

to 2 ppm each of Rh(III), V(V), and Fe(III) were avoided by using tartrate (20 ppm) as masking agent. Still large amounts of iron and aluminium could be tolerated in presence of fluoride ions. For removing interferences due to zinc, cadmium and nickel, the initial pH 5.5 was raised to 8.0 and after extraction with chloroform the pH of the aqueous phase brought again to 5.5 by adding acetic acid followed by acetate buffer of pH 5.5. Added 1 ml of 0.03% PAP again. The solution was heated on a water-bath for 50 min, cooled and extracted with 10 ml portions of freshly distilled chloroform and the extinction measured at 615 nm against chloroform blanks.

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### Potentiometric Estimation of Potassium Octacyanomolybdate(IV)

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**Potentiometric estimation of potassium octacyanomolybdate(IV) in hydrochloric acid medium in the presence of iodine monochloride using potassium iodate as titrant is described. The method affords satisfactory and reproducible results in 6 to 7M HCl.**

VERY few methods are available in literature on the estimation of octacyanomolybdates. The utility of Mn(VII), Ce(IV), Cr(VI) and Mn(III) compounds in potentiometric determination of potassium octacyanomolybdate(IV) in sulphuric acid medium have been investigated<sup>1</sup>. Applicability of halogen containing oxidants in the estimation of potassium octacyanomolybdate(IV) has not been explored as yet. Moreover at present no method is available for estimation of potassium octacyanomolybdate(IV) in hydrochloric acid medium. This communication deals with the potentiometric estimation of potassium octacyanomolybdate(IV) with potassium iodate in hydrochloric acid medium using iodine monochloride method.

Potassium octacyanomolybdate(IV) was synthesized by the recommended method<sup>2</sup> and its solution was prepared and standardized as reported earlier<sup>3</sup>. Iodine monochloride was prepared by the usual method<sup>4</sup>. The standard solution of potassium iodate

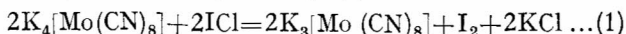
TABLE 1 — POTENTIOMETRIC ESTIMATION OF POTASSIUM OCTACYANOMOLYBDATE(IV) IN 6M HCl WITH POTASSIUM IODATE AFTER PRETREATMENT WITH IODINE MONOCHLORIDE

Potassium octacyanomolybdate(IV) (mmole)		Error %
Taken	Found	
0.0951	0.0950	-0.10
0.1237	0.1230	-0.57
0.1521	0.1510	-0.72
0.1807	0.1790	-0.94
0.2610	0.2580	-1.16
0.3420	0.3380	-1.16
0.5140	0.5180	+0.79
0.4285	0.4340	+1.30

was prepared by the recommended method<sup>5</sup>. The e.m.f. measurements were carried out on a OSAWA vernier potentiometer in conjunction with a spot galvanometer. A bright platinum foil was used as indicator electrode. A saturated calomel electrode served as reference electrode.

An aliquot of potassium octacyanomolybdate(IV) solution was placed in a titration cell and 6 ml of iodine monochloride solution was added. The requisite amount of conc. hydrochloric acid was added to the mixture so as to make the overall acidity 6M in a final volume of 50 ml. The reaction mixture was cooled and titrated potentiometrically with potassium iodate solution. The end point was located using analytical (derivative) method. The results are given in Table 1. It has been observed that an overall acidity of 6-7M with respect to HCl gives satisfactory and reproducible results. Erratic results are obtained if the acidity is less or more than 6-7M. In 2M HCl no inflection is observed.

In the present case, iodine monochloride is the real oxidant. Iodine monochloride oxidizes potassium octacyanomolybdate(IV) to octacyanomolybdate(V) according to Eq. (1).



The iodine liberated from iodine monochloride in amounts equivalent to that of octacyanomolybdate(IV) is oxidized by potassium iodate to iodine monochloride in concentrated hydrochloric acid medium.

The results are low below 5.5M HCl probably because of incomplete reaction (1) and air oxidation of octacyanomolybdate(IV). The over consumption of iodate above 7.5M HCl is perhaps due to partial decomposition of octacyanomolybdate(V) to an oxidizable Mo(V) species.

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