Art. XXIII. — *The Determination of Vanadium by Cupferron,* $C_6H_5N(ONH_4).NO$; by W. A. Turner.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cclxxvii.]

The present paper gives the results of experiments begun nearly two years ago on the determination of vanadium by means of cupferron (the ammonium salt of nitrosophenylhydroxylamine). At that time the actual determination of vanadium by this means was not so much sought as its separation from the element uranium.* A large number of experiments carried out for this purpose failed to reveal the proper conditions for a successful separation of these two elements. However something was learned of the reaction between vanadium and cupferron and it is with this reaction and its application to the estimation of vanadium that the present paper deals.

Vanadium in the form of its soluble vanadate in slightly acid solution (hydrochloric or sulphuric) gives with cupferron a mahogany red precipitate. This reaction is so delicate that it may well be used as a qualitative test for a vanadate. If the solution has a low concentration of vanadium a red coloration instead of a precipitate is obtained. A solution containing 0·000004 gm. vanadium per cubic centimeter gives a distinct coloration. Solutions of much lower concentration do not, in my experience, give the test.

A solution of ammonium metavanadate (prepared by precipitation from a solution of sodium vanadate by means of a saturated solution of ammonium chloride† and then washing until free from chlorides) was used for this work. The metavanadate was dissolved in water by constant stirring and gradual addition of concentrated hydrochloric acid.

To obtain the vanadium content of this solution the volumetric method, which involves a reduction of the vanadate by sulphurous acid and then oxidation by a measured amount of standard $KMnO_4$ solution, was used. There was some inconvenience in applying this method because of the fact that the vanadium solution contained hydrochloric acid, which acted upon the $KMnO_4$, giving too high results. This difficulty was overcome with some degree of success by evaporating the weighed portions of vanadium solution with sulphuric acid to remove the hydrochloric acid and then diluting and carrying out the process above mentioned.

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* The use of cupferron for this purpose was suggested by Dr. W. M. Thornton. While this work was in progress two papers by Rodeja have appeared to which reference will later be made.

† Ann. Phys., xcviii, 54, 1831.

In this way the following results were obtained:

TABLE I.

Exp.	Gms. of NH_4VO_3 solution taken	Gms. of V_2O_5 found	Gms. of V_2O_5 per 25 gms. of solution
1	25·9374	0·1714	0·1652
2	25·9846	0·1747	0·1681
3	25·6772	0·1699	0·1654
4	25·9426	0·1727	0·1664

These results not being wholly satisfactory in establishing the vanadium content of the solution, it was decided to try the apparently simple method of evaporating weighed portions of the solution, igniting the residues and weighing the amounts of vanadium pentoxide obtained. In this process also the presence of hydrochloric acid is an inconvenience. The results obtained were too low. It was noted that in the ignition some volatile product was formed which was deposited on the cover and the outer edges of the crucible. It is probable that some of the very volatile oxychloride, $VOCl_3$, is formed. An attempt was made to prevent this by evaporating the solution with sulphuric acid and thus remove hydrochloric acid, but under these conditions high results were obtained evidently due to the formation of a not readily decomposable vanadium sulphate. Simple evaporation and ignition of the ammonium vanadate solution was finally again resorted to and by a careful regulation of the heat (the temperature being very gradually increased from the lowest possible flame of a Bunsen burner to the high heat of the Meker burner) the following quite concordant results were obtained:

TABLE II.

Exp.	Gms. NH_4VO_3 solution taken	Gms. of V_2O_5 found	Gms. of V_2O_5 per 25 gms. of solution
5	25·4215	0·1679	0·1651
6	25·4215	0·1680	0·1652
7	25·4215	0·1683	0·1655
8	25·4215	0·1690	0·1662
9	25·4215	0·1681	0·1653
10	25·4215	0·1683	0·1655

The mean of these results was taken as the true value and the standard thus established as: 25 gms. solution ≎ 0·1655 gm. V_2O_5.

The determinations by means of the cupferron solution were carried out as follows:

Portions of about twenty-five cubic centimeters of the metavanadate solution, accurately weighed, were diluted to about 150–200 cm^3. The hydrochloric acid present in the metavanadate solution was sufficient for the complete precipitation of the vanadium. Not more than 1 per cent acid content (hydrochloric or sulphuric) is needed. Cupferron solution (6 per cent) prepared according to Baudisch* was then added with stirring until a slight excess was present as shown by the appearance of a white precipitate of nitrosophenylhydroxylamine (formed when cupferron comes in contact with an acid solution). Two or three cubic centimeters in excess are added and the precipitate is filtered on paper without delay and washed with a 1 per cent solution of sulphuric acid containing a little cupferron. The precipitate after being allowed to drain on the filter for a time is transferred with the paper to a platinum crucible, dried, ignited and weighed as vanadium pentoxide.

In this process there are several precautions which should be observed. The precipitate after being filtered on paper is transferred to a large platinum crucible and heated with a small flame to dry the mass and remove volatile substances from the precipitate and paper. This should be done cautiously in order not to produce a heat sufficient to fuse the vanadium oxide. If the attempt is made to hasten the ignition, the carbon of the unburned filter may mingle with the fused vanadium oxide, thus delaying the oxidation of the former, which is ultimately accomplished probably more or less at the expense of the latter. At best some of the oxide is likely to become reduced and must be thoroughly exposed to the action of the air by revolving the crucible held by the tongs in the flame and allowing the fused oxide to flow on the sides. By this means the oxide may be brought to its highest state of oxidation.

An apparently necessary condition for the formation of the vanadium-cupferron precipitate seems to be a slight acidity of the solution. Experiments made in this connection showed that if aqueous solutions of sodium vanadate and of cupferron, both made neutral to litmus, were mixed the resulting solution became alkaline (evidently due to ammonia liberated), no precipitate being formed. This alkalinity must be overcome by addition of acid (hydrochloric or sulphuric) and a slight excess must be used in order to bring about complete precipitation.

The precipitate, transferred to the filter, is washed with a solution containing about ten cubic centimeters of concentrated

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* Chem. Zeitung, xxxv, 223, 1911.

sulphuric acid and 1·5 gms. of cupferron per liter. The solutions and wash-liquid used should be cold; that is, their temperature should not exceed 20° C. If the temperature is allowed to rise much above this the precipitate tends to decompose and forms a gummy mass which clogs the pores of the paper and makes filtering almost impossible. The precipitate is ready to filter about as soon as formed and there should be no delay in the filtration and washing. If the precipitate is allowed to remain long on the filter it tends to crack and is then more difficultly washed, while if the process is carried out quickly and without interruption, it is readily filtered and washed.

By this process the following results were obtained:

TABLE III.

Exp.	Gms. NH_4VO_3 solution taken	Gms. of V_2O_5 found	Gms. of V_2O_5 per 25 gms. of solution found	taken
11	25·4236	0·1686	0·1658	0·1655
12	25·4193	0·1685	0·1657	0·1655
13	25·3242	0·1673	0·1652	0·1655
14	25·6816	0·1703	0·1658	0·1655

From the above data it appears that the vanadium in vanadates can be very accurately estimated by means of the cupferron reaction. Investigations are being made into the use of this reagent for the separation of vanadium from other elements, the results of which will appear at an early date.

Recently the statement has been made by Rodeja* that vanadium in the form of vanadates cannot be quantitatively precipitated by cupferron, but that if the vanadate is first reduced to the vanadyl condition a quantitative estimation of the vanadium may then be made. Experiments made according to the rather meager details given in the abstract of this work failed to confirm this statement.

Four portions of a solution of sodium vanadate, two of which were precipitated without reduction and the other two after reduction, gave the following results:

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* Abstract Journal of the Am. Chem. Soc., ix, 2201, 2202, 1915. Anales soc. Espan. fis. quim., xii, 305–9, 379–82, 1914.

TABLE IV.

Exp.	Gms. Na_3VO_4 solution taken	Gms. of V_2O_5 found	Gms. of V_2O_5 per 25 gms. of solution
	Without Reduction		
15	20·1067	0·0873	0·1085
16	20·4030	0·0882	0·1081
	With Reduction		
17	54·1156	0·2300	0·1063
18	46·2709	0·1954	0·1056

The filtrate from Exp. 17 was evaporated and the residue ignited. A solution of this residue gave with cupferron a distinct test for vanadium.

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