hydroxide by ammonium hydroxide is complete when $[H^+] = 10^{-6.5}$ to $10^{-7.5}$, points approximately defined by the color change of methyl red and of rosolic acid.

(2) The presence of ammonium chloride during precipitation is advantageous in limiting the alkalinity, and in coagulating the precipitate.

(3) Solutions of ammonium nitrate and chloride are equally satisfactory for washing the precipitate.

(4) The conditions of precipitation recommended are favorable for the simultaneous precipitation of aluminium and ferric hydroxides; and for their separation from calcium, strontium, barium, and magnesium.

(5) Crucibles containing ignited alumina should be kept covered in the desiccator and on the balance.

(6) For precipitates of from 0.1 to 0.2 g. Al_2O_3, five or ten minutes' blasting is sufficient.

(7) The presence of ammonium chloride during ignition causes no appreciable loss of alumina.

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THE ESTIMATION OF VANADIC ACID, AFTER REDUCTION BY METALLIC SILVER.

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Among the many reactions of vanadic acid to be found in the literature, that with metallic silver seems to have been almost overlooked by the numerous investigators who have studied the element vanadium. The only reference which the writer has been able to find bearing at all on this subject is the statement in a paper by Campbell and Griffin[1] that "silver, lead, copper and other elements were tried (as reducing agents on mixed uranyl and vanadyl solutions) but * * * offered no advantages for this purpose." It is true that Perkins[2] reduced vanadic acid to the tetroxide by the action of hydriodic acid and metallic silver, but he considered that the function of the silver was merely that of absorbing the iodine set free in the reaction, and the possibility of any direct action between the silver and vanadic acid seems not to have been thought of.

That silver should be capable of reducing pentavalent vanadium to tetravalent could be predicted with a considerable degree of certainty by consideration of the values obtained by Rutter[3] for the oxidizing potentials of solutions of vanadic acid, and also from the fact that silver is

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[1] *J. Ind. Eng. Chem.*, 1, 661 (1909).

[2] *Am. J. Sci.*, [4] 29, 540.

[3] *Z. anorg. Chem.*, 52, 368 (1907).

capable of reducing ferric salts, which are less easily reduced than solutions of vanadic acid. That the reduction cannot proceed further than the tetravalent stage (as it does in the case where zinc, magnesium or aluminum is used as the reducing agent) could also be predicted from the fact that divalent and trivalent vanadium salts precipitate metallic silver from solutions of silver salts.[1] We should expect therefore that the reaction

$$\mathrm{Ag} + \mathrm{VO}^{+++} \longrightarrow \mathrm{Ag}^{+} + \mathrm{VO}^{++}$$

should be strictly quantitative—an expectation which is fully confirmed by the results given in this paper.

The course of the reaction can obviously be measured in three ways: (*a*) from the loss in weight of the metallic silver (if a weighed excess is used to effect the reduction); (*b*) by estimation of the dissolved silver (for example by titration with standard NH_4CNS solution); and (*c*) by oxidimetric estimation of the reduced vanadium, say, with standard $KMnO_4$. Provided the reaction is strictly quantitative, any one or all of these methods might be used for the quantitative estimation of vanadium.

To test the validity of these conclusions a series of experiments was carried out to determine the conditions, if any, under which a quantitative reduction of pentavalent vanadium to tetravalent might be expected.

Reagents and Apparatus.

Solutions of pure sodium vanadate (free from chloride) were carefully standardized against $KMnO_4$, after reduction with sulfur dioxide, and also by the very accurate method of Holverscheit.[2]

Potassium permanganate, approximately 0.05 *N*, was standardized against sodium oxalate.

Ammonium thiocyanate, approximately 0.05 *N*, was standardized against 0.1 *N* silver nitrate.

Metallic silver was prepared by electrolysis of a silver nitrate solution, using a platinum anode enclosed in a porous cup, and a fine platinum wire suspended near the top of the solution, as cathode. Under these conditions if a moderately heavy current is passed through the solution the silver is deposited as a "bush" of very fine crystals which drop continually from the cathode to the bottom of the beaker, and which can be later removed by filtration. The finely divided crystals were boiled with dilute sulfuric acid in order to remove any impurities which might be soluble in this medium, and were then filtered off through an alundum crucible, washed, and ignited at low red heat. In certain of the preliminary experiments other forms of silver were used, for instance, that formed by precipitation by zinc dust from dilute silver nitrate solution, or by

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[1] Rutter, *Loc. cit.*

[2] *Inaug. Diss.*, Berlin, 1890.

igniting silver oxide, or in one case a spiral of pure fine silver wire. Mention is made of this in later discussion.

All pipets and burets used had been calibrated carefully and carried certificates of accuracy, and the greatest care was taken in making all measurements and readings. In all titrations the amount of the reagent necessary to produce the color change of the end point was determined by "blank" experiments and the readings were corrected accordingly. The amount was usually between 0.03 and 0.05 cc.

Experimental Results.

After certain preliminary experiments which will not be recorded here, a number of determinations were made as follows:

Carefully measured portions of a standard solution of sodium vanadate were acidified with about 2 cc. of conc. H_2SO_4, diluted to about 75 cc., and treated with 1 to 2 g. of metallic silver, the exact weight of which had been previously determined. The small flasks containing the solutions were then placed upon a quartz plate, and the solutions were boiled gently for twenty minutes, or in some cases for one-half hour. Usually the boiling was continued for about ten minutes after the appearance of the pure blue color which signifies practically complete reduction of the vanadium. The solutions were then filtered upon asbestos in weighed perforated porcelain crucibles, and the residue of silver was washed with hot water. The crucibles were then placed inside of a larger nickel crucible and heated therein for about one-half hour, the outer crucible being subjected to the full heat of a large Bunsen burner. Under these conditions the inner porcelain crucible is at very low red heat. After cooling in a desiccator the crucibles were weighed, and the loss of weight of the silver was calculated.

The filtrates from the silver, containing all of the vanadium in the tetravalent condition, together with the dissolved silver, were titrated hot with 0.05 N $KMnO_4$. At the completion of this titration the solutions were cooled and titrated for silver with 0.05 N NH_4CNS, after the addition of ferric alum as indicator.

TABLE I.

No.	V_2O_5 taken, g.	Loss Ag, g.	$KMnO_4$ $N/20$ × 1.4212, cc.	NH_4CNS $N/20$ × 0.9862, cc.	V_2O_5 calc. from Ag.	V_2O_5 calc. from $KMnO_4$.	V_2O_5 calc. from NH_4CNS.	Mean error, g.
1	0.0702	0.0830	10.85	15.65	0.0701	0.0702	0.0702	±0.0000
2	0.0702	0.0832	10.85	15.68	0.0702	0.0702	0.0703	±0.0000
3	0.0702	0.0828	10.87	15.60	0.0700	0.0700	0.0700	—0.0001
4	0.1260	0.1492	19.50	28.10	0.1260	0.1261	0.1260	±0.0000
5	0.1260	0.1497	19.50	28.15	0.1264	0.1261	0.1262	+0.0002
6	0.1260	0.1490	19.50	28.20	0.1259	0.1261	0.1264	+0.0001
7[1]	0.1260	0.1490	19.50	28.10	0.1259	0.1261	0.1260	—0.0000

[1] Reduced with silver wire; see below.

The amount of vanadic acid present was calculated (*a*) from the loss in weight of the metallic silver, (*b*) from the permanganate titration, and (*c*) from the silver equivalent to the thiocyanate titration. The results given in Table I show that the reaction is strictly quantitative, and that not only the gravimetric method, but also the volumetric ones are very accurate measures of the amount of vanadic acid present.

The value of these results is obvious. They afford an accurate and simple *gravimetric* method for the estimation of vanadium, which can in the same operation be checked by *two volumetric* estimations with very little additional trouble. Furthermore, if the gravimetric estimation is not desired, the operation can be very materially shortened and still permit the employment of the two volumetric estimations. In Table II are given the results of experiments in which the acid vanadate solutions were heated as above with unweighed amounts of metallic silver, filtered through paper or asbestos, and the filtrates titrated first with permanganate and then with thiocyanate as in the first set of experiments.

TABLE II.

No.	V_2O_5 taken, g.	$KMnO_4$ $N/20$ × 1.4212. cc.	V_2O_5 found calc. from $KMnO_4$, g.	NH_4CNS $N/20$ × 0.9862, cc.	V_2O_5 found calc. from NH_4CNS.	Mean error, g.
1	0.0702	10.85	0.0702	15.65	0.0702	±0.0000
2	0.0702	10.90	0.0704	15.70	0.0704	+0.0002
3	0.0702	10.85	0.0702	15.68	0.0703	+0.00005
4	0.1260	19.48	0.1259	28.10	0.1260	—0.00005
5	0.1260	19.50	0.1261	28.15	0.1262	+0.00015
6	0.1260	19.50	0.1261	28.10	0.1260	+0.00005

These results show that vanadic acid can be very accurately determined by titration with permanganate or thiocyanate, or both, after reduction by metallic silver.

Discussion of Factors Influencing the Completion of the Reaction (based partially upon the above experiments and partially upon the preliminary experiments, not here recorded).

Time.—The time necessary for complete reduction varied, naturally, with the total amount of vanadium present, with the amount of silver used, and with its state of subdivision. With as much as 2 g. of finely divided crystalline silver complete reduction of about 0.1200 g. of vanadic acid occurred after ten minutes' boiling. On the other hand, when only 0.5 g. of silver was used, reduction in some cases was incomplete after as much as one-half hour's boiling. The influence of the state of subdivision of the silver was shown by an experiment in which about 1.5 g. of fine silver wire was used as the reducing agent. In this case the gravimetric and volumetric estimation (Table I, No. 7) showed that reduction was complete, but this was only after an hour's boiling. The best practice seemed to be to continue boiling gently for about ten minutes after the solution had become a pure blue in color. Longer boiling, though unnecessary, is not harmful. Certain of the preliminary experiments showed that heating on the water bath for about two hours could usually be substituted for the boiling, but the results were not quite so certain.

Preparation of Silver.—No appreciable difference could be observed in the action of electrolytic silver, silver reduced by zinc, and silver prepared by heating the oxide, provided the purity was the same, and provided that preliminary treatment with dilute sulfuric acid was given. The electrolytic silver is, however, recommended as being more apt to be pure, and as giving somewhat more uniform results. It is easily prepared by the method given above.

Acidity.—The acidity of the solutions was varied between 0.5 cc. and 3 cc. of conc. H_2SO_4 in a total volume of 75 cc. No very marked differences in behavior were observed, but somewhat more uniform results were obtained when 1 to 2 cc. in 75 cc. were used.

The reduction takes place readily when hydrochloric acid is used instead of sulfuric. In this case the dissolved silver is precipitated as chloride, and the vanadic acid present may be calculated from the *increase* in weight of the silver used for the reduction, as well as by permanganate titration of the filtrate. The gravimetric method is not quite so accurate as when loss of weight is determined, for, of course, the increase of weight due to chlorine is only about one-third of the decrease in weight caused by the solution of an equivalent amount of silver. Furthermore, the permanganate titration in the hot solution containing hydrochloric acid is not so accurate as in the presence of sulfuric acid alone, even when all precautions are observed. If it is desired, however, to determine vanadium in a solution containing hydrochloric acid, the silver reduction followed by permanganate titration may be used with a fair degree of accuracy. A better method is to remove the hydrochloric acid with silver sulfate in slight excess, and then determine vanadium as described above for solutions containing sulfuric acid. Either the gravimetric method or the permanganate titration may be employed, and even the thiocyanate titration also, provided a blank is run to determine the silver already present.

Nitric acid must not be present, for obvious reasons, nor any other substance acted upon by finely divided silver under the conditions of the experiment. The application of the reaction to the determination of vanadium in technical products, and in the presence of other substances, will be the subject of further investigation.

Filtration.—Where the gravimetric method is to be carried out, filtration through asbestos in a perforated porcelain crucible (or through alundum) is far preferable to filtration through paper. Where only the volumetric processes are to be carried out, filtration through paper is probably more convenient. It is even possible to wash the silver residue by decantation entirely, but filtration in this particular case is so rapid that decantation gains no time, and there is always the risk that fine particles of silver may be carried into the solution to be titrated, and thus spoil the determination.

Accuracy.—The accuracy with which duplication of results can be obtained is very unusual. This is especially true of the permanganate titration, where the writer had had as many as six consecutive titrations show no readable difference in the volume of permanganate used. Slightly greater variations were obtained in the thiocyanate titration, but here also the results are excellent. The writer has had experience with nearly all of the standard methods for the estimation of vanadium, and has obtained better results with the method proposed here than with any other of his experience. The fact that three check determinations may be made on the same solution should make the method admirably adapted to the exact standardization of vanadic acid solutions, or to other cases where high accuracy is desired.

Another useful feature of the method is the opportunity which it offers for the gravimetric standardization of permanganate solutions against metallic silver, or of comparing permanganate and thiocyanate solutions against one another. For this purpose complete reduction of the vanadic acid is not necessary, as the three factors, loss of weight of silver, permanganate titration, and thiocyanate titration are always strictly proportional, regardless of the extent to which the vanadium is reduced.

Summary.

Vanadium is quantitatively reduced from the pentavalent to the tetravalent condition by metallic silver in acid solution under proper conditions.

The reaction may be used to determine vanadium (*a*) gravimetrically, from the loss in weight of the silver; (*b*) oxidimetrically, by titration with standard potassium permanganate; or (*c*) by titration of the dissolved silver with ammonium thiocyanate. All of these operations may be carried out on the same solution, and serve to check each other.

The results are of the highest order of accuracy.

The reactions may be also used for the standardization of permanganate solutions against silver, and of permanganate and thiocyanate solutions against each other.

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