

N-(4-Hydroxy-3-methoxybenzylidene)hydrazine carbothioamide as a selective and sensitive reagent for the rapid spectrophotometric determination of osmium(VI)

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Received 20 December 1988; revised and accepted 8 June 1989

N-(4-Hydroxy-3-methoxybenzylidene)hydrazine carbothioamides is proposed as a selective and sensitive reagent for the rapid spectrophotometric determination of osmium (VI). The reagent forms a brownish-yellow complex with osmium(VI) at room temperature in 1-4M acetic acid medium. The complex exhibits absorption maximum at 364 nm with a molar absorptivity of $1.2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Beer's law is valid over the concentration range of 0.02-1.2 ppm of osmium(VI) with an optimum concentration range of 0.1-1.1 ppm. The apparent stability constant of the complex is $\log K = 6.79 \pm 0.1$ at 28°C. The method has been used for the determination of osmium in sysskrite.

N-(4-Hydroxy-3-methoxybenzylidene) hydrazine carbothioamide, HMBCT, which is used in chemotherapy and seed treatment was proposed as a spectrophotometric reagent for the determination of cobalt¹ and mercury². In the present note we have investigated the complexation reaction between osmium(VI) and HMBCT. It is found that HMBCT is one of the most selective and sensitive reagents for the spectrophotometric determination of osmium(VI). The proposed method is simple and rapid and involves no extraction, heating or catalyst.

The stock solution of osmium(VI) was prepared from potassium osmate (M/s Johnson Matthey Ltd, London) in doubly distilled water. It was standardised³ and diluted to get a standard solution containing 5 µg/ml of osmium (VI).

HMBCT was prepared by the condensation of hydrazine carbothioamide with vanillin⁴. A 0.3% solution of HMBCT was prepared in 85% ethanol. A Beckmann Model DB spectrophotometer with matched 1 cm silica cells was used for absorbance measurements.

Procedure

An aliquot of the stock solution containing 2.5-27.5 µg of osmium (VI), ethanol (5ml), 0.3% HMBCT solution (3 ml) and 10M acetic acid (6.5 ml) was transferred to a 25 ml volumetric flask and the volume made upto the mark with doubly distilled water. The solution was mixed well and the absorbance was measured at 364 nm against the reagent blank prepared similarly. The amount of osmium(VI) in the sample solution was deduced from the standard calibration curve.

Results and discussion

HMBCT formed a brownish-yellow complex instantaneously with osmium(VI) in acetic, phosphoric, sulphuric or hydrochloric acid medium at room temperature ($28 \pm 1^\circ\text{C}$). Osmium(VIII) and osmium(IV) did not react with the reagent in any of the acid media. The absorbance readings were unstable in sulphuric or hydrochloric acid medium. The sensitivity and stability of the complex was found to be more in acetic acid (1-4M) than in phosphoric acid (1-6-3.5M). The absorbance values remained constant over 16-56% (v/v) (ethanol). Below 16% (ethanol) turbidity was observed and above 56% (ethanol) the maximum intensity of the colour was not obtained. Hence, 2.6M acetic acid medium containing 29% ethanol, in which the absorbance readings were stable for 2 hr was selected for the present study. An 84-fold molar excess of the reagent was necessary for the maximum development of colour intensity. There was no appreciable change in the absorbance if the order of addition of reactants was varied. The absorbance was not affected in the temperature range 5-55°C. Above 55°C, the absorbance gradually decreased with increase in temperature.

Beer's law was found to be valid over the concentration range 0.02-1.2 ppm of Os(VI). The optimum range for the effective spectrophotometric determination, evaluated by Ringbom's method, was found to be 0.1-1.1 ppm. According to Sandell's expression, the sensitivity of the reaction was 1.5 ng cm^{-2} and the molar absorptivity was $1.2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The standard deviation calculated from six determinations in a solution containing 0.4 ppm of Os(VI) was 0.006 and the relative error is less than 2%.

The ion-exchange experiments showed that the complex is cationic in nature as the complex was retained by Dowex 50W-X8. The job's method of

continuous variations and mole-ratio method indicated the stoichiometry of the complex to be 1:2 (metal:ligand). The apparent stability constant of the complex evaluated by the mole-ratio method was $\log K = 6.79 \pm 0.1$ at 28°C .

Interference study

In order to assess the possible analytical applications of the osmium complex, the effect of some foreign ions which often accompany osmium was studied by adding different amounts of diverse ions to a solution containing $0.4 \mu\text{g/ml}$ of osmium. The following amounts (ppm) of foreign ions were found to give less than 2% error in the determination of 0.4 ppm of Os(VI):Ru(III) , 2; Rh(III) , 5; Os(IV) , 18; Os(VIII) , 12; Ir(III) , 21; Pt(IV) , 4; Au(III) , 4; Pd(II) , 0.2; Mo(VI) , 105; W(VI) , 160; Cu(II) , 0.4; Zn(II) , 880; Fe(III) , 36; Co(II) , 590; Ni(II) , 1200; Al(III) , 1020; As(III) , 486; Pb(II) , 2000; Ag(I) , 53; Mn(II) , 210; Mg(II) , 600; U(VI) , 110; Te(VI) , 314; Sb(III) , 46; Zr(IV) , 36; Bi(III) , 52; Ti(IV) , 132; Cr(III) , 218; Hg(II) , 32; V(V) , 49; sulphate, 10,000; nitrate, 8000; phosphate, 15,000; thiosulphate, 600; oxalate 1600; citrate, 6400; tartrate, 5100; fluoride 6500; chloride, 7000; bromide 10,000; iodide 38,000 and EDTA 1600. The tolerance limits of Cu(II) , Ru(III) , Os(IV) , Os(VIII) , and Au(III) could be raised to 2.5, 3, 32, 32 and 18 ppm, respectively, by adding 5000 ppm of citrate, those of Rh(III) and Pt(IV) to 12 and 14 ppm, respectively, by adding 1500 ppm of phosphate and that of Pd(II) to 0.5 ppm by adding 4000 ppm of tartrate.

Determination of osmium in synthetic mixtures

Synthetic mixtures corresponding to a typical sample of syserskite (27.3% Os; 55.2% Ir; 10.1% Pt; 5.9% Ru; and 1.5% Rh) were prepared and the osmium content was determined using the standard procedure. The results in Table 1 show that iridium, platinum, ruthenium and rhodium do not interfere in the determination of osmium (VI).

Table 1 — Determination of osmium(VI) in synthetic mixtures corresponding to syserskite

Os(VI) taken (ppm)	Metal ion added (ppm)				Os(VI) found (ppm)*
	Ir(III)	Pt(IV)	Rh(III)	Ru(III)	
0.2	0.50	0.10	0.02	0.06	0.203
0.3	0.65	0.15	0.03	0.10	0.306
0.6	1.30	0.30	0.06	0.20	0.608
0.8	1.70	0.45	0.09	0.30	0.809
1.0	2.20	0.60	0.12	0.40	1.010

*Average of five determinations

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