6. By combination of 2, 3, 4 and 5, periodate, iodate, bromate and chlorate can be determined differentially in the presence of each other and in the presence of perchlorate.

The differential deportment of other oxidizing agents will also be studied.

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THE ELECTROMETRIC TITRATION OF VANADIUM.

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The titration of chromates with ferrous sulfate, using as an end point the change in potential of a platinum electrode immersed in the solution has been recently used by Hildebrand[1] and Forbes and Bartlett.[2] While working on the application of this method to the determination of chromium in steel, it was found that vanadium in the pentavalent condition may be titrated in a very similar manner. If both chromates and vanadates are present, the titration includes both elements. We, therefore, determined to test this as a possible new method for the determination of vanadium.

Volumetric methods for the determination of vanadium usually involve the titration of vanadyl salt with potassium permanganate. To a less extent the determination is made with ferrous sulfate, using potassium ferricyanide as either inside or outside indicator, more often the latter.

In the first class of methods, reduction is accomplished by hydrochloric acid, sulfur dioxide, hydrogen peroxide, oxalic acid, and other reducing agents. The chief objections which have been made to these methods are (1) that the state of oxidation of the vanadium after reduction is uncertain[3] and (2) that the residual solution after reduction may not be entirely free from the reducing agent. The second class of methods is criticized by Cain[4] as being faulty in that vanadyl salts reduce ferricyanide which then reacts with ferric salts, with the result that the values obtained are too low. Clark[5] replies to this that well-washed ferricyanide crystals in fresh solution are not acted upon by vanadyl salts, and that the result is correct. Bleecker[6] states that vanadyl salts added to ferric salts immediately reduce a part to the ferrous condition. One of us (Kelley) in trying Clark's method, which involves reduction with ferrous sulfate and back titration with potassium dichromate, using potassium ferricyanide as an outside indicator, found it to give variable and high results. This seems to be contrary to the experience of Cain and Bleecker as well as Clark. The tendency of Clark's method to give high results has been shown again in this investigation, for the addition of appreciable amounts of ferrous sulfate solution was found necessary to obtain the end point of Clark's method after our own end point had been reached. We take occasion to mention these points concerning the reduction of vanadates with ferrous sulfate because our method depends upon this, although it differs from other methods in the manner of obtaining the end point. In the experimental portion of the paper, we show results obtained by several methods and compare them with our own.

[1] THIS JOURNAL, 35, 869 (1913).

[2] *Ibid.*, 35, 1527 (1913).

[3] Auchy, *J. Ind. Eng. Chem.*, 1, 455 (1909).

[4] *Ibid.*, 3, 477 (1911).

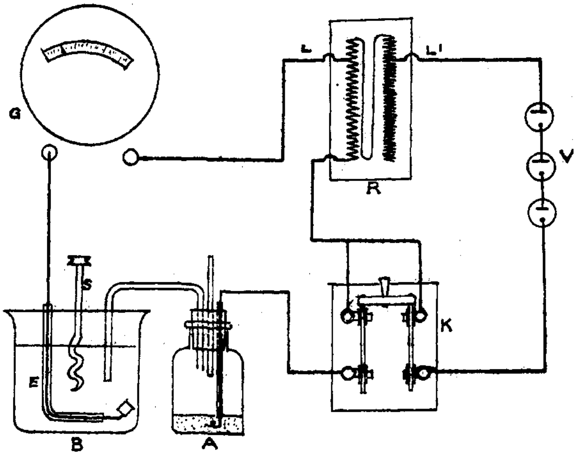
[5] *Met. Chem. Eng.*, 11, 195-7.

[6] *Ibid.*, 9, 209 (1911).

Apparatus.

Since the aim of the investigation was the analytical determination of vanadium no attempt was made to measure the actual potentials involved. It was required only that the apparatus be of such a nature that we could readily detect the sudden changes of potential which corresponded to the disappearance of the higher state of oxidation of the element in question. This enabled us to replace the reflecting galvanometer which Forbes and Bartlett used with an ordinary suspension galvanometer, and the slide-wire bridge with a resistance box containing two sliding contacts. The latter change was possible because we made no readings of the resistances involved, the changes of position of the galvanometer needle alone being noted. The resistance box, which consisted of two coils and sliding contacts with resistances of 195 and 5 ohms, was wired so that one resistance served to vary the e. m. f. of the dry cells used as the source of current and the other served as the potentiometer box.

In the diagram of our apparatus, A represents a calomel electrode conveniently made from a small wide-mouth bottle filled with a solution of KNO_3. The dotted area in A indicates the portion of bottle occupied by the mercury. It is provided with a plunger, slight pressure on which causes the ejection of a portion of the liquid through a capillary tube. B represents the beaker in which the titration is made and containing the platinum electrode E and the stirrer S. The galvanometer is shown at G and the resistance box at R, with its two sliding contacts L and L′. The batteries, ordinary dry cells, are shown at V, and K is a double knife switch which throws in both the galvanometer and main circuits at one operation.



The Titration of a Solution.

The solution containing the unknown amount of vanadium as vanadate is placed in the beaker and 25 cc. of H_2SO_4 (sp. gr. 1.4) are added with water enough to bring the volume up to 200 cc. The connections are then made and resistances so adjusted that the needle comes to rest on the scale. Standard ferrous sulfate solution is then run in from the buret. At the first addition of ferrous sulfate the needle begins to move off of the scale, showing a drop in potential. The sliders on the resistance box are then changed in such a manner as to keep the needle on the scale during the addition of further quantities of the reducing agent. This movement of the needle is slow and continues until one-half to three-fourths of the equivalent quantity of ferrous sulfate solution has been added. During the addition of the last quarter the needle remains practically at rest until the end point is reached, when the addition of a few tenths of a cubic centimeter in excess causes a sudden movement. To obtain exact adjustment, dilute standard dichromate solution is added in small amount until the needle is returned to the position which it occupied before ferrous sulfate was added in excess. The addition of two or three drops of the ferrous sulfate solution is now usually enough to cause a sudden movement over several divisions. This is followed by the addition of exactly the quantity of dichromate necessary to return the needle to the original stationary position. The end point in the reaction is thus indicated by a sharp throw of the needle which is easily distinguished from the slow movement which occurs when the first portions of ferrous sulfate are added. The final adjustment to get the exact end point will rarely require the addition of more than 0.5 cc. of standard dichromate solution, for, even if the addition of ferrous sulfate has been rapid, the end point will not usually be passed by more than this amount. However, this titration is much more sensitive to conditions than is the titration of chromates. Accordingly, we give below a few of our experiments which show favorable and unfavorable conditions for the titration.

Conditions for Titrating Vanadates.

The object of these experiments was to find the conditions which gave the maximum throw of the needle for a given excess of ferrous sulfate, that is, the sharpest end point. To this end varying amounts of pure ammonium vanadate solution were titrated with ferrous sulfate and potassium dichromate as described above under conditions differing as to temperature, and concentration of foreign salts and acid. Solutions having a volume of 250 cc. of the composition given in Table I were titrated to within a few drops of the end point. The resistance was then adjusted until the needle came to rest at zero on the galvanometer. Record was then made of the deflection following the addition of each drop of ferrous sulfate. In this way a rough but serviceable idea could be obtained of the sharpness of the end point under the given conditions. After the addition of these several drops of ferrous sulfate, enough dichromate was added to bring the needle back to the position which it occupied before the first deflection caused by the addition of ferrous sulfate. From the buret readings the vanadium content was calculated for comparison with the known weight in the solutions taken.

TABLE I.—EFFECT OF CONDITIONS UPON END POINT.

Temp. ° C.	H_2SO_4. Sp. gr. 1.40. cc.	Additions.	Change in reading of galvanometer with successive drops of ferrous sulfate.							Vanadium	
			1.	2.	3.	4.	5.	6.	7.	present.	found.
10	30	....	0.0	0.2	1.0	1.0	1.5	1.7	1.7	0.1178	0.1179
25	30	....	0.0	0.3	0.5	0.5	1.0	1.5	2.0	0.1178	0.1174
40	30	....	1.0	1.0	0.5	0.5	0.7	1.0	1.2	0.1178	0.1178
22	5	....	0.0	0.2	0.3	0.3	0.2	0.2	0.8	0.1178	0.1176
25	100	....	0.0	1.0	2.5	2.5	2.5	...	...	0.1178	0.1180
20	30	....	0.0	1.5	3.5	3.5	...	...	...	0.0236	0.0232
20	30	....	0.0	0.6	2.3	3.5	...	...	...	0.0471	0.0470
22	30	2 cc. conc. HCl	0.0	0.6	2.5	3.0	...	...	...	0.0471	[1]
20	30	0.004 g. Cr	0.0	1.0	3.5	3.5	...	...	...	0.0236	0.0230
20	30	0.02 g. Cr	0.0	0.5	1.5	2.5	3.0	3.5	...	0.0471	0.0470
23	30	1 g. Fe	0.0	0.5	1.0	2.0	3.0	3.0	...	0.0471	0.0473
23	30	2 g. Fe	0.0	0.5	1.0	2.0	2.5	...	...	0.0471	..

In Expt. 4 the end point was taken at the fourth drop. The chromium and iron were added as the corresponding alums.

As is readily seen, the deflection of the galvanometer needle caused by the addition of a given excess of ferrous sulfate (and thus the sharpness of the end point varies greatly with conditions). From the experiments given above, together with others not recorded here, we feel that this titration is favorably influenced by the following conditions:

1. Low temperature, preferably 10° C. (first three experiments).
2. High acid concentration (fourth and fifth experiments).
3. Small rather than large amounts of vanadium (second, sixth and seventh experiments).
4. Low concentration of chromic and ferric salts.

From the excellent agreement among the results, it will appear that successful determinations may be made even under the most unfavorable of these conditions if the galvanometer be closely watched. However it is obviously much easier to note large movements of the needle than small ones; and to facilitate accurate and rapid work it is desirable to fulfil the conditions for titration as outlined above.

The potentials of vanadium solutions in which the vanadium was in the quadrivalent and pentavalent states have been studied by Rutter.[2] He found that the potential of a platinum electrode in a solution of ammonium vanadate was 1.121 volts, taking the normal hydrogen element as zero. With a solution in which 91.9% of the vanadium was in the quadrivalent state he found the voltage to be 0.936. The e. m. f. of a solution containing no pentavalent vanadium was 0.644 volt. Beyond showing that the addition of the last portion of the reducing agent would be expected to cause a large change in the e. m. f. these measurements throw no light

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[1] Not determined.

[2] *Z. anorg. Chem.*, 52, 370 (1907).

on the present problem. We have already pointed out that the change in potential is apparently gradual until half to three-fourths of the vanadium has been reduced, when no further change occur until the excess of ferrous salt has been added. This corresponds to a flattening of the potential-concentration curve beginning at the point where half of the ferrous sulfate has been added, and continuing until the end point is closely approached. This, and the effect of acid concentration and temperature, Rutter's paper does not explain.

The authors hope that other experimenters in whose field this problem lies will be interested in undertaking an electrochemical study of vanadium which lately has become so important technically.

A Comparison of the Electrometric Method with Other Methods for Determining Vanadium.

Attempts to compare the electrometric end point with the ferricyanide spot plate test were given up, since it was found that at least 0.5 cc. of ferrous sulfate solution must be added above that necessary for the electrometric end point before a faint blue color was perceptible after twenty to thirty seconds. Moreover, the solution gave a faint blue color on standing one or more minutes with ferricyanide, even in the absence of ferrous iron. Thus it would appear that titrations employing this substance as outside indicator would give high results if only a short time were allowed for the indicator to act, and low values if the time allowed were longer. These comments apply, of course, only to the volumes with which we worked, 200 to 300 cc., and in which the concentration of sulfuric acid was between 10 and 25% by weight.

For the purpose of comparing the results given by other methods for determining vanadium with those given by our own method, we prepared an indeterminate solution of vanadium by dissolving a quantity of ammonium vanadate in water with the aid of a little sodium hydroxide. Analyses of this solution were then made by several of the volumetric methods most in use and by ours.

Method I. Reduction with Hydrochloric Acid.—Fifty cubic centimeters of concentrated hydrochloric acid were added to a measured volume of the solution of vanadate. This was evaporated to a small volume, the same amount of hydrochloric acid again added and the evaporation repeated. At this point 50 cc. of sulfuric acid were added and the solution evaporated until fuming was well established. (Care at this point is necessary for (1) if all hydrochloric acid is not removed it interferes with the subsequent titration of the hot solution with permanganate, and (2) if the fuming is continued too long there is danger[1] of reoxidizing the vanadium tetroxide to vanadium pentoxide by the action of the sulfur

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[1] Cain, *J. Ind. Eng. Chem.*, 3, 477 (1911).

trioxide.) The solution was cooled slightly, diluted to 400 cc., warmed to 80° and titrated with potassium permanganate.

Method II. Reduction with Sulfur Dioxide.—This method was applied as recommended by Cain.[1] The vanadate solution was diluted to 350 cc., 30 cc. of H_2SO_4 (sp. gr. 1.40) added, the solution heated to boiling and sulfur dioxide, washed with water, passed in during 5 minutes. Continuing the boiling, a rapid stream of carbon dioxide, washed with sodium acid carbonate solution, was passed in during ten minutes. At the end of this time no sulfur dioxide could be detected in the steam. Water was added to make the volume 400 cc., and the temperature was then brought to 70 to 80° for the titration with potassium permanganate.

Method III. Reduction by Hydrogen Peroxide.—This method was applied substantially as recommended by Cain and Hostetter.[2] The solution was mixed with 30 cc. of concentrated sulfuric acid, 3 cc. perhydrol added, and the solution evaporated to the appearance of fumes. As a precautionary measure, a second portion of perhydrol was added and the evaporation repeated. (3% hydrogen dioxide may be used in place of perhydrol.) The solution was then diluted to 400 cc. volume, warmed to 80° and titrated with permanganate.

Method IV. Reduction with Oxalic Acid.—The solution was treated with 30 cc. of concentrated sulfuric acid, 0.20 g. oxalic acid added and the solution evaporated to the appearance of fumes. The fuming was continued 10 minutes, after which the solution was diluted to 300 cc., warmed to 80°, and titrated with permanganate.

Method V. Electrometric.—Titration was made at 10 to 20° with 30 cc. H_2SO_4 (sp. gr. 1.40) in a volume of 250 cc.

The ferrous sulfate and potassium dichromate solution were approximately 0.0625 *N*.

The potassium permanganate was approximately 0.1 *N* and was standardized against sodium oxalate. This solution was used to standardize both the ferrous sulfate and dichromate solutions.

Of the five different methods for determining vanadium, in our hands the electrometric method has given the most consistent results. The mean of the results obtained by our method is substantially identical with the mean of results obtained by reduction with sulfur dioxide, hydrogen dioxide and oxalic acid, but higher than that obtained by reduction with hydrochloric acid. We are at a loss to explain the discordant results obtained with hydrochloric acid as a reducing agent in the analysis of this solution, for as will be shown later it is capable of giving consistent results in other cases. Our experience with this reagent has been chiefly in the analysis of iron-vanadium alloys, in which use it has always given

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[1] *Idem.*, p. 479.

[2] THIS JOURNAL, 34, 274 (1912).

excellent results. It may be possible that the iron or some other element present has a favorable influence upon the reduction in such instances.

TABLE II.—COMPARISON OF METHODS.

NH_4VO_3 solution. cc.	Method.	Vanadium found. Gram.	Gram per cc.	Average.
25	I	0.1140	0.00456	
25		0.1139	0.00456	
25		0.1164	0.00466	
25		0.1158	0.00463	0.00460
25	II	0.1170	0.00468	
25		0.1177	0.00471	
50		0.2354	0.00471	
50		0.2348	0.00470	0.00470
25	III	0.1172	0.00470	
25		0.1177	0.00471	
50		0.2360	0.00472	
50		0.2330	0.00466	0.00470
25	IV	0.1177	0.00471	
25		0.1182	0.00473	0.00472
25	V	0.1177	0.00471	
25		0.1177	0.00471	
25		0.1179	0.00472	
25		0.1174	0.00470	
25		0.1180	0.00472	
10		0.0470	0.00470	Av., 0.00471

Oxidation of Vanadium to Vanadate.

In order that the electrometric titration of vanadium may be applied to the analysis of ores and metals, it is necessary to have some convenient quantitative method for insuring oxidation of the vanadium to vanadate. It is further necessary that the solution as prepared shall contain no substance other than the vanadate which may be reduced by ferrous sulfate.

Nitric acid was tried as an oxidizing agent and at first seemed to be quite promising, especially as chromium seems not to be oxidized under the most vigorous oxidizing conditions, while vanadium is quite rapidly oxidized. We were eventually disappointed, however, for the oxidation was invariably incomplete, as is shown in the following experiment:

A vanadium solution was prepared by dissolving ferro-vanadium in a mixture of dilute sulfuric and nitric acid. This was evaporated until fumes appeared and diluted with water. This solution, when reduced with either hydrochloric acid or hydrogen dioxide, was found to be of such strength that 10 cc. required 17.7 cc. of our permanganate solution for its oxidation. In our experiments, 10 cc. portions of the solution were reduced with a slight excess of ferrous sulfate solution and 45 cc. of sulfuric acid (sp. gr. 1.4) and 50 cc. of water added. Different amounts of nitric acid were then added and the solutions boiled for varying lengths of time. The solutions were then cooled slightly and titrated with permanganate, the amount of permanganate required being a measure of the failure of the nitric acid to oxidize the vanadium.

TABLE III.—OXIDATION OF VANADIUM BY NITRIC ACID.

HNO_3. cc.	Period of boiling. Min.	$KMnO_4$ used. cc.	% oxidation.
0	0	17.7	..
5	5	6.0	66
10	5	2.0	89
15	5	1.5	91.5
5	15	5.0	72
10	15	1.8	90
15	15	1.0	94
10	20	0.4	97.7

From the above it will be clear that nitric acid could not be depended upon to oxidize the vanadium. Nitric acid also was found to produce a harmful effect upon the electrometric titration, probably by reaction with $FeSO_4$. This was less noticeable with low acid concentration and low temperatures. The trouble manifested itself in the irregular behavior of the galvanometer, in that the addition of ferrous sulfate would cause a movement of the needle indicating that the end point had been reached, but, after a moment, the needle would return to its original position. This would occur repeatedly, requiring the addition of a large excess of ferrous sulfate. The influence of the acid concentration is shown in Table IV.

TABLE IV.—EFFECT OF NITRIC ACID ON TITRATION.

Temperature 20°. Total volume 100 cc.

		Electrometric titration			Vanadium		
HNO_3.[1] cc.	H_2SO_4 (Sp. gr. 1.40). cc.	$FeSO_4$. cc.	$K_2Cr_2O_7$. cc.	Corrected Vol. $FeSO_4$. cc.	present. G.	found. G.	Remarks.
2.5	10	35.30	0.20	35.10	0.1026	0.1025	good
10	10	35.30	0.25	35.05	0.1026	0.1022	end point
10	45	No end point could be found					
10	45						

We thought to complete the oxidation with nitric acid by evaporating to the appearance of fumes, which would also avoid the difficulty of titrating in the presence of much nitric acid. To test this, we oxidized 10 cc. of our vanadium solution with permanganate to a faint pink, added 40 cc. of sulfuric acid (sp. gr. 1.40) and evaporated to the fuming point. When cooled and titrated electrometrically the vanadium found was 0.0955 g. instead of 0.1026 g., showing that the vanadate had been reduced by the treatment. Another similar portion treated with 40 cc. of sulfuric acid and 60 cc. of water was made barely pink with permanganate. After boiling 15 minutes, the solution turned pink on the addition of the first drop of permanganate, showing that simply boiling with dilute sulfuric acid had no reducing effect on the vanadium. It is possible that

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[1] The nitric acid used here is in excess of that necessary for oxidation.

dust in the sulfuric acid caused the liberation of sulfur dioxide which in turn caused the reduction of the vanadate. For these reasons all attempts to oxidize vanadium with nitric acid were abandoned.

Oxidation with Permanganate.

Vanadium may be completely oxidized to the pentavalent condition in hot solution by potassium permanganate, as is well known. The method chosen to accomplish this in the absence of chromium was to treat the solution at 80° with dilute potassium permanganate solution until a slight permanent pink color resulted. The solution was then treated with a few drops of hydrochloric acid (1 to 3), and boiled for five minutes. All of the potassium permanganate was thus decomposed and the chlorine removed, the vanadate remaining unchanged. As an alternative to this method, the permanganate may be added carefully to the hot solution until the first change of color appears. This point may be found very accurately and in fact most of the volumetric methods for determining vanadium depend upon it. The solution, after cooling to 20° or lower, is ready to titrate electrometrically. The last process is available for use when small amounts of chromium are present.

Oxidation with Ammonium Persulfate.

This method involves oxidation with ammonium persulfate in the presence of silver nitrate. To carry out the process, the solution containing the vanadium is treated with nitric acid to oxidize the iron. Enough sulfuric acid is added to make the total present equal to 25 to 40 cc. of acid of sp. gr. 1.40. The solution is then diluted to a volume of 300 cc. with hot water and 10 cc. of solution of silver nitrate (2.6 g. to 1 liter) and 5 g. of ammonium persulfate added. After boiling the solution for ten minutes it is treated with 5 cc. of dilute hydrochloric acid (one to three). Five minutes' boiling decomposes the permanganic acid which will form if manganese is present. The solution was then cooled and titrated electrometrically.

The Determination of Vanadium in the Presence of Chromium.

Of the methods given below for the oxidation and determination of vanadium only one is available in the presence of chromium. This follows from the fact that reagents which oxidize vanadium completely tend to oxidize chromium, at least in part. We were, therefore, unable to accomplish the oxidation by ammonium persulfate or permanganate in excess even though the solution were subsequently boiled with hydrochloric acid. The method which we were able to use involves oxidation of the hot solution with permanganate to the first change of color, taking care not to add an excess. An account of our experimental work in the application of the this method will be given in a paper which we expect shortly to publish on the analysis of chrome-vanadium steels.

TABLE V.—ANALYSIS OF SOLUTIONS OF FERRO-VANADIUM[1] (METHODS I–IV).

Solution A.

		Vanadium.		
Cc. soln.		Found. G.	Wt. per cc. G.	Av. per cc.
25	I	0.2575	0.01029	0.01027
25		0.2572	0.01029	
10		0.1030	0.01030	
10		0.1020	0.01020	
10	III	0.1029	0.01029	0.01032
10		0.1023	0.01023	
25		0.2590	0.01036	
25		0.2596	0.01038	
10	V[2]	0.1038	0.01038	0.01027
10		0.1030	0.01030	
10		0.1022	0.01022	
10	V[3]	0.1025	0.01025	0.01025
10		0.1025	0.01025	

Solution B.

		Vanadium.		
Cc. soln.		Found. G.	Wt. per cc. G.	Av. per cc.
200	I	0.3861	0.00193(0)	0.00193(2)
200	I	0.3866	0.00193(3)	
50	III	0.0970	0.00194(0)	
50	V[4]	0.0966	0.00193(1)	
50	V[3]	0.0963	0.00192(6)	
		Solution C.		
200	I	0.3652	0.00182(6)	0.00182(5)
200	I	0.3640	0.00182(0)	
50	III	0.0907	0.00181(5)	
50	V[4]	0.0915	0.00183(0)	
50	V[3]	0.0917	0.00183(5)	

Summary.

(1) Vanadates may be successfully titrated with ferrous sulfate, using a change in the electromotive force of a suitable cell as the indicator.

(2) The most suitable conditions for obtaining a quick and accurate determination by this method have been defined.

(3) Several interesting theoretical problems which arise from a study of the change of potential during the titration are indicated.

(4) A comparison has been made of four of the methods in widest use for the determination of vanadium and the results are found to be in close agreement with those found by the method here outlined.

(5) The oxidation of vanadium to the pentavalent condition with nitric acid has been found unsatisfactory for quantitative purposes.

(6) The oxidation with potassium permanganate or ammonium persulfate has been found entirely satisfactory for this method in the absence of chromium.

(7) The method has been applied to the analysis of ferro-vanadium and with small changes in the preparation of solutions could be applied to the analysis of ores.

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[1] These solutions were prepared by dissolving ferro-vanadium in dilute sulfuric acid, using about 10 cc. of sulfuric acid of sp. gr. 1.40 in 100 cc. or less of water for each gram of the alloy. When solution was complete, nitric acid was added in small amounts to oxidize the iron and break up carbides of vanadium. 200 cc. of Solutions B and C correspond to 1 gram of ferro-vanadium.

[2] Oxidized with $KMnO_4$ to a faint pink color.

[3] Oxidized with $KMnO_4$ and boiled with a little dilute HCl.

[4] This solution was oxidized with ammonium persulfate in the presence of silver nitrate as described on p. 350.