

## Spectrophotometric determination of osmium using molybdate and Nile blue in the presence of polyvinyl alcohol

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A sensitive spectrophotometric method for the determination of osmium(VIII) has been developed, based on the reaction of osmium(VIII) with molybdate and Nile blue (NB) to form an ion association complex in the presence of polyvinyl alcohol. The molar absorptivity at 585 nm is  $2.81 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . Beer's law is obeyed over the range 0-1.8  $\mu\text{g}$  of osmium per 25 ml. The method can also be applied for the determination of trace amounts of osmium in some catalysts and metallurgical products.

The spectrophotometric determination of zirconium<sup>1</sup>, hafnium<sup>2</sup> and gold<sup>3</sup> as the ion association complexes of the metal ion with molybdate and Nile blue in aqueous solution in the presence of polyvinyl alcohol have been reported. However, the possibility of the determination of osmium using an ion association complex of this type has not been studied so far. This note presents a detailed investigation of various factors for the spectrophotometric determination of osmium in aqueous solution, e.g., the acidity, the concentration of reagents, the effects of foreign ions and so on. The method is also applied for the determination of osmium in some catalysts and metallurgical products, with relative standard deviation of less than 5%.

### Experimental

A 721A spectrophotometer, wavelength range 360-800 nm, was employed for absorbance measurements, and a Shimadzu IR-450S (Japan) was used for infrared measurements. All reagents used were of AR grade. All solutions were prepared with doubly distilled water and kept in polyethylene bottles.

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A standard solution of osmium was prepared by dissolving 1 g of osmium tetroxide from a sealed ampoule in about 100 ml of 0.2 mol  $\text{dm}^{-3}$  sodium hydroxide solution in a glass-stoppered 1 litre volumetric flask. The solution was then diluted to volume with water and standardized iodometrically by the method of Gowda<sup>4</sup>. The working solutions were made by appropriate dilutions.

A molybdate solution (0.01 mol  $\text{dm}^{-3}$ ) was prepared by dissolving 1.0 g of ammonium heptamolybdate in 500 ml of water. Nile blue (NB) solution ( $6.9 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) was prepared by dissolving 0.5 g of Nile blue in water and diluting it to 1  $\text{dm}^3$  with water. Polyvinyl alcohol (PVA) solution (2%, w/v) was prepared by dissolving 4.0 g of commercially available PVA in 200 ml water. Perchloric acid solution (5.8 mol  $\text{dm}^{-3}$ ) was prepared by diluting commercially available concentrated perchloric acid (70%, 11.6 mol  $\text{dm}^{-3}$ ) with water.

### General procedure

Place 1.0  $\mu\text{g}$  of osmium(VIII) in a 25 ml calibrated flask, then add 1-2 drops of *p*-nitrophenol indicator and neutralize with 0.5 mol  $\text{dm}^{-3}$  sulphuric acid until the indicator colour changes from yellow to colourless. Add 2.0 ml of 0.01 mol  $\text{dm}^{-3}$  ammonium molybdate solution, dilute to about 10 ml with water and mix, and let the mixture react by heating on a boiling water bath for about 15 min. Allow the contents to cool to room temperature with water. In the following order, add 5.0 ml of 5.8 mol  $\text{dm}^{-3}$  perchloric acid, 1 ml of 2% polyvinyl alcohol solution and 2.0 ml of  $6.9 \times 10^{-4}$  mol  $\text{dm}^{-3}$  NB solution. Dilute up to the mark with water and mix. Measure the absorbance in a 1.0 cm cell at the maximum absorbance wavelength against the reagent blank solution.

### Results and discussion

The absorption spectra of the ion association complexes of osmium(VIII) with molybdate and Nile blue was recorded against the corresponding reagent blank. The maximum absorption wavelength was at 585 nm. Hence, further studies were carried out at 585 nm.

Experiment showed that the colour reaction could be performed in hydrochloric, nitric, sul-

Table 1—Sensitivity of various methods for the spectrophotometric determination of osmium

Reagent	$\lambda_{\max}$ (nm)	$\epsilon$ ( $10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ )	Ref.
4-(2-Pyridylazo)resorcinol	540	0.24	5
<i>p</i> -NPF	570	1.0	6
2-Thiobarbituric acid	332	14	7
Rhodamine B	560	6.2	8
Methylene blue	655	2.2	9
Rhodamine 6G	530	4.0	10
1,5-Diphenylcarbazine	570	3.5	11
Malachite green	690	16	12
Ethyl violet	560	11	13
Nile blue	585	28.1	this work

phuric or perchloric acid media, but the sensitivities differed according to the acid used. The highest and most constant absorbance was obtained with perchloric acid. The appropriate acidity range was between 0.93–1.4 mol dm<sup>-3</sup> perchloric acid, hence, 5.0 ml of 5.8 mol dm<sup>-3</sup> perchloric acid was used in this work.

The sensitivity of the system depended upon the NB concentration. If it was too low, the decolouration rate was faster. If it was too concentrated, the reagent blank solution was deeply coloured. Both extremes reduce the sensitivity of the colour reaction system. The optimum concentration of NB was between  $5.5 \times 10^{-5}$ – $8.2 \times 10^{-5}$  mol dm<sup>-3</sup>, hence, 2.0 ml of  $6.9 \times 10^{-4}$  mol dm<sup>-3</sup> NB solution was adopted in this work. Under the experimental conditions, higher concentration of molybdate was required for complete formation of the molybdoosmic acid. The complex gave maximum and almost constant absorbance in the range  $6.8 \times 10^{-4}$ – $23 \times 10^{-4}$  mol dm<sup>-3</sup>. In the general procedure, 2.0 ml of 0.01 mol dm<sup>-3</sup> ammonium molybdate was adopted.

In the absence of an enhancing agent, the ion association complexes precipitated out of the aqueous solution due to their hydrophobicities. When an enhancing agent such as gum arabic, OP, gelatin, PVA, Triton X-100 or Tween-80 was added, the solution remained clear and there was a marked colour change. PVA was the best in all systems. The amount of 2% PVA solution examined was over the range 1.0–4.0 ml for the system. The absorbance of the colour system was constant in this range. The use of 1.0 ml of 2% PVA solution was recommended.

The reaction of osmium(VIII) with molybdate to form a heteropoly acid anion was difficult

when the room temperature was between 10 and 30°C. The complexing reaction was carried out by heating on a boiling water bath for at least 10 min; 15 min was recommended. Once the ion association complex was formed, it was stable for at least 6.5 h.

Under the optimum conditions, different amounts of osmium were used for colour development, and calibration graph was plotted. The molar absorptivity was  $2.81 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The concentration range of osmium obeying Beer's law was 0–1.8  $\mu\text{g}$  per 25 ml. The linear regression equation obtained was  $A = 0.5917C - 0.0006$  ( $r = 0.9993$ ), where A was absorbance at 585 nm, C was expressed as  $\mu\text{g}$  of Os per 25 ml and r was the correlation coefficient. A 0.04  $\mu\text{g ml}^{-1}$  of osmium was analysed seven times, the relative standard deviation being 1.6%. The limit of detection, calculated three times as the standard deviation of the blank, was 2.0 ng ml<sup>-1</sup> ( $n = 11$ ). A comparison of the sensitivities for the determination of osmium by various methods is shown in Table 1. Obviously, the sensitivity and selectivity of the method were superior to those of other published methods.

The molar ratio of osmium to NB was 1 : 4 as established by the equilibrium shift method. The IR spectra of the ion association complex and pure NB were compared. The spectrogram showed both spectra to be very similar above 1000 cm<sup>-1</sup>, which is characteristic of the NB cations. The differences between both spectra were marked below 1000 cm<sup>-1</sup>. In the IR spectrum of the ion association complex, the four new absorptive peaks occurred at 910, 800, 390 and 350 cm<sup>-1</sup>. This is characteristic of the formation of an ion association bond.

#### Effect of foreign ions

The selectivity of the method using the NB system was investigated in the determination of 1.0  $\mu\text{g}$  of osmium in the presence of a series of other ions. The following foreign ions examined (in mg) did not interfere (relative deviation  $\leq \pm 5\%$ ): sulphate (4), nitrate (3), chloride (1), bromide (1), iodide (1) and fluoride (0.4). Of the metal ions examined, Co(II) (0.5), Zn(II) (0.4), Pb(II) (0.3), Fe(III) (0.3), Cu(II) (0.1), Mn(II) (0.1), Ag(I) (0.1), Hg(II) (0.05), V(V) (0.05), Ni(II) (0.03), Tl(I) (0.03), P(V) (0.02), Cr(VI) (0.02), Bi(III) (0.01), Cd(II) (0.01), La(III) (0.01), Th(IV) (0.01), Se(IV) (0.005), Ce(IV) (0.005), Te(IV) (0.005). The main interfering ions were Pt(IV), Pd(II), Rh(III), Ir(IV), Ru(III), Au(III), Ge(IV), Ti(IV),

Table 2 — Determination of osmium in real samples

Sample	Osmium found (%)		RSD (%)	Standard added $\mu\text{(g)}$	Recovery (%)
	AAS	Present method			
Metallurgical product	0.242	0.244	2.4	0.2	98
Catalyst 1	0.0349	0.0350	1.6	0.2	102
Catalyst 2	0.0636	0.0639	4.8	0.2	103

Zr(IV), Hf(IV), Si(IV) and As(III). Hence, osmium was separated by distillation.

#### Analyses of samples

The treatment of samples and distillation separation are similar to the method established in ref. 14, but the absorbing solution of ruthenium and osmium are  $6.0 \text{ mol dm}^{-1}$  hydrochloric acid and 2.0% sodium hydroxide, respectively. Take a known volume of distilled solution containing not more than  $1.8 \mu\text{g}$  of osmium in a 25 ml calibrated flask, then follow the general procedure for the

determination of osmium. The results are presented in Table 2.

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