Spectrophotometric Determination of Traces of Osmium with 4-Sulpho-2-aminothenothiol

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Received 20 April 1987; revised and accepted 10 August 1987

Spectrophotometric method for the determination of ultratrace quantities of osmium(VI) with 4-sulpho-2-aminothenothiol is described. Os(VI) forms a violet 1:2 complex with the reagent; it is stable for 3 hr and has $\lambda_{\text{max}}$ at 490 nm. Beer’s law is obeyed from 0.5 to 16 ppm of Os with a photometric error of 2.7%. The molar absorptivity and Sandell’s sensitivity values are $1.08 \times 10^4$ 1.mol$^{-1}$cm$^{-1}$ and 0.175 $\mu$g/cm$^2$ Os(VI) respectively at 490 nm.

The osmium determination is important due to its well-known association with other Pt-group metals and lack of suitable micro-chemical techniques. The separation process as well as its individual determination, specially in presence of iridium and palladium matrices, is a real problem in both the pure and applied analytical chemistry.

The osmium content of many biological species (0.01-0.1 ppm range) is required to be determined accurately and reasonably rapidly. Although many this reagents have been proposed$^{1-4}$ for the determination of trace amounts of osmium, and they are highly sensitive, they require strict control of several parameters.

In this note, a sensitive and selective method for the determination of osmium in presence of other Pt-group metals is presented. It is based on the formation of a 1:2 complex by Os(VI) with 4-sulpho-2-aminothenothiol.

Absorbance measurements were made on Hilger-Uvispek and Perkin-Elmer digital spectrophotometers using 2-cm matched glass cuvettes.

Osmium solution was prepared by dissolving OsO$_4$ (Johnson & Methey) in 50 ml of 0.2 M NaOH and diluted to 100 ml. A standard stock solution (0.1 mg/ml) was prepared from this solution.

4-Sulpho-2-aminothenothiol was synthesised as reported earlier$^5$. A freshly prepared 1% reagent solution in water was used. All chemicals used were of A R or G R quality.

Procedure
An aliquot of standard osmium (0-400 $\mu$g) solution was mixed with 4 ml of 1% reagent solution and 4 ml of 12 M hydrochloric acid in a 25 ml volumetric flask. The solution was mixed thoroughly and the volume was made up to the mark. A reagent blank was prepared exactly in the same way; it did not absorb in the range of $\lambda_{\text{max}}$ of the complex. A water blank was found almost satisfactory. The absorbance of the violet osmium(VI) complex was measured at 490 nm.

The spectrum was recorded over the wavelength range 400-600 nm. The complex showed maximum absorption at 490 nm in aqueous medium. The reagent showed no absorption in the range. All measurements were made at 490 nm. The Os(VI) complex is formed in the presence of 0.2-3.8 M HCl. The optimum acidity range was found to be 1.7-2.9 M HCl. Therefore, 4 ml of 12 M HCl was used in the estimations.

Effect of reagent concentration and stability of colour—A 1% reagent solution was used to study the effect of reagent concentration on the complexation of osmium. The optimum range was 2.0-6.0 ml of 1% reagent; 3 ml of 1% solution was found sufficient for complete formation of the violet coloured complex.

The complex formation was independent of the mode of addition of variables and it formed immediately on addition of the acid and the reagent solutions. The system is stable for more than 3 h at room temperature (30°C).

Beer’s law, optimum range, photometric error, molar absorptivity and sensitivity—The osmium(VI) complex obeyed Beer’s law over the range 0.5-16 ppm of Os(VI) at 490 nm. The optimum range of determination obtained from Ringbom’s plot$^6$ was 2-14 ppm. The relative photometric error was 2.7% (cf. Ayres’ plot$^7$). The molar absorptivity (Beer’s law) and Sandell’s sensitivity$^8$ were $1.08 \times 10^4$ 1.mol$^{-1}$cm$^{-1}$ and 0.0175 $\mu$g cm$^{-2}$ Os(VI) at 490 nm, respectively.

Effect of diverse ions—The foreign ions were mixed with 8 ppm of Os(VI) in the final volume and the tolerance limit was set at 0.005 scale unit at 490 nm. A 25-fold excess of Fe(III), Fe(II), Cr(III), Cr(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II), Ca(II), Ba(II), Sr(II), Bi(III), Al(III), Sb(III), As(V), Mo(VI), W(VI), U(VI), Nb(V), Ti(IV), Sn(II), Ti(II), Cu(II) and a 15-fold excess of Ru(III), Rh(III), Ir(III), Pt(IV), Pt(II) did not i-
terfere in the normal procedure. Pd(II) did not interfere when present in 1:1 ratio. Fifty-fold excess of EDTA, citrate, oxalate, tartrate, acetate chloride, bromide, iodide, phosphate, iodate, borate, perchlorate, sulphate and nitrate did not interfere. Hg(II), thiocyanate, Ag(I) and cyanide showed strong interference.

Composition of osmium(VI) complex and stability constant—The composition of the complex was determined by the continuous variation and mole-ratio methods\(^9,10\). The plot of absorbance against M/M + R (M = metal, R = reagent) ratio showed a 1:2 [OS(VI):thiol] composition at 490 nm. The composition was verified by mole ratio method using the equimolar solutions and a constant metal concentration.

The instability constant \(K' = [(n\alpha c)^2/(\alpha c)]/\left[c(1 - \alpha)\right]\) and the degree of dissociation \(\alpha = A_m - A_r/A_m\) were calculated from the M:R ratio in reagent effect studies for 1:2 osmium(VI) complex. The value of \(\alpha\) and thermodynamic stability constant \((K)\) as evaluated by the Harvey-Mannings method\(^11\) came out to be 0.2093 and 8.89 (log \(K\)) respectively at 30°C.

The author gratefully acknowledges the CSIR, New Delhi for a position in the Scientist Pool.

References