Art. XXII.—*The Gravimetric Estimation of Vanadium as Silver Vanadate;* by Philip E. Browning and Howard E. Palmer.

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

Silver nitrate has long been known as a precipitant of solutions of vanadic acid, but, so far as the authors are aware, no method for the quantitative estimation of vanadium, based on the use of this reagent, has been published. The work to be described was undertaken to determine the conditions under which vanadium could be estimated gravimetrically as silver vanadate.

For this work an exactly neutral solution of ammonium vanadate was used, whose standard had been determined by evaporating accurately measured portions to dryness in a platinum crucible and weighing as V_2O_5 after gentle ignition.

Attempts were first made to precipitate the silver vanadate in acetic acid solution. The solution of ammonium vanadate, acid with acetic acid, was heated to boiling, and a solution of silver nitrate was added, with stirring to coagulate the precipitate. The precipitate, after settling, was filtered off on asbestos, washed thoroughly, and weighed after gentle ignition. The experiments made in this way, under different conditions of acidity, and with different amounts of silver nitrate, are recorded in Table I, and indicate a variation in the composition of the precipitate which is formed in acetic acid solution.

Table I.

	V_2O_5 taken grm.	Silver vanadate found grm.	V_2O_5 found grm.	Error grm.
(1)	0·0569	0·1978	0·0871	+0·0302
(2)	0·0569	0·1202	0·0529	−0·0040
(3)	0·1139	0·2275	0·1002	−0·0137
(4)	0·0569	0·2671	0·1176	+0·0607
(5)	0·0569	0·1717	0·0756	+0·0187

The effect was next tried of making the precipitation in exactly neutral solution as follows: The neutral solution of ammonium vanadate, about 200^{cm^3} in volume, was heated to boiling, and a solution of silver nitrate was added in excess, with vigorous stirring to coagulate the precipitate. The precipitate was then filtered off on an asbestos felt contained in a platinum crucible, washed thoroughly, ignited at a gentle heat below the fusing point of silver vanadate, and weighed as $AgVO_3$.

The results, recorded in Series A of Table II, indicate that the composition of the precipitate formed in neutral solution approximates closely to the meta-form.

In the experiments recorded in Series B of Table II, the solution of ammonium vanadate was made ammoniacal with ammonium hydroxide, and this solution was made neutral by boiling until the ammonia was completely expelled. To this solution, diluted to about 200^{cm^3}, and heated to boiling, silver nitrate was added, and the procedure given above was followed. The results indicate that the precipitate formed by adding silver nitrate to a solution made neutral by boiling off the ammonia from an ammoniacal solution, is of constant composition.

The experiments of Series C were made to determine whether any solution containing vanadium could be brought into the condition in which the silver metavanadate would be precipitated on the addition of silver nitrate, by making ammoniacal and boiling off the ammonia. To this end the solution of ammonium vanadate was made acid with nitric acid, then made ammoniacal with ammonium hydroxide, and boiled to expel the ammonia; the solution was then treated as in the experiments of Series A. This method, as will be seen, gave the most satisfactory results. In this connection it should be noted that the ammoniacal solution, which is yellow at first, becomes colorless during the boiling, until finally, when the ammonia is almost completely expelled, the solution begins to turn yellow; the boiling should be stopped as soon as the solution begins to turn faintly yellow, because, if the boiling is continued further, the solution becomes too acid, and the precipitate which forms on the addition of silver nitrate has a varying composition which does not correspond to the meta-condition.

The ease with which the silver vanadate settled out on stirring suggested that the vanadium might be estimated volumetrically with a fair degree of accuracy, by adding a standard solution of silver nitrate to the hot neutral solution containing the vanadium, and noting the point at which the precipitation ceased: but attempts to do this met with unsatisfactory results.

The gravimetric estimation of silver by the addition of an excess of a solution of ammonium vanadate to the solution containing the silver was also tried, but was abandoned on account of the unsatisfactory character of the precipitate and the difficulty with which it filtered.

TABLE II.

	V_2O_5 taken grm.	$AgVO_3$ found grm.	V_2O_5 found grm.	Error grm.
		(A)		
(1)	0·1139	0·2595	0·1143	+0·0004
(2)	0·0569	0·1291	0·0569	+0·0000
(3)	0·0569	0·1277	0·0562	+0·0007
(4)	0·0569	0·1303	0·0574	+0·0005
(5)	0·1066	0·2436	0·1073	+0·0007
		(B)		
(1)	0·1066	0·2430	0·1070	+0·0004
(2)	0·1066	0·2429	0·1070	+0·0004
(3)	0·0533	0·1224	0·0539	+0·0006
(4)	0·0533	0·1221	0·0538	+0·0005
(5)	0·0569	0·1312	0·0578	+0·0009
		(C)		
(1)	0·0569	0·1293	0·0569	−0·0000
(2)	0·1066	0·2419	0·1065	−0·0001
(3)	0·1066	0·2424	0·1068	+0·0002
(4)	0·1066	0·2422	0·1066	+0·0000
(5)	0·0533	0·1215	0·0535	+0·0002