A NEW METHOD FOR THE ELECTROMETRIC TITRATION OF VANADIUM IN THE PRESENCE OF IRON AND CHROMIUM

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Introduction

Of the two accepted methods for the selective oxidation of vanadium in the presence of chromium, titration with potassium permanganate and boiling with nitric acid, neither is free from inaccuracies due to manipulation. The end-point in the former, especially in the presence of relatively large amounts of chromium, is extremely difficult to detect,[1] and the latter requires an extended period of boiling with a high and regulated concentration of nitric acid.[2] It seemed desirable, therefore, to investigate further the selective reactions of these 2 elements with a view to simplifying the analytical procedures now in wide use.

Gooch[3] calls attention to a method worked out by H. E. Palmer for the separation of chromium and vanadium which is based upon the reduction of chromate by hydrogen peroxide in acetic acid solution, leaving unchanged the vanadate which may then be precipitated directly by the addition of lead acetate. As it stands, the method is of little more than theoretical interest but it offers possibilities as the basis of a volumetric method for vanadium involving an electrometric titration of the vanadate with ferrous sulfate. When the concentration of hydrogen ion is low, hydrogen peroxide readily oxidizes a chromic salt to chromic acid; as it rises, the amount of oxidation decreases until finally the peroxide reduces chromic acid to a chromic salt. Perchromic acid is often an intermediate product in this reduction. The presence of chromium and iron also influences the action of hydrogen peroxide on vanadic acid, and it was necessary, therefore, to make a careful study of this reaction before it could be applied to the determination of vanadium in the presence of these other elements.

Character of the Titration

First, it is advisable to discuss the electrometric titration of vanadic acid with ferrous sulfate. The electrode system used was the polarized bimetallic system previously described,[4] consisting of 2 identical platinum wires polarized with a current of 0.5×10^{-5} amp. (0.5 volt through 100,000 ohms). Preliminary titrations made on solutions containing vanadic acid alone, and also in the presence of chromium and chromium and iron, with various mixtures of mineral and acetic acids, showed that the end-

[1] Kelley and Conant, J. Ind. Eng. Chem., 8, 722 (1916).

[2] Kelley, Wiley, Bohn and Wright, ibid., 11, 632 (1919).

[3] Gooch, "Methods in Chemical Analysis," J. Wiley and Sons, 1912, p. 412.

[4] Willard and Fenwick, THIS JOURNAL, 44, 2516 (1922).

point was sharp and much less affected by the concentration of hydrogen ion and the presence of foreign salts than that given by a monometallic system. The initial voltage of a solution containing vanadic acid lies considerably above that of a solution of chromic acid of equivalent normality and the same concentration of hydrogen ion, as is to be expected from a consideration of the relative oxidizing strengths of the two acids and the concentration of oxygen ion given by each.[4] An increase in acidity lowers the potential of either oxidizing agent, thereby increasing its apparent strength.

Taking into consideration the inherent characteristics of the two systems, the titration of vanadic acid with ferrous sulfate, using the bimetallic system, is perfectly analogous to that with the monometallic.[5] The voltage rises slowly from the first addition of reducing agent, more slowly as the concentration of vanadyl salt increases. Just preceding the end-point, this velocity increases very slightly, then decreases again to an almost imperceptible rise. At the end-point the galvanometer appears to have momentarily lost its sensitivity and then reverses the direction of its swing as more ferrous sulfate is added. In carrying out a titration it is best to follow the rising voltage with the potentiometer, keeping about 0.5 mv. behind it. With so sensitive an electrode system this is quite sufficient to give an easily determined swing of the galvanometer. Ferrous sulfate is added more and more slowly as the rate of the potential rise decreases until the deflection indicates a diminishing potential. The end-point lies just beyond the brief period of insensitivity. An excess of the reducing agent causes the voltage to decrease with rapidly increasing velocity until the approximate limiting concentration is passed and the stable condition reached. The reversal is very sharp, easy to detect, and normally sensitive to 0.03 cc. of 0.02 N solution. The total magnitude of the preliminary rise varies considerably with the composition of the solution. With a pure, strongly acid solution of ammonium vanadate it may amount to from 200 to 300 mv., while in the determination of vanadium in a low-vanadium steel 10 to 20 mv. is common. The initial potential also alters with the concentration of acid and foreign salts. It usually lies between 350 and 500 mv. with a polarizing potential of 0.5 volt. The sharpness of the end-point, however, is hardly affected by these factors. It is advisable to keep the concentration of mineral acid fairly high, but it may vary within wide limits without causing any material difference in behavior.

Experimental

Since most of the analytical work on vanadium is devoted to special steels and similar alloys, experimental conditions were chosen closely resembling a sulfuric acid solution of an alloy steel.

[5] Kelley and Conant, THIS JOURNAL, 39, 341 (1916).

The iron was taken in the form of a solution of ferrous sulfate. To this was added 4.0 cc. of conc. sulfuric acid, then the chromium as potassium dichromate and the vanadium in the form of a solution of pure ammonium vanadate, standardized by titration electrometrically with ferrous sulfate which had been compared with a standard solution of potassium dichromate. A slight excess of a concentrated solution of potassium permanganate was run in; a known amount of sodium acetate and acetic acid added, then the reducing agent, either the ordinary 3% solution of hydrogen peroxide or a solution of sodium perborate neutralized with acid. After the solutions had been boiled to destroy the excess of the peroxide they were cooled to at least 20–25°, and 25–50 cc. of conc. hydrochloric acid was added before titration. The standard ferrous sulfate solution was compared with a standard 0.05 N vanadate solution by diluting 25.00 cc. of the latter to about 40 cc., acidifying with 15–20 cc. of conc. hydrochloric acid and titrating electrometrically.

As chromium is but slightly oxidized by hydrogen peroxide in weak acid solution, it seemed possible that the method might be made one of selective oxidation by leaving the vanadium all in the vanadyl form, oxidizing the iron with nitric acid and depending upon the peroxide for a complete conversion to vanadic acid. This attempt to eliminate the permanganate oxidation was unsuccessful.

Nitric or hydrochloric acid solution may be substituted for the sulfuric acid without affecting the results.

The period of boiling necessary to destroy completely all excess of the peroxide was one of the first points of importance to be determined. Samples were made up as outlined containing 1 g. of iron, 64 mg. of chromium, 31.9 mg. of vanadium, 4.0 cc. of conc. sulfuric acid; 20 cc. of glacial acetic acid; 20 g. of sodium acetate trihydrate, and 0.7 g. of sodium perborate in an initial volume of 200 cc. After boiling for periods of 5, 10, 15, and 40 minutes, the amounts of vanadium found were 32.4 mg., 32.4 mg., 31.83 mg., and 31.87 mg., respectively. As 15 minutes was sufficient and 40 minutes not excessive, 20 minutes was adopted as the standard period. Very long boiling causes a slight reduction of vanadic acid.

When a solution of hydrogen peroxide was used instead of perborate, vanadic acid was very appreciably reduced if the time of boiling was prolonged or considerable peroxide was added. This was probably due to a preservative in the hydrogen peroxide. As a solution of sodium perborate neutralized with acid was free from this objection it was regularly used.

When insufficient acid is present the chromic acid is not completely reduced; this error increases rapidly with the concentration of chromium. Both these factors must, therefore, be controlled. The upper limit of acidity is that at which pervanadic acid is formed, inasmuch as this decomposes on boiling to form some vanadyl salt. This limit was found to be equivalent to 0.075 N sulfuric acid. However, an attempt to decrease the amount of acetate added so as to leave a calculated amount of free sulfuric acid was unsuccessful. Iron precipitated, carrying with it much of the chromate. A high concentration of free acetic acid is necessary for quantitative results.

Effect of Varying the Concentration of Acetic Acid and Sodium Acetate

The effect of the concentration of acetic acid upon the accuracy of the vanadium determination, both in the presence and absence of chromium and iron, is taken up in Table I.

TABLE I

EFFECT OF THE CONCENTRATION OF ACETIC ACID[6]

The solutions titrated contained 31.9 mg. of V, the stated amount of Cr, Fe, and glacial acetic acid, 4.0 cc. of H_2SO_4 (sp. gr. 1.83) 20 g. of $NaC_2H_3O_2.3H_2O$, and 0.7 − 2.5 g. of $NaBO_3.4H_2O$; they were boiled for 20 min.   The standard $FeSO_4$ solution was 0.02 N.

Cr Mg.	Fe G.	CH_3COOH % by vol.	Initial vol. Cc.	Error Mg. V
0	0	0	200	0.0
32	1	0	200	−0.08
320	1	0	400	Fe pptd. on boiling. Considerable H_2CrO_4 present.
32	0	5	200	+0.05
32	0	10	200	+0.3
160	0	10	200	0.0
320	0	10	200	+1.0
320	1	16	400	+0.10
320	1	19	400	+0.10
320	1	25	200	+2.0
320	1	25	400	−0.04
320	1	33	225	−0.25

The presence of iron is distinctly beneficial, and with large amounts of chromium the error may be reduced by dilution.   The last 5 experiments show that in the presence of iron with proper regulation of acidity and volume the interference of chromic acid may be prevented.

The results in the last two experiments in Table I are a little low, indicating a possible reduction of vanadic acid.   To test this point ammonium vanadate alone, acidified with sulfuric acid and treated with acetic acid and acetate, was titrated.   In high concentrations of acetic acid the reduction of vanadic acid was appreciable but between 20 and 30% the error was negligible.

Later work on steels indicated that with 1 g. of iron its catalytic effect had not quite reached its finite value.   With still larger amounts the limits are extended somewhat but it is safe to state as a general rule that in the presence of at least 1 g. of iron the reaction is selective and independent of the vanadium present if the concentration of the acetic acid added is from 20 to 25%.   The initial volume should be 200 cc. when the chromium is not more than 150 mg., and 400 cc. when it rises as high as 300 mg.

In view of the enormous repression of the dissociation of acetic acid by sodium acetate it seemed possible that any excess of the latter over that required for combination with the mineral acid might have a very appreciable tendency toward lowering the effective acetic acid concentration.

[6] The results stated in Tables I and II are, in each case, the averages of several determinations.

Throughout the work so far some excess of acetate has been present; 4.0 cc. of conc. sulfuric acid was regularly added to the ferrous sulfate used in making up the samples. This is the equivalent of 19.4 g. of sodium acetate trihydrate. In the oxidation process with permanganate part of this acid is used up. This consumption amounts to 0.5 cc. per g. of iron, or the equivalent of 2.4 g. of acetate. No account was taken of this; therefore, with all samples containing iron, excess acetate was present. It seemed desirable to extend the investigation.

TABLE II

EFFECT OF THE CONCENTRATION OF ACETATE

The samples contained 31.9 mg. of V, 1 g. of Fe, the stated amount of Cr and excess of sodium acetate, 4.0 cc. of H_2SO_4 (sp. gr. 1.83) 20% glacial acetic acid, and 0.7 g. of $NaBO_3.4H_2O$. The initial volume was 200 cc. The actual weight of $NaC_2H_3O_2.3H_2O$ added in each case was 19.4 g. plus the given excess.

Cr Mg.	Excess $NaC_2H_3O_2.3H_2O$ G.	Error Mg. V
32	2.5	0.0
32	12	−0.3
100	2.5	−0.09
100	12	+0.08
100	17	+0.07
100	22	Large quantities of Fe pptd. on boiling. No titration.
160	2.5	−0.09
160	12	+0.2

Considerable excess of sodium acetate has no deleterious effect upon the titration. Apparently with at least moderate amounts of chromium, provided the acetic acid content is fairly high, the limiting concentration of acetate is that at which considerable iron is precipitated on boiling. Increasing the amount of iron to 5 g. has only a slight effect on the results in Tables I and II.

Determination of Vanadium in Artificial Mixtures and in Steels

Before testing the method on actual steels, samples were made up for titration corresponding to a 5g. sample of a steel containing 0.204% of vanadium and 4.0% of chromium. This was done essentially as outlined above. Ammonium vanadate and potassium dichromate were added to a solution of ferrous sulfate containing sulfuric acid, the mixture was heated to boiling and most of the iron oxidized with nitric acid. The oxidation was completed with a slight excess of potassium permanganate, the calculated amount of sodium acetate to combine with the sulfuric acid added, then the acetic acid and neutralized solution of perborate in the amount stated in Table III.

In Samples 1 and 2, where the negative error was large, there was present a considerable quantity of a light yellow, crystalline precipitate which did not go into solution when the hydrochloric acid was added just before titrating. In Samples 3 to 8 the amount of the precipitate was much

smaller and the results were better.   Reducing the iron content in Expts. 9 to 12 by the use of smaller samples eliminated this precipitate alto-

TABLE III

DETERMINATION OF VANADIUM IN SYNTHETIC STEELS

All solutions contained 10.2 mg. of V, 200 mg. of Cr, 4.0 cc. of H_2SO_4 (sp. gr. 1.83), 20 g. of $NaC_2H_3O_2.3H_2O$, and Fe, glacial acetic acid and $NaBO_3.4H_2O$ in the amounts stated.

Expt.	Fe G.	CH_3COOH %	$NaBO_3.4H_2O$ G.	Initial vol. Cc.	Error Mg. V
1	4.75	15	2.0	400	−0.85
2	4.75	15	2.0	400	−0.70
3	4.75	10	1.5	200	−0.25
4	4.75	20	1.5	200	−0.11
5	4.75	20	0.7	200	−0.01
6	4.75	20	0.7	200	−0.11
7	4.75	20	0.7	300	−0.14
8	4.75	20	0.7	400	+0.02
9	3	20	0.7	200	+0.02
10	3	20	0.7	200	+0.02
11	3	20	0.7	300	+0.19
12	3	20	0.7	400	+0.12

gether.   It seldom appeared even with 5 g. of *steel*.   It contained no vanadium but its composition was not further investigated.   The presence of the finely divided solid seems to cause low results,[7] and any precipitate should be filtered off to avoid this error.

TABLE IV

DETERMINATION OF VANADIUM IN CHROMIUM-VANADIUM
Steels from the Bureau of Standards

Sample	V found %	B. of S. certificate value %	Cr found %	B. of S. certificate value %
30a	0.201			
	0.200			
	0.205		1.037	
	0.201		1.042	
	Av. 0.202	0.21	Av. 1.04	1.02
24	0.139			
	0.139			
	Av. 0.139	0.15[a]		

° B. of S. results, 0.143% of V.

Two samples of vanadium steel from the U. S. Bureau of Standards were now analyzed according to the above procedure, using 5g. samples of No. 30a and 4 g. of No. 24.   For the sake of completeness, the chromium was determined in No. 30a by persulfate oxidation and electrometric titration as given by Kelley and others[2] but using the bimetallic electrode system.   The end-point is the previously described vanadium end-point.

[7] This Paper, p. 91.

The effect of tungstic acid on the determination of vanadium was investigated, using 2 steels containing tungsten, chromium, and vanadium. An exact analysis of the steels was not available but it was known that Steel a was approximately 2.8% of chromium, 1.3% of vanadium and 16.8% of tungsten, and Steel b, 5.2% of chromium, 0.3% of vanadium and 10.0% of tungsten. The process of solution was somewhat different from that followed by Kelley and others.[2] One-g. samples of a and 4 g. of b were treated with hydrochloric acid, sp. gr. 1.13, until action ceased, then 8 cc. of conc. nitric acid was added and the solution evaporated to 20 cc. After the liquid was diluted with hot water and heated until the soluble salts were dissolved, the procedure was exactly as usual. The results of the analysis were erratic and all low. Other samples were dissolved and the tungstic acid filtered out after the evaporation and solution of the salts. Under these conditions no difficulties were encountered.

The filtered and washed precipitates of tungstic acid were dissolved in sodium carbonate, oxidized with hydrogen peroxide, the excess of which was destroyed by boiling, and then acidified with 3 to 5 cc. of conc. phosphoric acid. After adding the equivalent of 3 to 5 cc. of conc. sulfuric acid, the occluded vanadium was titrated with ferrous sulfate. The results are stated in Table V.

TABLE V

DETERMINATION OF VANADIUM IN CHROMIUM-VANADIUM-TUNGSTEN STEELS

Steel	Uncorrected % V	Occluded % V	Corrected % V	% W	V occluded per % W
a	1.319	0.016			
	1.321	0.013			
	Av. 1.320	Av. 0.015	1.335	16.8	0.0009
b	0.281	...			
	0.278	0.033			
	0.282	0.028			
	Av. 0.280	Av. 0.031	0.31	19.0	0.0017

The correction for Steel a corresponds very closely to that given by Kelley,[2] 0.001% for each per cent. of tungsten, but in the second case it is much higher. The sample used was, however, twice as large as specified by him.

The occluded vanadium did not account for the error encountered when the tungstic acid was not removed. In view of former difficulties it was concluded that the presence of any finely divided precipitate causes the reduction of vanadic acid in this reaction.

Synthetic molybdenum-chromium-vanadium steels were analyzed for their vanadium content. Under the conditions of the titration the reduction of molybdic acid by ferrous sulfate is so slow as to render the reaction selective. There is no appreciable alteration in the end-point.

Recommended Procedure

The recommended procedure for the determination of vanadium in special alloy steels is as follows.

a. **For Vanadium and Chromium-vanadium Steels.**—A sample requiring about 10 cc. of 0.02 N ferrous sulfate is convenient. Place it in a 600cc. beaker, add 20 to 30 cc. of water and run in a measured volume of conc. sulfuric acid from a buret. Each gram of steel requires 1.0 cc. of the acid to form ferrous sulfate and a 4cc. excess is sufficient to effect a rapid solution. Heat gently until the sample is completely dissolved and the salts begin to separate. Dilute with 20 cc. of hot water and heat until dissolved. Add 4 or 5 cc. of conc. nitric acid cautiously and boil. Complete the oxidation of iron and vanadium with a slight excess of a solution of potassium permanganate. Add sufficient sodium acetate (a moderate excess does no harm), to combine with the acid used in excess of that required for solution (1 cc. of conc. sulfuric acid, = 4.8 g. of sodium acetate trihydrate), and 40 to 50 cc. of glacial acetic acid. Add about 0.5 g. of sodium perborate, previously neutralized; dilute, if necessary, to 200 cc. and boil for 20 min. Cool to room temperature, add 25 to 30 cc. of conc. hydrochloric acid and titrate with 0.02 N ferrous sulfate solution standardized against potassium dichromate.

b. **For Chromium-vanadium-tungsten Steels.**—Treat the samples with 40 cc. of hydrochloric acid, 3 parts of conc. acid to 1 of water, and heat until action ceases. Add 8 to 10 cc. of conc. nitric acid, dropwise, until the first violent action has ceased. Boil and evaporate to about 20 cc. Dilute with hot water and heat to insure complete solution of soluble salts. Filter and wash with hot 2% hydrochloric acid. Oxidize the filtrate with permanganate solution and add sufficient sodium acetate to combine with the free acid. This may be estimated accurately enough by putting the weight of hydrochloric acid as equal to 20% of the volume after concentrating the solution to about 20 cc. and adding 5 or 6 g. more as a safeguard; 1 g. hydrochloric acid = 3.73 g. of sodium acetate trihydrate. From here the determination is carried on as outlined above.

To determine the vanadium occluded by the tungstic acid, dissolve the latter in sodium carbonate. Add a few tenths of a gram of perborate and boil {vigorously for 10 minutes. Acidify with 3 to 5 cc. of phosphoric acid, add 25 to 40 cc. of sulfuric acid, 1 part of acid to 3 of water, and titrate with ferrous sulfate electrometrically to the permanent drop in potential.

c. **For Molybdenum-chromium-vanadium Steels.**—Exactly as in (a).

The Electrometric Titration of Small Amounts of Vanadium in Tungstic and Molybdic Acids

Samples of pure tungstic acid were dissolved in sodium carbonate solution, and acidified with phosphoric acid; dil. sulfuric acid and a known

amount of ammonium vanadate were added and the mixture was titrated with ferrous sulfate. The character of the vanadium end-point is quite materially altered by the presence of the phosphotungstic acid. As the titration progresses the solution becomes a deep amethyst color, believed to be due to the formation of a vanadyl phosphotungstate, and some distance from the end-point each drop of ferrous sulfate causes a fall in potential followed by a slow return to the former maximum. The period of depression increases slowly to longer than a minute. The first decrease in voltage lasting 2 minutes or longer may be assumed to be permanent and accepted as the true end-point.

TABLE VI

DETERMINATION OF SMALL AMOUNTS OF VANADIUM IN TUNGSTIC ACID

WO₃ taken G.	% V in sample	V taken Mg.	Error Mg. V
10	0.10	10.20	+0.06
5	0.20	10.20	0.00
2	0.50	10.20	−0.03

In spite of the disadvantage of the slow end-point the results are perfectly satisfactory.

Similar samples of pure molybdic acid were dissolved in sodium carbonate solution, acidified with phosphoric and hydrochloric acids, ammonium vanadate was added and the mixtures were titrated. When sulfuric acid alone is used the end-point is slow but the use of hydrochloric acid overcomes this difficulty and the method is rapid and accurate.

It may be pointed out that the method outlined here may be applied to the direct titration of the vanadium occluded by the phosphomolybdate precipitate.[8]

Summary

1. A polarized, bimetallic electrode system affords a more sensitive means of determining the end-point in the reduction of vanadic acid by ferrous sulfate than the usual monometallic combination.

2. In acetic acid solution the reduction of chromic acid by hydrogen peroxide in the presence of vanadic acid may be made selective and gives an excellent means of determining the latter element in all alloy steels. Results checking to 0.005% when using 5g. samples are readily obtained. One advantage over the method involving selective oxidation of vanadium with nitric acid lies in the shortened period of required boiling.

3. Traces of vanadium may be titrated directly in the presence of large quantities of phosphotungstate and phosphomolybdate.

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[8] Cain and Hostetter, *J. Ind. Eng. Chem.*, **4**, 250 (1912). THIS JOURNAL, **43**, 2552 (1921).