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WATERTOWN ARSENAL LABORATORIES

AMPEROMETRIC TITRATIONS

1. Determination of Trace Amounts of Vanadium in Steels and Cast Irons

TECHNICAL REPORT WAL TR 823.3/1

BY

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AND

GEORGE H. CAREY

DATE OF ISSUE - MARCH 1963

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BASIC RESEARCH IN PHYSICAL SCIENCES
D/A PROJECT 1-A-0-10501-B-010

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AMPEROMETRIC TITRATIONS

I. Determination of Trace Amounts of Vanadium in Steels and Cast Irons

Technical Report WAL TR 823.3/1

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TITLE

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I. Determination of Trace Amounts of Vanadium in Steels and Cast Irons

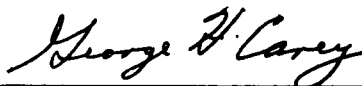
ABSTRACT

An amperometric titration method has been developed for the determination of trace amounts of vanadium in steels and cast irons. This method does not require chemical separations, except in the case when more than 3 percent chromium is present, and may be used on the solution remaining from a routine chromium determination by visual titration.

The method is applicable down to the 0.0002 percent level.

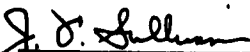


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INTRODUCTION

Potassium permanganate oxidation is generally used as the basis for the visual titrimetric determination of vanadium; however, the oxidation proceeds slowly and, in many instances, offers an end-point difficult to determine. The ferrous ammonium sulfate reduction of vanadium, a rapid reaction, is used as the basis for the somewhat less popular but very accurate potentiometric titration; but, here too, the determination of the end-point is rather tricky and requires numerous readings near the end-point.

Both of the above titration techniques have been employed successfully in the analysis of vanadium steels; however, in the case of trace amounts of vanadium, say less than 0.01 percent, these techniques leave much to be desired. In addition to the difficulties noted above, sample weight must be increased to improve the titrant-to-blank ratio and the bulk of the iron should be removed by bicarbonate and/or mercury cathode separation.

Vanadium content of steels has also been determined by colorimetric and spectrochemical methods. In the colorimetric method, interference caused by the presence of strong acids and elements such as iron, tungsten, chromium, nickel, and molybdenum has been minimized but only with difficulty. For very low concentrations of vanadium, i.e., less than 0.05 percent, spectrochemical methods are generally recommended and have been found satisfactory down to the 0.005 percent level where error as high as 50 percent may be acceptable.

An amperometric titration of vanadium offers an excellent solution to the difficulties and limitations exhibited by the above methods. This technique allows the ferrous ammonium sulfate reduction of vanadium, a rapid reaction, and offers an easily determinable end-point. Data of the titration is required not in the area of the end-point, as in a potentiometric titration, but considerably before and after it. The titration is performed by noting the current which flows as the titrant is added to a solution across which a specific constant potential is applied through an indicator electrode and reference electrode. Depending on the potential applied, this current may be proportional to the concentration of species being titrated, the concentration of excess of titrant, or the concentration of a product of the reaction.¹ In the proposed titration of vanadium with ferrous ammonium sulfate there is no major change in current until excess ferrous ions are present. A plot of the current versus volume of titrant would consist of two straight lines which intersect at the end-point of the titration. The sensitivity of this type of titration should permit the accurate determination of vanadium in the range of 0.0002 to 0.1 percent, the lower limit of which is now undeterminable by other chemical methods.

Parks and Agazzi² amperometrically determined vanadium in samples of steel containing 0.97 percent and 0.03 percent vanadium by ferrous ammonium sulfate reduction in a sulfuric-perchloric acid medium. A rotating platinum electrode at +1.0 volt versus the saturated calomel electrode (S.C.E.) was

used to indicate the changes in ferrous concentration. Rulfs, Lagowski, and Bahor³ used a similar procedure in a sulfuric acid medium on several steel samples containing 0.273 percent to 2.04 percent vanadium. In addition they found 0.005 percent vanadium in a steel with a certified value of 0.003 percent. Titrations were performed with a rotating platinum electrode at +0.65 volt (versus S.C.E.). Hiett and Kobetz⁴ determined the vanadium in silica-alumina cracking catalysts by an amperometric ferrous titration based on the method of Parks and Agazzi.

With the results of the previous workers in mind, it was undertaken to show that extremely small amounts, in the range of 0.0002 to 0.1 percent, of vanadium can be determined accurately and quickly by the use of an amperometric titration with ferrous ammonium sulfate. Furthermore, it can be shown that the sulfuric-phosphoric acid medium used in this laboratory for preparation of steel samples for chromium determination will act as a suitable medium for the titration and that many solutions analyzed for chromium may be subsequently analyzed for traces of vanadium.

EXPERIMENTAL

I. Background

A. Chemistry of the Method

In the usual determination of chromium and vanadium in steel in this laboratory a sample is dissolved in dilute sulfuric-phosphoric acid and the resulting solution oxidized with a solution of silver nitrate-nitric acid. This leaves a solution containing Fe^{+3} , Cr^{+3} , Mn^{+2} , and V^{+5} . Further oxidation with ammonium persulfate (catalyzed by the Ag^{+} present) changes the chromium to Cr^{+6} and the manganese to Mn^{+7} . Excess persulfate is decomposed by boiling the solution and a small amount of hydrochloric acid is added to reduce Mn^{+7} to Mn^{+2} and precipitate the Ag^{+} as AgCl .

The solution is then analyzed for chromium by adding a measured excess of standardized ferrous ammonium sulfate, which reduces Cr^{+6} to Cr^{+3} and V^{+5} to V^{+4} , and back-titrating with standardized potassium permanganate, which oxidizes the excess Fe^{+2} to Fe^{+3} and V^{+4} to V^{+5} . Thus, the milliequivalents of permanganate ion added can be subtracted from the milliequivalents of ferrous ion added and a value obtained for the chromium content of the sample.

This solution is then used for the determination of vanadium. Excess ferrous ammonium sulfate is added to reduce the vanadium to V^{+4} and to reduce the excess permanganate required to observe the end-point in the titration of chromium. Ammonium persulfate is added to oxidize the excess of ferrous ammonium sulfate, and standardized potassium permanganate is then added to oxidize the vanadium to V^{+5} . As stated previously, this reaction proceeds slowly and the end-point of the titration is difficult to

determine accurately, especially if the solution is colored by other elements in the steel sample. By this method the lowest amount of vanadium determinable in a two-gram sample is about 0.03 percent.

Our aim was to use the solution from which the chromium was determined for the amperometric titration of vanadium with ferrous ammonium sulfate. To do this ferrous ions must react with the V^{+5} only. Therefore, the following chemical manipulations were performed on the solution: potassium permanganate was added in excess to insure complete oxidation of vanadium to V^{+5} ; potassium nitrite was added to destroy the excess permanganate; and urea was added to remove the excess nitrite. The solution was then titrated amperometrically with ferrous ammonium sulfate using a rotating platinum electrode at +1.0 volt (versus S.C.E.).

B. Amperometric Titration Technique

1. Apparatus - Figure 1 is a sketch of the apparatus arrangement used in this study.

A Sargent Model XXI Polarograph with synchronous rotating platinum electrode and saturated calomel reference electrode was used to observe the changes in current during a titration.

Standardized ferrous ammonium sulfate was added from a 5-ml micro-buret with the tip immersed in the solution to insure accurate delivery of amounts observed on the buret.

A magnetic stirrer, operating at constant speed, mixed the solution rapidly as titrant was added.

To allow ease of handling, an agar- KNO_3 salt bridge was used between the solution (in a 600-ml beaker) and the working compartment of an H-cell containing saturated KCl. This H-cell had an agar-KCl salt bridge between its working compartment and the S.C.E. compartment.

2. Preliminary Investigations - To find the optimum potential for a titration several current-voltage curves were determined (Figure 2). Sulfuric-phosphoric acid (0.6 molar and 0.24 molar respectively) was tested and found to produce a small residual current from +1.40 to +0.50 volts (versus S.C.E.) (Curve A). The addition of 1 ml of 0.010 normal ferrous ammonium sulfate to 325 ml of this acid mixture produced a significant anodic current from +1.40 to about +0.50 volts with an apparently diffusion-controlled process occurring from +1.40 to about +0.90 volts (Curve B). The addition of 1 ml of concentrated hydrochloric acid to this solution narrowed the potential range of the diffusion-controlled current to +1.10 to +0.90 volts (Curve C).

To determine the effect of a large amount of ferric ions, two grams of "electrolytic-pure" iron powder were dissolved in sulfuric-phosphoric acid and carried through the proposed chemical analysis procedure. A

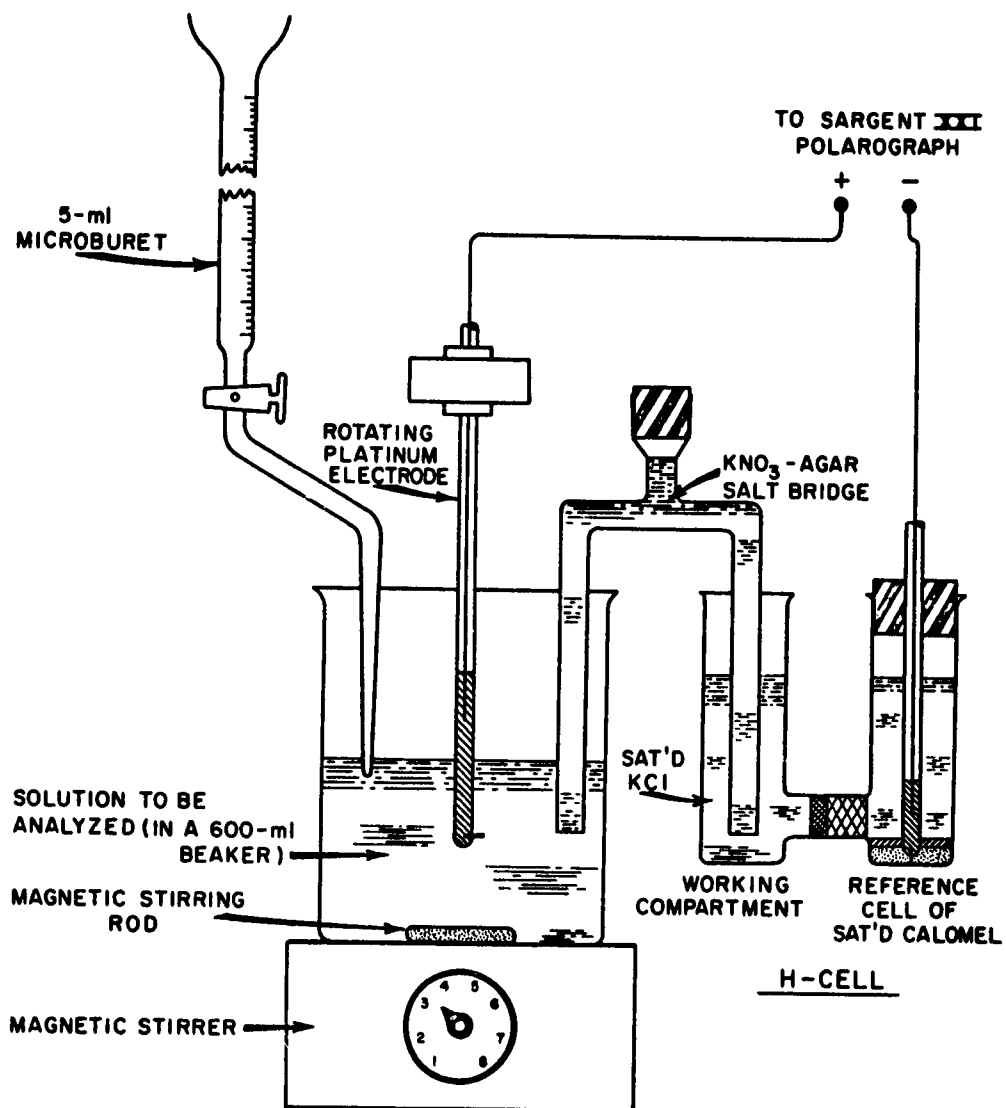


Figure 1. SKETCH OF APPARATUS

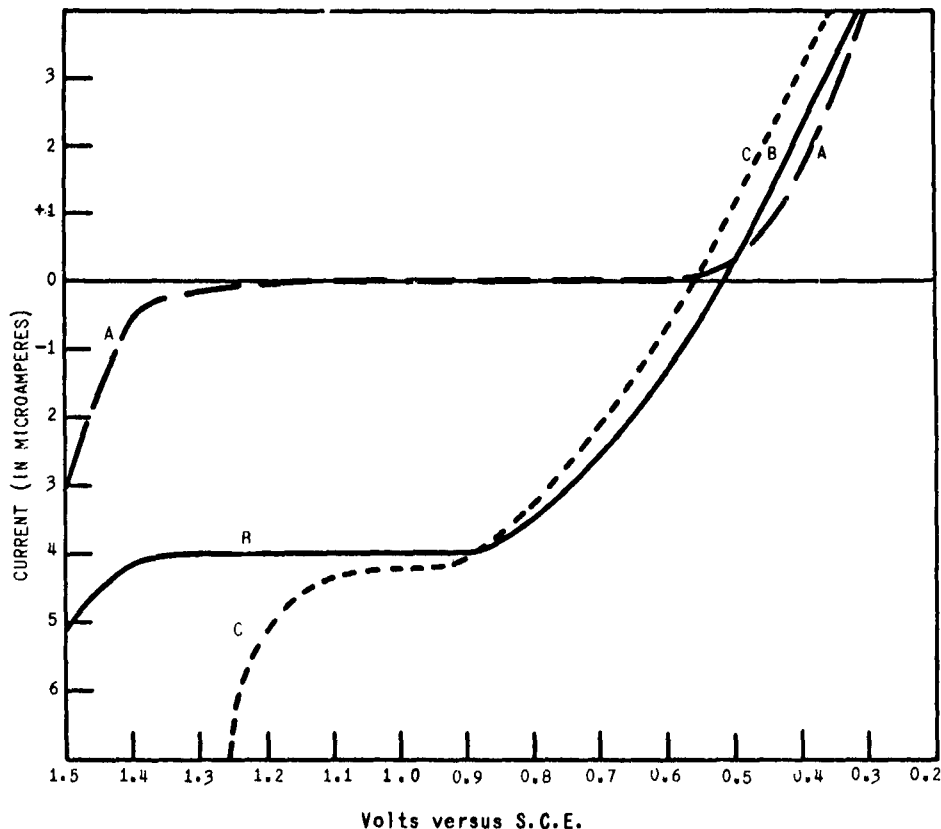


Figure 2. CURRENT-VOLTAGE CURVE OF $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ (0.6 molar and 0.24 molar respectively):
 (A) with no additions; (B) with 1 ml of 0.010 normal $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$; and
 (C) with 1 ml of 0.010 normal $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ and 1 ml of concentrated HCl .

current-voltage curve (Figure 3, Curve A) of this solution showed a residual current line from +1.10 volts to about +0.65 volt after which the platinum indicated either the presence of large amounts of ferric ions or the start of a dissolution pattern of oxide film.⁵ The addition of 0.10 ml of ferrous ammonium sulfate to this solution caused an apparently diffusion-controlled anodic current from +1.10 to +0.90 volts. This last current-voltage curve (Curve B) indicated that at a potential of about +1.00 volt (versus S.C.E.) the platinum electrode acts as a good indicator of ferrous ions in the presence of a supporting electrolyte of ferric, sulfate, phosphate and chloride ions. At this very positive potential there is no reaction from dissolved air and, therefore, no need to remove it. Elements generally found in steel and subjected to the chemical reactions of the proposed procedure should not react at the indicator electrode at this potential.

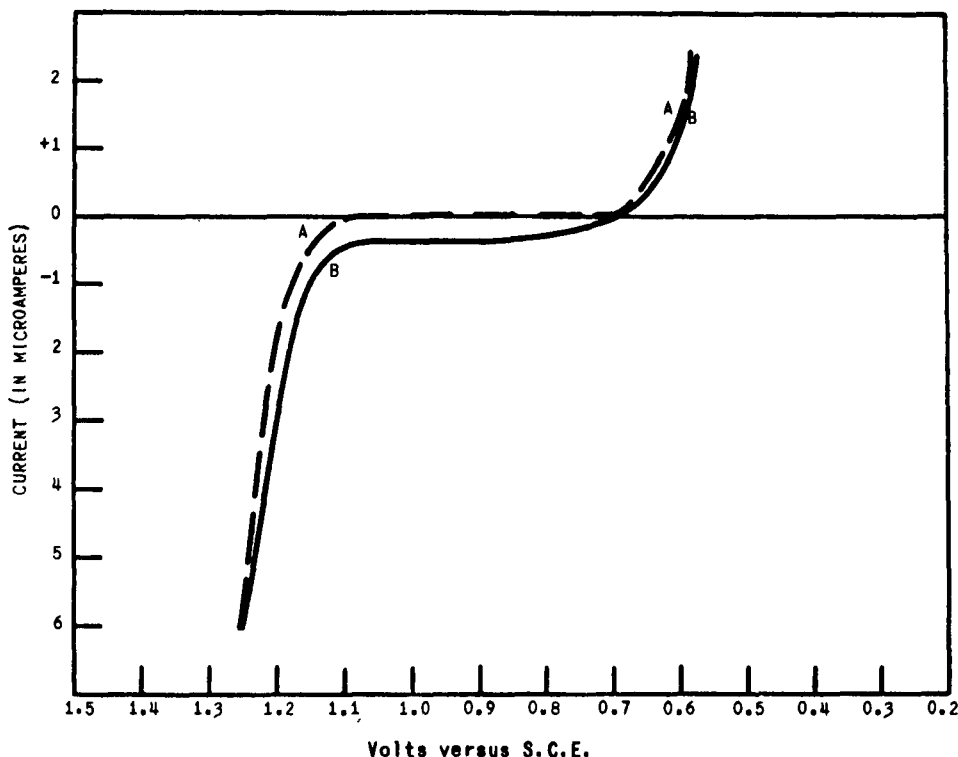


Figure 3. CURRENT-VOLTAGE CURVE OF "ELECTROLYTIC-PURE" IRON CARRIED THROUGH THE PROPOSED PROCEDURE: (A) prior to addition of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$; and (B) with the addition of 0.10 ml of 0.010 normal $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$.

II. Experimentation and Results

A. Current versus Excess Titrant

Ferrous ammonium sulfate (0.010 N) was added to 325 ml of sulfuric-phosphoric acid (0.6 M and 0.24 M respectively) to observe the changes in current with increase in ferrous concentration (Figure 4). Prior to the addition of any ferrous ammonium sulfate, a small residual cathodic current, characteristic of all titrations, was observed. Because of the large volume of acid solution used, the curve of current versus milliliters of titrant did not require corrections for dilution in order to observe the desired straight line relationship. An increase in anodic current of about 0.4 microampere was observed for each 0.10-ml addition of ferrous ammonium sulfate. With a sensitivity setting of 0.008 microampere per millimeter on the polarograph this increase produced a 50-mm deflection of the recorder pen, a very sensitive means of observing current changes.

Figure 5 is a titration curve of the standardization with 20 ml of 0.001804₄ normal potassium dichromate and is representative of most titration curves. Prior to the equivalence point there is slight, if any, change in current. Around the equivalence point there is a rise in current due to equilibrium between reactants. Following this there is linear increase in current with excess of ferrous ammonium sulfate. The intersection of two straight lines drawn from the linear portions of the curve is the equivalence point of the titration.

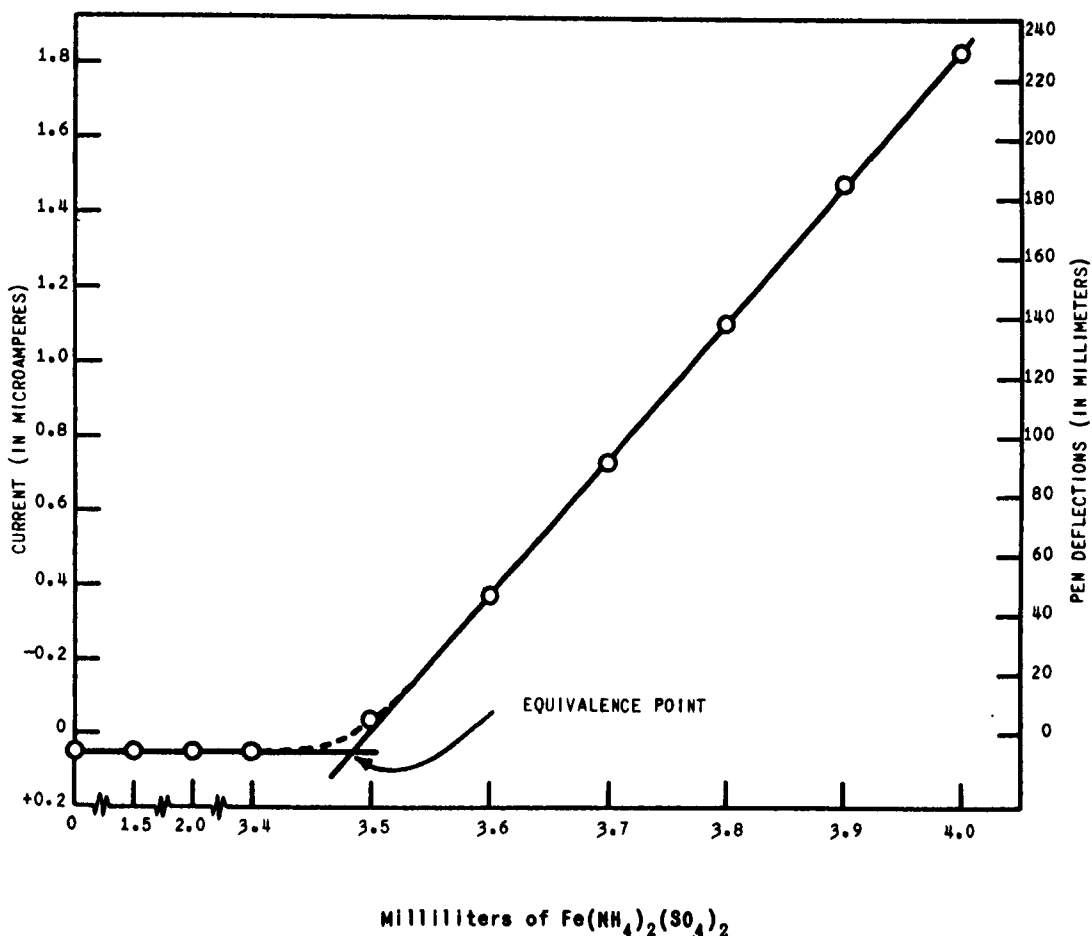


Figure 5. TITRATION CURVE OF THE STANDARDIZATION OF 0.010 NORMAL $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ WITH 20 ml OF 0.001804₄ NORMAL $\text{K}_2\text{Cr}_2\text{O}_7$ IN 325 ml OF H_2SO_4 - H_3PO_4 (0.6 molar and 0.24 molar respectively). Equivalence point equals 3.488 ml.

C. Standardization of Sodium Vanadate

Using the titer of the ferrous ammonium sulfate derived from standardization with potassium dichromate, a solution of 0.0017 normal sodium vanadate (Appendix I), which was to be used in recovery testing, was standardized by amperometric techniques. The results showed the vanadium content to be significantly less than that indicated for the salt employed. This was to be expected as another method used in this laboratory for determining vanadium had shown a comparable deviation, i.e., about 5 percent less than expected.

Two methods of solution preparation were tested in determining amperometrically the vanadium value of the sodium vanadate solution. In the first method the sodium vanadate solution was added to the usual 325 ml of sulfuric-phosphoric acid and titrated directly. In the second method the sodium vanadate from the first titration was reoxidized by permanganate; excess permanganate was destroyed by nitrite; excess nitrite was destroyed by urea; and the titration with ferrous ammonium sulfate was performed in the usual way. This double standardization confirmed the vanadium content of the sodium vanadate and also showed that all the vanadium in the salt was present in the +5 valence state.

D. Vanadium Recovery from Synthetic Standards

Standardized sodium vanadate solution was added to 2.000 grams of NBS 55d iron and the sample dissolved in sulfuric-phosphoric acid. After solution preparation according to the procedure in Appendix II, vanadium was determined amperometrically. Several such synthetic standards were prepared, using 0.0017, 0.00017, and 0.000017 normal sodium vanadate, and analyzed for vanadium. Table I shows the recovery.

From this data it can be seen that vanadium can be determined accurately in the range of 0.1 percent (2 mg V) to 0.0002 percent (0.004 mg V).

TABLE I
Recovery of Vanadium Added to Iron-base* Solutions

mg V added	mg V found (less blank)
2.18	2.18
1.74	1.74
1.31	1.31
.870	.865
.435	.435
.218	.215
.087	.086
.044	.043
.022	.022
.013	.011
.004	.004
.000 (blank)	(.0016)

*Two grams of NBS 55d iron sample. Based on the titration of the blank (0.0016 mg V found) this sample contains <0.0001% V.

E. Effect of Excess Reagents

Titration were performed on excesses of reagents used subsequent to the oxidation with ammonium persulfate. A five-fold excess of urea, five-fold excess of nitrite, ten-fold excess of permanganate, and a five-fold excess of hydrochloric acid did not increase the required number of milliliters of titrant for the titration of the high purity iron sample (NBS 55d). In all cases the sample and excess reagents required only 0.003 ml of ferrous ammonium sulfate (0.010 %). It may be assumed that this is due to traces of vanadium in the iron sample.

F. Analysis of NBS Standard Samples

Several samples of NBS Standard Steels and Cast Irons with certified vanadium values were analyzed by the proposed method. Column C, Table II, shows excellent reproducibility of several duplicate analyses. When these results are compared to their respective certificate values, column B, close agreement to average values is observed and, in all but two samples (30e and 36a), amperometric titration results are within the range of values reported in the certification of the samples.

Samples 4g and 107, cast irons, were titrated without removal of the heavy carbide solids formed during the dissolution of the samples. With these carbides present the recorder pen oscillated considerably at currents greater than 0.4 microampere; but this did not prevent the determination of the end-point. The analytical result on a sample of 107 which was filtered prior to final oxidation with potassium permanganate did not differ significantly from the results on unfiltered solutions.

TABLE II
Determination of Vanadium in NBS Standard Samples

A NBS Standard Sample Number (and Type)	B Certificate Value for % V		C % V Found by Amperometric Titration	
	Average	Range		
4g (Cast Iron)	0.011	0.007-0.016	0.0093	0.0096
10f (Steel, 0.4C)	.003	.002- .004	.0036	.0038
10f (Steel, 0.2C)	.007	.005- .009	.0070	.0070
20d (Steel, 0.4C)	.049	.045- .055	.0457	
30e (Cr-V Steel)	.149	.146- .152	.145	.145
36a (Cr-V Steel)	.006	.005- .007	.0039	
55a (Iron)	<.0005	<.0002-.001	<.0002	<.0002
55d (Iron)	<.001	<.001- .001	<.0001	<.0001
106a (Cr-Mo-Al Steel)	.002*	----	.0030	
107 (Ni-Cr-Mo Cast Iron)	.015	.011- .017	.0146	.0129
			.0140**	

*Only one value reported.

**Solution of sample filtered prior to final oxidation with potassium permanganate.

G. Interference from Chromium

From the analysis of the standard steels and cast irons it appeared that elements normally found in such samples would not interfere. However, on attempting to apply this method to samples with more than 3 percent chromium, high vanadium results would occur. Upon "spiking" pure iron with more than 3 percent chromium and about 1 mg of vanadium it was found that vanadium recovery usually approximated 103 percent. Therefore, it is recommended that this method be limited to samples containing less than 3 percent chromium. Additional experimentation is required to overcome this interference.

CONCLUSIONS

Trace amounts of vanadium in iron-base metals can be determined without chemical separation by an amperometric titration technique.

In addition, the solutions of such metals used for routine chromium determination can be subsequently used for the amperometric titration of vanadium.

Vanadium content down to the 0.0002 percent level can be determined without difficulty.

When more than 3 percent chromium is present, the chromium should be removed, as vanadium results may tend to be high.

APPENDIX I

PREPARATION OF STANDARD SOLUTIONS

A. Standard Ferrous Ammonium Sulfate (0.010 normal) - Dissolve 3.9215 grams of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in about 250 ml of water containing 2.8 ml of concentrated sulfuric acid and dilute to 1 liter. This solution should be standardized daily as the titer changes on standing.

B. Potassium Dichromate (0.001804₄ normal) - Dissolve 0.4424 gram of NBS 136a $\text{K}_2\text{Cr}_2\text{O}_7$ in water and dilute to 500 ml. Transfer 100 ml of this solution to a 1-liter volumetric flask and dilute to the mark. (This dilute solution (0.001804₄ normal) was used in all standardizations of the ferrous ammonium sulfate.)

C. Sodium Vanadate (0.0017 normal) - Dissolve 0.219 gram of NaVO_3 in about 250 ml of water containing a drop (0.05 ml) of concentrated sulfuric acid and dilute to 1 liter. Standardize this solution with the above standard ferrous ammonium sulfate.

D. Sodium Vanadate (0.00017 normal) - Transfer 100 ml of 0.0017 normal sodium vanadate solution to a 1-liter volumetric flask and dilute to mark.

E. Sodium Vanadate (0.000017 normal) - Transfer 100 ml of 0.00017 normal sodium vanadate solution to a 1-liter volumetric flask and dilute to mark.

APPENDIX II

PROPOSED CHEMICAL PROCEDURE

A. Reagents:

Sulfuric-phosphoric Acid Mixture - To 760 ml of water add 160 ml of concentrated sulfuric acid and 80 ml of concentrated phosphoric acid.

Silver Nitrate-Nitric Acid Mixture - To 1350 ml of water add 625 ml of concentrated nitric acid and 135 ml of silver nitrate solution (2.25 percent in water). This mixture is in general use in this laboratory for chromium and manganese determinations.

Ammonium Persulfate Solution - Dissolve 15 grams of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in water and dilute to 100 ml. This solution must be freshly prepared.

Potassium Permanganate Solution - Dissolve 0.3 gram of KMnO_4 in water and dilute to 200 ml.

Hydrochloric Acid Solution - Dilute 50 ml of concentrated hydrochloric acid to 200 ml with water.

Potassium Nitrite Solution - Dissolve 5 grams of KNO_2 in water and dilute to 100 ml.

Urea.

B. Procedure:

1. Transfer 2.000 grams of steel sample to a 600-ml beaker. Add 65 ml of sulfuric-phosphoric acid mixture to dissolve the sample. Heat gently until action ceases.

2. Oxidize the solution with 17 ml of silver nitrate-nitric acid mixture and boil to expel the oxides of nitrogen.

3. Dilute to 300 ml with water and bring to a boil. Carefully add 25 ml of ammonium persulfate solution. If no permanganate color develops within 2 to 3 minutes, add dropwise potassium permanganate solution until a pink color persists.

4. Boil the solution gently for 10 minutes.

5. Carefully add 3 ml of hydrochloric acid solution and boil for 5 minutes after the disappearance of the permanganate color. Small additions of hydrochloric acid may be made if the color does not fade within a few minutes.

6. Cool the solution to room temperature and, if desired, determine the chromium by conventional ferrous ammonium sulfate-potassium permanganate titration. In general the titer of these standardized solutions is about 0.06 normal.

7. After the determination of chromium, or after complete reduction of chromium with ferrous ammonium sulfate, add potassium permanganate solution dropwise to oxidize the vanadium to the +5 valence state. Add about 12 drops in excess after the permanganate color no longer fades.

8. After 2 to 3 minutes add potassium nitrite solution dropwise to dispel the permanganate color, that is, to reduce the permanganate. Add 2 drops in excess.

9. Add one gram of urea and allow the solution to stand for about 10 minutes before performing the amperometric titration.

10. Amperometrically titrate the vanadium with standardized ferrous ammonium sulfate (See Appendix III).

C. Calculation:

$$\text{Percent Vanadium} = \frac{\text{ml}_{\text{FAS}} \times N_{\text{FAS}} \times 0.05095}{w_s} \times 100$$

where

ml_{FAS} = milliliters of ferrous ammonium sulfate required,

N_{FAS} = normality of ferrous ammonium sulfate,

0.05095 = milliequivalent weight of vanadium, and

w_s = weight of sample (in grams).

APPENDIX III

AMPEROMETRIC TITRATION TECHNIQUE

The amperometric titration of vanadium described here is based on the use of a Sargent Model XXI Polarograph. Other apparatus capable of impressing +1.00 volt (versus S.C.E.) on a rotating platinum electrode and capable of determining small currents may be used.

1. Assemble the apparatus as shown in Figure 1, with the beaker containing the titrate (solution to be titrated) in the field of the magnetic stirrer.

2. Introduce the magnetic stirring bar (a Teflon-coated bar was found quite satisfactory).

3. Connect an agar-KNO₃ salt bridge from the titrate to the working compartment of the H-cell. This working compartment contains saturated KCl to minimize changes in the reference compartment due to ionic migration.

4. Introduce the tip of the microburet (5-ml) to a position below the surface of the titrate. The tip should not approximate the same horizontal plane as the rotating platinum wire as this may result in ferrous ammonium sulfate migrating directly to it before mixing with the bulk of the titrate. Such a condition will cause local high concentrations of ferrous ions around the wire, anodically depolarizing this electrode. Additional time will then be required for the electrode to regain equilibrium.

5. With the EMF switch of the polarograph constant at +1.00 volt, the sensitivity setting at 0.008 μ a/mm, the platinum electrode rotating and the damping switch "off", throw the DME switch to the proper polarity and wait until a constant current is reached. This will most likely require a minute or two.

6. After constant current is established add ferrous ammonium sulfate in increments of 0.1 to 0.2 ml from the microburet and note the changes in recorder pen deflection (or in the current). Pen deflection may pass through a maximum but it is the final unchangeable pen deflection which should be recorded. It is suggested that about three additions of ferrous ammonium sulfate be made in order to determine the base line of the titration curve; however, in cases of very small amounts of vanadium this is impractical and the base line may be considered the initial constant current line.

Continue adding the ferrous ammonium sulfate at a moderate rate and until the recorder pen rises about 20 mm and does not return to the vicinity of the base-line current. From this point on add ferrous ammonium sulfate in increments of 0.1 ml or 0.05 ml and note the accompanying pen deflections. Three to five such observations are recommended for increased certainty in the construction of the titration curve.

7. Plot the number of milliliters of titrant added versus the recorder pen deflection. Draw a straight line for the base current and a straight line for the excess ferrous ammonium sulfate. The point of intersection is the equivalence point of the titration. (See Figure 5).

8. Compute the vanadium content of the sample as shown in Appendix II.

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