 0.1% w/v. Prepared with absolute methanol (Merck).

Potassium chloride (Merck) solution, 3.5 M. Prepared with triply distilled water.

Apparatus. All spectra were obtained with a Beckman DK-2A ratio recording spectrophotometer and the absorbance measurements were made with a Perkin-Elmer 35 spectrophotometer. The pH values were determined with a Corning 125 pH meter using a combined electrode.

Procedure. An aliquot of the sample solution containing 5—180 μg of Os(VIII) was placed in a 10-cm^3 flask. One cm^3 of 1.5% TBAB and 3 cm^3 of 3.5 M KCl solution were added and pH was adjusted between 3.0 and 3.5 with dilute HCl. The solution was diluted to the mark with triply distilled water. Next, the solution was transferred into a 60-cm^3 separatory funnel, 10 cm^3 of 1:10 MIBK–chloroform solvent was added and the mixture was shaken vigorously for 10 min. The phases were allowed to separate and the organic layer was collected in a 25-cm^3 flask. To ensure the complete extraction of osmium, the aqueous layer was treated with another 5-cm^3 protion of fresh organic solvent. To the combined organic extracts 1 cm^3 of 0.1% PAR solution and 3 cm^3 of methanol were added and the mixture was diluted to the mark with chloroform. For complete color development, the solution was heated in a thermostated water-bath at 50 °C for 2 h. The absorbance of the orange-red solution was measured at 530 nm against a reagent blank.

Results and Discussion

Absorption Spectra. The absorption spectra of the mixed complex of osmium with PAR and blank reagent are shown in Fig. 1. As it is seen, the orange-red complex shows a maximum at 530 nm with a molar absorptivity of 2.5×10^4 dm^3 mol^{-1} cm^{-1}, whereas the reagent blank shows a negligible absorbance at this wavelength.

Effect of pH. The extraction of Os(VIII) with TBAB was carried out over the pH range 0.8—12.6 and the results are given in Fig. 2. It is seen that the extraction is quantitative at pH range of about 1—4, the percent of

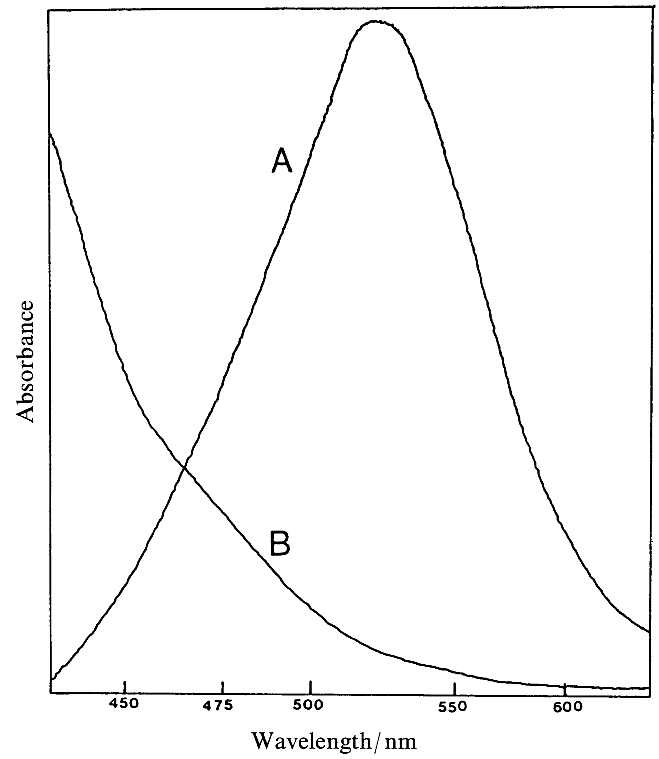

Fig. 1. Absorption spectra of the mixed complex of Os(VIII) with PAR (A) and the reagent blank (B) in organic phase.

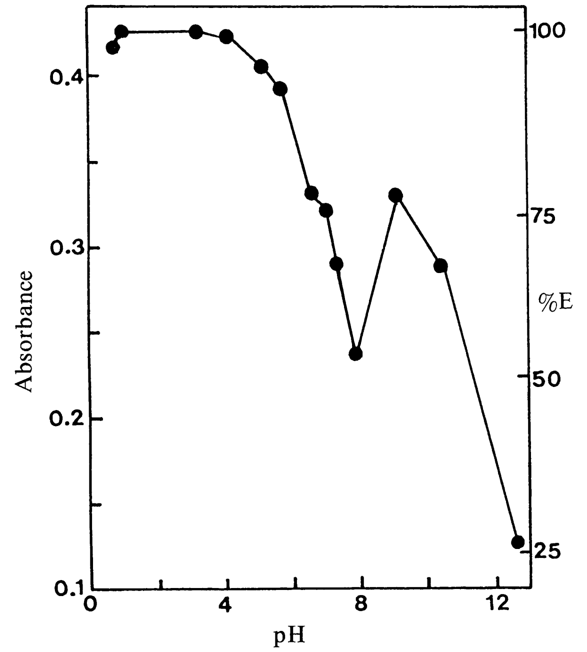

Fig. 2. Effect of pH on the extraction of Os(VIII). Conditions: Os, 10.24 μg cm^{-3}; TBAB, 3 cm^3 of 0.5% in H_2O; PAR, 1 cm^3 of 0.1% in CH_3OH; λ_{max}, 530 nm; color, orange-red.

extraction (%E) decreases drastically by an increase in pH from 4 to 12.6.

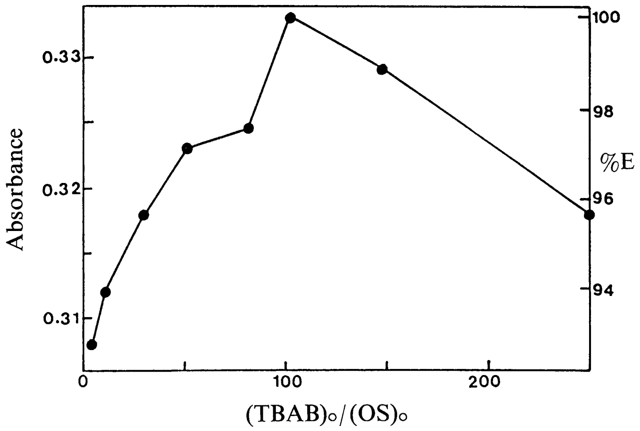

Fig. 3. Effect of TBAB concentration on the extraction of Os(VIII). Conditions: Os, 8.0 μg cm^{-3}; PAR, 1 cm^3 of 0.1% in CH_3OH; pH, 3.2; λ_{max}, 530 nm.

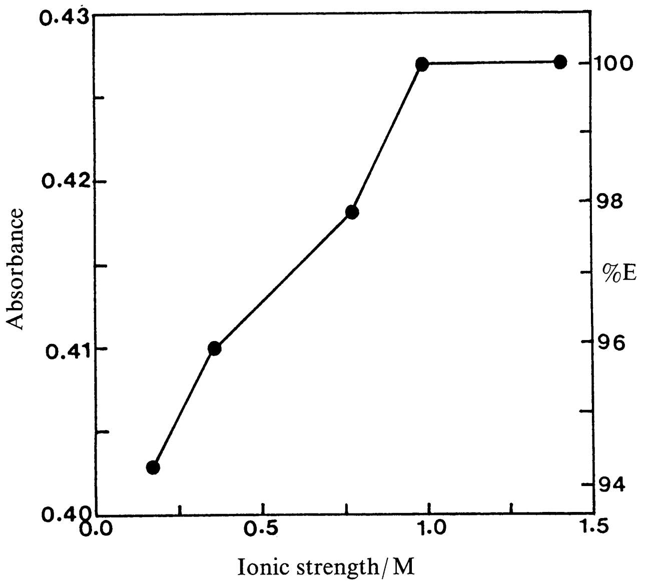

Fig. 4. Effect of ionic strength on the extraction of Os(VIII). Conditions: Os, 10.24 μg cm^{-3}, TBAB, 1 cm^3 of 0.1% in CH_3OH; pH, 3.2; λ_{max}, 530 nm.

Effect of TBAB Concentration. The influence of the TBAB concentration on the extraction of osmium is shown in Fig. 3. The extraction was found to be quantitative when the TBAB to osmium mole ratio is about 100. A further excess of TBAB would cause a decrease in %E, probably due to a change in the extent of ion pairing.

Effect of Ionic Strength. The ionic strength of aqueous solution was found to influence the extraction process (Fig. 4). There is an increase in %E with ionic strength of the solution, maintained by addition of KCl; quantitative extraction results at ionic strength 0.99 M. No change in %E was observed upon further addition of the KCl solution.

Effect of Organic Solvent. The extraction process was performed in a single stage at optimal condition with pure MIBK and pure chloroform. The amount of remaining osmium in aqueous phase was checked by the reported catalytic methods.[12,13)] It was found that the exctraction was more complete with MIBK, but the color intensity of the resulting complex with PAR was much higher in chloroform. However, a 1 : 10 MIBK–chloroform mixture was chosen in this study in which the effect of MIBK on the color intensity was negligible, while in a single stage process the %E was found to be >97.

Effect of Shaking Time. The extraction of osmium(VIII) under the conditions recommended in the procedure is rapid. A shaking time of 8—12 min was found sufficient for the complete extraction.

Effect of PAR Concentration. Addition of methanolic solution of PAR to the chloroform extract of osmium forms a turbid red adduct. In order to overcome the turbidity, absolute methanol was added to the solution until a 5 : 1 v/v ratio of chloroform to CH_3OH is reached and a completely clear solution was obtained. Studies with various concentration of PAR showed that 1.0 cm³ of a 0.1% (w/v) of PAR in methanol was adequate for the complete color development (Fig. 5). A further excess of PAR increased the absorbance of reagent blank.

Effect of Temperature and Time. The influence of temperature on the color development of osmium–PAR system was studied. There is an increase in the rate of complex formation, and hence in the color development, with temperature. However, 50 °C was chosen in the procedure because of the considerable evaporation of the solvent at higher temperatures. Measurements of absorbance against time at 50 °C showed that, a duration of about 2 h is needed for complete color development. Absorbance of the resulting colored solution was found to remain unchanged for 48 h, if it was protected from the direct sunlight.

Beer's Law Study. A calibration graph for osmium was obtained under the recommended conditions in procedure. Beer's law was obeyed over the concentration range 0.5—18 μg cm^{-3} of Os(VIII) and Sandell's sensitivity[17)] for 0.001 absorbance was 0.0076 μg cm^{-2}. The relative error (95% confidence level) for 10.24 μg cm^{-3} of osmium was ±1.3% (12 replicates).

Stoichiometry of the Complex. The ratio of osmium to PAR in the resulting complex in organic phase was studied by continuous variations method,[18)] and found to be 1 : 2.

Effect of Diverse Ions. Osmium(VIII) was extracted according to the recommended procedure in the presence of several other ions to determine the sensitivity and validity of the method. The results are shown in Table 1. An error of ±2% in the absorbance reading was considered tolerable. As it is seen, most of the common anions and cations associated with osmium did not interfere in the extraction of Os(VIII), except Ag^+, Cd^{2+}, Hg^{2+}, Zn^{2+}, and Pd^{2+}. Interferences form these cations were eliminated by either in situ masking or pre-separation using appropriate methods indicated in Table 1.

Conclusion. The method described provides a reliable means of determining trace amounts of osmium. It has a wide range and is free from interferences from many anions and cations, including some platinum

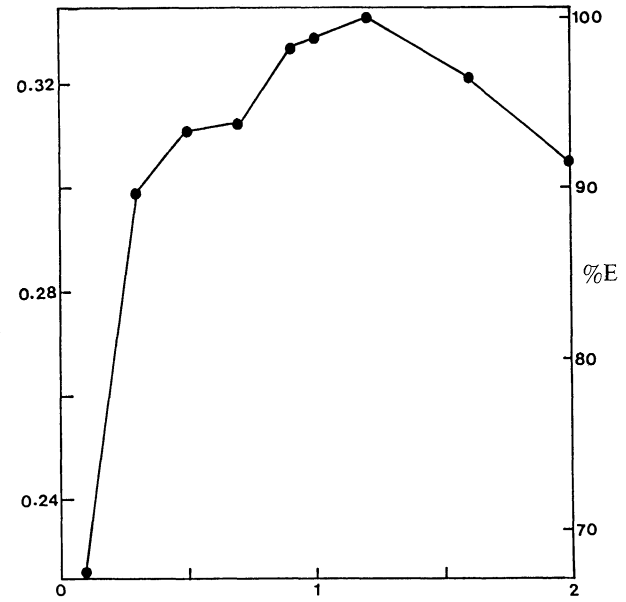

Fig. 5. Effect of PAR concentration on the absorbance of Os–PAR complex. Conditions: Os, 8.0 μg cm^{-3}; TBAB, 1 cm³ of 1.5% in H_2O; pH, 3.2; λ_{max}, 530 nm.

Table 1. Tolerance of the Os(VIII)–TBAB–PAR System to Diverse Ions. Conditions: Os, 10.24 ppm, TBAB, 1 cm³ of 1.5% in H_2O; PAR 1 cm³ of 0.1% in CH_3OH; pH, 3.2; λ_{max}, 530 nm

Foreign ion	Molar ratio	Foreign ion	Molar ratio
Ag(I)	72[a,b)]	W(VII)	300[a)]
Al(III)	1000	Zn(II)	600[c)]
Bi(III)	94[a)]	Br^-	933[a)]
Cd(II)	330[c)]	BrO_3^-	146
Co(II)	831	CH_3COO^-	63
Cr(III)	1072	Cl^-	2097[a)]
Cu(II)	614	ClO_4^-	94
Hf(III)	417[a)]	CO_3^{2-}	310[a)]
Hg(II)	100[d)]	F^-	3913[a)]
Mn(II)	39	$H_2PO_4^-$	153
Mo(VII)	465[a)]	I^-	586[a)]
Ni(II)	1260	IO_3^-	106[a)]
Pb(II)	50[a)]	NO_2^-	404
Pd(II)	17[e)]	NO_3^-	150
Pt(IV)	97[a)]	OCN^-	88
Rh(III)	723[a)]	SCN^-	128
V(V)	40	SO_4^{2-}	775[a)]

a) Above of which was not tested. b) After centrifugation and separation of the resulting precipitate with Cl^-. c) After masking with 3.0 cm³ of 0.1 M EDTA at pH=4. d) After addition of 3.0 cm³ of 10000 μg cm^{-3} of I^- and removal of the precipitate. e) Preliminary extraction with tetrabutylammonium iodide in a highly acidic media into chloroform, Ref. 19.

metals. The method compares favorably in sensitivity with most published methods for the determination of osmium by use of ion-association compounds, and it can certainly be classed among the most sensitive.

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