

CATALYSIS IN VOLUMETRIC ANALYSIS.

PART IV. ESTIMATION OF VANADATE IN THE PRESENCE OF IRON, MOLYBDENUM AND TUNGSTEN.

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In view of the great importance of vanadium steels and other alloy steels containing vanadium, the estimation of vanadium in the presence of iron, chromium, molybdenum and tungsten is a matter of considerable importance. Numerous methods have been suggested for the purpose but they are all cumbersome.

We have now found that the iodimetric method developed by Gopala Rao, Viswanadham and Ramanjaneyulu (1945) for the estimation of vanadate can be employed even in the presence of a considerable excess of ferric salt, provided a large excess of oxalate is added to the reaction mixture. The ferric ions get bound by the oxalate in the form of complex anions, and therefore do not interact with hydriodic acid. The addition of oxalate serves yet another important purpose. It catalyses the reaction between vanadate and hydriodic acid. By separate experiments, we have found that the oxalate must be largely in excess of that required for the formation of the complex $K_3Fe(C_2O_4)_3$.

We have found that molybdic acid reacts only extremely slowly with iodide at the acid concentration (approx. N/4) prescribed in our experiments. It is only when the concentration of sulphuric acid is raised to the overall level of 2N that there is a slight reaction. Tungstate reacts with hydriodic acid even more slowly than molybdic acid.

EXPERIMENTAL.

The mixed solution containing vanadate, ferric and other salts is kept in a narrow gas washing bottle fitted with a ground glass stopper with fused inlet and outlet tubes, 25 ml. of N/4 oxalate solution were then added, followed by 20 ml. of M/4 potassium iodide solution. A current of carbon dioxide was passed through the mixture for about half an hour, at the end of which 5 ml. of 4N sulphuric acid, free from oxygen, was added and the reaction was allowed to continue for about 5 minutes in an atmosphere of carbon dioxide. The liberated iodine was titrated, with standard sodium thiosulphate solution, using starch indicator towards the end. Typical results given in the following table show that ferric salts, molybdate and tungstate do not interfere in the iodimetric estimation of vanadate under the conditions prescribed by us.

TABLE I.

X ml. of vanadate + 10 ml. of ferric alum (N/20) + 20 ml. of potassium iodide (M/4) + 10 ml. of molybdate (M/200) + 10 ml. of tungstate (M/200) + 5 ml. of sulphuric acid (4N) + 25 ml. of oxalate (N/4).

Amount of vanadate taken in millimoles.	Amount of vanadate found in millimoles.
0.0975	0.0974
0.0488	0.0494
0.0244	0.0245
0.0195	0.0199

We have ascertained that neither oxalate nor ferrous salt can catalyse the reaction of hydriodic acid with molybdic acid or tungstic acid.

SIMULTANEOUS ESTIMATION OF TRIVALENT IRON AND PENTAVALENT VANADIUM.

In the absence of oxalate or any other substance which is capable of binding ferric ions in the form of complex anions, both trivalent iron and pentavalent vanadium react with hydriodic acid, liberating iodine quantitatively under suitable conditions. The reaction between trivalent iron and hydriodic acid is quantitative, if enough hydrochloric acid is present to bring its overall concentration up to 0.1 N-0.4N. Good results are not obtained in solutions that are not acid enough. Furthermore, the iodide must be present in large excess to favour the reduction of ferric iron. The concentration of the acid cannot be too high, lest there should be excess liberation of iodine due to the oxidation of hydriodic acid by atmospheric oxygen. The reaction between vanadate and hydriodic acid, though slow, is catalysed by ferric or ferrous ions.

We recommend the following procedure for the conjoint estimation of ferric iron and pentavalent vanadium. To about 25 ml. of the reaction mixture, 5 ml. of sulphuric acid (4N) are added, a current of carbon dioxide is passed through for about fifteen minutes, at the end of which 2 gm. of potassium iodide are added, and the reaction allowed to proceed for ten minutes in the absence of air. The liberated iodine is then titrated with standard sodium thiosulphate solution. Typical results are given below.

TABLE II.

Amount of ferric iron taken in milli-equivalent.	Amount of vanadate taken in milli-equivalent.	Amount of iron and vanadium found by the authors' method.	Amount of iron and vanadium calculated in milli-equivalent.
0.75500	0.00000	0.7520	0.75500
0.50300	0.00000	0.5030	0.50300
0.25200	0.00000	0.2500	0.25200
0.12100	0.00000	0.1250	0.12100
0.75470	0.09788	0.8510	0.85258
0.50310	0.09788	0.5990	0.60098
0.25160	0.09788	0.3510	0.34948
0.12080	0.09788	0.2250	0.21868
0.75470	0.04894	0.8040	0.80364
0.50310	0.04894	0.5490	0.55204
0.25160	0.04894	0.3040	0.30054
0.12080	0.04894	0.1740	0.16994

It will be evident, from the foregoing, that the iodimetric methods developed by us for the estimation of trivalent iron and pentavalent vanadium in the presence of molybdate and tungstate are simpler and more elegant than the methods now in use.

In conclusion, we desire to express our thanks to Prof. N. R. Dhar, D.Sc. (Lond.), Dr. es' Sciences (Paris), F.R.I.C., F.N.I., for his kind interest in this investigation.

REFERENCE.

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