

## Spectrophotometric Determination of Os(VIII) Using 2,3-Dihydroxypyridine & 5-Chloropyridine-2,3-diol

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Osmium(VIII) forms 1:1 brown complexes with 2,3-dihydroxypyridine (DHP) (80-fold excess) and 5-chloropyridine-2,3-diol (CPD) (120-fold excess), exhibiting  $\lambda_{\max}$  at 230 and 310 nm in the pH range 8.5-11 when the contents are heated on a boiling water-bath for 150 and 210 min respectively. However, studies of both the complexes have been made in the visible region only (at 500 nm) using water blank. The colour systems obey Beer's law up to 7 and 8 ppm of Os(VIII) in the case of DHP and CPD respectively. The metal-ligand composition of the complexes has been determined by Job's and Bent and French methods. The sensitivities of the colour reactions between osmium and DHP and osmium and CPD are 0.0058 and 0.0098  $\mu\text{g cm}^{-2}$  respectively. The method is very sensitive and fairly selective and compares well with many known methods.

A LARGE number of reagents<sup>1-6</sup> have been used for the spectrophotometric determination of Os(VIII), but the inherent disadvantages are the interferences due to diverse ions and rigid control of working conditions. In some of the known methods prior separation of osmium as a volatile tetroxide is necessary. In view of this, there is a need for better reagents for easy manipulation and better sensitivity and selectivity. The efficacy of 2,3-dihydroxypyridine (DHP) and 5-chloropyridine-2,3-diol (CPD) for the spectrophotometric determination of Os(VIII) was therefore investigated and the results are presented in this paper. DHP and CPD have earlier been used for the spectrophotometric determination of iron and palladium<sup>7</sup>. In the present method, although platinum and some other base metals interfere during the normal course of determination, these interferences can be easily circumvented by choosing the appropriate masking agents. DHP has also been used for the determination of Os(VIII) in synthetic mixtures.

### Materials and Methods

Unicam SP 600 and Beckman DU-2 spectrophotometers were used for measuring absorbance in the visible and UV regions respectively. A Metrohm E 350 pH meter, with saturated calomel and glass electrode assembly, was used for pH measurements.

DHP (Fluka) and CPD (K & K Laboratories) were used as such. Stock solutions of DHP and CPD were prepared in ethanol by refluxing on a water-bath.

The stock solution of Os(VIII) was prepared by dissolving ampoules of OsO<sub>4</sub> (Johnson Matthey, London) in 2N NaOH as described by Ayres and Wells<sup>8</sup> and standardized by the method of Klobbie<sup>9</sup>.

All other chemicals used were of AR grade. Buffer solutions were prepared following the conventional methods.

*Procedure* — To an aliquot containing 1.5-5.2 or 1.2-7.1 ppm of osmium was added an excess

(80-fold in the case of DHP and 120-fold in the case of CPD) of the reagent solution. After adjusting the pH to 10 by adding 3 ml of ammonium chloride-ammonium hydroxide buffer (pH 10), the resulting solution was heated for the required time period (105 min for DHP and 210 min for CPD) on a boiling water-bath, cooled, transferred into a 10 ml measuring flask, volume made up by adding doubly distilled water, and the absorbance measured at 500 nm. The amount of osmium was evaluated from the calibration curves drawn under similar conditions.

### Results and Discussion

The absorption spectra of solutions containing a fixed amount of Os(VIII) and different concentrations of the ligands and at different pH values were recorded after the solutions were heated under reflux. In all the cases, the complexes showed two absorption maxima at 230 and 310 nm. However, the studies have been carried out in the visible region (500 nm) because there is less steep fall in the absorbance at 500-520 nm and the interferences due to many colourless ions, which would otherwise interfere seriously in the UV range, are much less pronounced. The absorption maxima of the complexes remained unchanged even when different proportions of osmium and ligands were mixed suggesting the formation of only one complex in both the cases.

It was observed that almost no complex formation took place in the cold, but when solutions were heated on a boiling water-bath for 105 min in the case of DHP and for 210 min in the case of CPD, the colour started developing and finally a brown colouration resulted. Further heating did not have any effect on the absorbance. Therefore, in both the cases, the contents were heated for 15 min more than the minimum heating time required for full colour development. The absorbance was measured against water blank as the same due to the reagents

was practically negligible at 500 nm. The complexes were found to be stable for at least 24 hr, after which the absorbance started decreasing slowly.

It was observed that the absorption of complexes increased with the increasing pH, attained a maximum value in the pH range 8.5-11, and thereafter started falling. Hence, the studies were carried out at pH 10 using ammonium chloride-ammonium hydroxide buffer, the constituents of which do not cause variation in the absorbance.

It was also observed that the excess ligands (80-fold in the case of DHP and 120-fold in the case of CPD) were necessary for full colour development.

*Beer's law and sensitivity*—The system obeyed Beer's law up to 7 ppm of Os(VIII) in the case of DHP and up to 8 ppm in the case of CPD. The sensitivities of the colour reactions in terms of Sandell's definition are 0.0058 and 0.0098  $\mu\text{g}$  of Os  $\text{cm}^{-2}$  for DHP and CPD respectively. The optimum ranges within which accurate determination of Os(VIII) can be carried out, as deduced from Ringbom plot, are from 1.5 to 5.2 and from 1.2 to 7.1 ppm of Os using DHP and CPD respectively.

*Composition of the complexes*—The composition of the complexes was determined by Job's (final molarity of the solutions being  $1 \times 10^{-3}M$ ) and Bent and French (final molarities of the metal and ligand

TABLE 2 — DETERMINATION OF Os(VIII) IN SYNTHETIC MIXTURES

Os(VIII) added (ppm)	Ir added (ppm)	Ru added (ppm)	Pd added (ppm)	Os(VIII) found (ppm)
5	11	0.1	0.55	4.90
5	11	2.2	1.4	4.95
5	15	5.5	0.55	4.90

solutions being  $5 \times 10^{-5}M$  and  $1 \times 10^{-3}M$  respectively) methods. Both the methods showed the formation of 1:1 (metal-ligand) complexes.

Both the complexes were shown to be ionic in nature, as they were not extracted into the common organic solvents. Further, they were retained almost completely by the anion exchange resin (Amberlite IR-400, chloride form) and their solutions passed unchanged through the cation exchange resin, establishing thereby their anionic nature. However, in the absence of further proofs, no tentative structure can be assigned.

*Effect of added ions*—The study was carried out in solutions containing 5 ppm of osmium and the desired amounts of foreign ions. After following the recommended procedure the absorbances were noted. The results are recorded in Table 1. Some of the ions such as thiosulphate, thiocyanate and sulphide and thiourea inhibit the colour formation even when present in traces. Iron interferes seriously in the determination.

In the case of DHP, EDTA and fluoride were used as masking agents to remove the interferences of the ions. Following are the results, the maskable amounts (in ppm) being given in the parentheses: Ru(III) (20), Rh(III) (20), Pd(II) (20), Ir(III) (20), Pt(IV) (20), Cu(II) (50), Ni(II) (50) and Pb(II) (50) with EDTA, and Fe(III) (50), Al(III) (50), Sn(IV) (50) and Mn(II) (50) using fluoride.

*Determination of Os(VIII) in synthetic mixtures*—On account of the difficulty in getting the naturally occurring ores of osmium, different synthetic mixtures were prepared and analysed as follows:

To the synthetic mixtures were added excess of EDTA (1100 ppm) followed by DHP solution and the amount of Os(VIII) was determined as described above. The results are recorded in Table 2.

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#### References

1. BEAMISH, F. E., *The analytical chemistry of the noble metals* (Pergamon Press, London), 1966.
2. AGARWALA, B. V. & GHOSE, A. K., *Talanta*, **20** (1973), 129.
3. McDONALD, C. W. & CARTEL, R., *Analyt. Chem.*, **41** (1969), 1478.
4. SANDELL, E. B., *Analyt. Chem.*, **16** (1944), 342.
5. STEIGER, B., *Mikrochemie*, **16** (1934), 193.
6. BOLTZ, D. F. & MELLON, M. G., *Analyt. Chem.*, **46** (1974), 233R.
7. KUSHWAHA, V., KATYAL, M. & SINGH, R. P., *Talanta*, **21** (1974), 763.
8. AYRES, G. H. & WELLS, W. N., *Analyt. Chem.*, **22** (1950), 317.
9. KLOBBIE, E. A., *Chem. Zentbl.*, **11** (1898), 65.

TABLE 1 — EFFECT OF DIVERSE IONS

Foreign ion added	Tolerance limits using*	
	DHP (ppm)	CPD (ppm)
Fluoride	500	50
Oxalate	500	50
Tartrate	500	50
Borate	100	500
Citrate	500	50
Phosphate	80	500
Persulphate	500	150
Nitrite	500	90
Nitrate	800	70
Cyanide	50	25
Bromide	500	80
Iodide	80	100
Sulphite	500	100
Acetate	800	500
Ru(III), rhodium(III), palladium(II), iridium(III), and platinum(IV)	3	20
Cu(II)	20	15
Zn(II)	20	25
Cd(II)	10	50
Hg(II)	25†	50†
Ni(II)	20	50
Mn(II)	25†	15
Al(III)	15†	25†
Mg(II)	50	50
Sc(III)	25†	30†
Ba(II)	50	50
Mo(VI)	25	30
Sn(IV)	25†	20†
In(III)	25†	20†
Pb(II)	10†	15†
Gd(III)	50†	50†
U(VI)	15	50
Co(II)	25†	50†
EDTA	1,100	200

\*Concentration at which not more than 2% deviation in the absorbance is obtained.

†Got precipitated and removed by centrifugation.