Designation: E 365 – 99

Standard Test Method for the Determination of Vanadium in Ferrovanadium and Vanadium Alloying Additives[1]

1. Scope

1.1 This test method covers the chemical analysis of ferrovanadium, vanadium carbide, and vanadium-aluminum having chemical compositions within the following limits:

Element	Concentration Range, %
Aluminum	0.01 to 65
Carbon	0.01 to 20
Chromium	0.01 to 1
Manganese	0.01 to 1
Silicon	0.05 to 10
Vanadium	25 to 90

1.2 The test methods in this standard are contained in the sections below:

	Sections
Vanadium by the Permanganate Oxidation—Ferrous Ammonium Sulfate Titration Method	9 to 15

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 5 and in special "Warning" paragraphs throughout these test methods.

2. Referenced Documents

2.1 *ASTM Standards:*

A 102 Specification for Ferrovanadium[2]

D 1193 Specification for Reagent Water[3]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[4]

E 32 Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition[5]

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals[5]

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[5]

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory[6]

3. Significance and Use

3.1 These test methods for the chemical analysis of metals and alloys are primarily intended as referee methods to test such materials for compliance with compositional specifications, particularly those under the jurisdiction of ASTM Committee A1 on Steel, Stainless Steel, and Related Alloys, specifically Specification A 102. It is assumed that all who use these methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory under appropriate quality control practices such as those described in Guide E 882.

4. Reagents

4.1 *Reagents*:

4.1.1 *Purity of Reagents*—Unless otherwise indicated, all reagents used in these test methods shall conform to the "Reagent Grade" Specifications of the American Chemical Society.[7] Other chemicals may be used, provided it is first ascertained that they are of sufficiently high purity to permit their use without adversely affecting the expected performance of the determination, as indicated in the section on "Precision and Bias."

4.1.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

5. Hazards

5.1 For precautions to be observed in the use of certain reagents in these test methods, refer to Practices E 50.

6. Sampling

6.1 For procedures for sampling the material, refer to Practices E 32.

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[1] These test methods are under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.01 on Iron, Steel, and Ferroalloys.

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[2] *Annual Book of ASTM Standards* Vol 01.02.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

[5] *Annual Book of ASTM Standards*, Vol 03.05.

[6] *Annual Book of ASTM Standards*, Vol 03.06.

[7] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

7. Rounding Calculated Values

7.1 Calculated values shall be rounded to the desired number of places as directed in 3.4 to 3.6 of Practice E 29.

8. Interlaboratory Studies

8.1 These methods have been evaluated in accordance with Practice E 173 unless otherwise noted in the precision and bias section.

VANADIUM BY THE PERMANGANATE OXIDATION—FERROUS AMMONIUM SULFATE TITRATION TEST METHOD

9. Scope

9.1 This test method covers the determination of vanadium in ferrovanadium, vanadium carbide, and vanadium-aluminum in concentrations from 25 to 75 %.

10. Summary of Test Method

10.1 Vanadium in a sulfuric acid solution is oxidized at room temperature to V(+V) state by potassium permanganate. The excess permanganate ions are reduced with sodium nitrite and the excess nitrite is destroyed by urea. Vanadium is then titrated with ferrous ammonium sulfate to the V(+V) state with sodium diphenylamine sulfonate as the indicator.

11. Interferences

11.1 The elements ordinarily present do not interfere if their concentrations are under the maximum limits shown in 1.1.

12. Reagents

12.1 *Ferrous Ammonium Sulfate Standard Solution* (0.1 *N*)—Dissolve 39.2 g of ferrous ammonium sulfate ($Fe(NH_4)(SO_4)_2 \cdot H_2O$) in 500 mL of cold H_2SO_4(5 + 95) and dilute to 1 L with H_2SO_4(5 + 95). Standardize the solution as follows: Using a pipet, transfer 50 mL of .10 *N* potassium dichromate solution to a 600-mL beaker containing 280 mL of water to which 10 mL of H_2SO_4(1 + 1), 10 mL of H_3PO_4, and 1.0 mL of sodium diphenylamine sulfonate solution have been added. Using a 100-mL buret, titrate with the ferrous ammonium sulfate solution while stirring. As the end point is approached, add the titrant dropwise. Finally, add fractions of a drop by rinsing the tip of the buret with a stream of water from a wash bottle after forming a partial drop. Continue the titration until the color changes from blue to green. Record the buret reading to the nearest 0.05 mL. Calculate the normality of the ferrous ammonium sulfate solution as follows:

$$\text{Normality} = 0.1\,A/B \tag{1}$$

where:

A = millilitres of 0.1 N $K_2Cr_2O_7$ solution, and
B = millilitres of ferrous ammonium sulfate solution.

12.2 *Potassium Dichromate Standard Solution* (0.1000 *N*)—Dissolve 4.90315 g of primary standard grade potassium dichromate ($K_2Cr_2O_7$) in water, transfer to a 1-L volumetric flask, dilute to volume, and mix. This is a primary standard solution.

12.3 *Potassium Permanganate Solution* (20 g/L)—Dissolve 20 g of potassium permanganate ($KMnO_4$) in water and dilute to 1 L.

12.4 *Sodium Diphenylamine Sulfonate Indicator Solution* (2 g/L):

12.4.1 *Test Method A* (Preparation from Barium Diphenylamine Sulfonate)—Dissolve 0.32 g of barium diphenylamine sulfonate in 100 mL of hot water. Add 0.5 g of sodium sulfate (Na_2SO_4), stir, and filter through a fine paper to remove the $BaSO_4$. Store in a dark-colored bottle.

12.4.2 *Test Method B* (Preparation from Sodium Diphenylamine Sulfonate)—Dissolve 0.20 g of sodium diphenylamine sulfonate in 100 mL of water. Store in a dark-colored bottle.

12.5 *Sodium Nitrite Solution* (10 g/L)—Dissolve 10 g of sodium nitrite ($NaNO_2$) in water and dilute to 1 L.

12.6 *Urea* (NH_2CONH_2).

13. Procedure

13.1 Transfer a 0.50-g sample, weighed to the nearest 0.1 mg, to a 600-mL beaker. Add 50 mL of H_2SO_4(1 + 1), 30 mL of HNO_3, and 3 to 5 drops of HF (Note 1). Cover the beaker and heat at 85 to 100°C until dissolution is complete. Evaporate to the first fumes of H_2SO_4(Note 2). Cool, add 10 mL of H_3PO_4, dilute to 300 mL, and heat at 70 to 90°C until soluble salts are dissolved.

NOTE 1—When the silicon concentration is greater than 1%, increase the amount of HF to 1 to 2 mL.

NOTE 2—Excessive fuming will make dissolution of the salts difficult.

13.2 Add $KMnO_4$ solution to the hot solution, while stirring, until a deep pink color persists, and then boil 2 min. Cool to 15°C or less.

TABLE 1 Statistical Information Permanganate Oxidation-Ferrous Ammonium Sulfate Titration Test Method—Vanadium

Test Specimen	Vanadium Found %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Ferrovanadium (Nominal: 30 V)	28.27	0.15	0.42
2. Vanadium-Aluminum (Nominal: 50 V, 50 A1)	51.73	0.30	0.42
3. Ferrovanadium (BAS No. 205/3, 54.9 V)	54.94	0.18	0.63
4. Ferrovanadium (Nominal: 70 V)	71.99	0.32	0.51

13.3 Add rapidly, while stirring, 0.1 *N* ferrous ammonium sulfate solution until the solution is bright blue with no trace of green color (Note 3). Add $KMnO_4$ solution, while stirring, until the solution remains a deep pink color, and continue stirring for 1 min. Add $NaNO_2$ solution dropwise, while stirring, until the solution is clear yellow, and then add 1 mL in excess. Immediately add 5 g of urea and stir for 2 min. Add 1.0 mL of sodium diphenylamine sulfonate solution. Using a 100-mL buret, titrate with 0.1 *N* ferrous ammonium sulfate solution while stirring. As the end point is approached, add the titrant dropwise; finally add fractions of a drop by rinsing the tip of the buret with a stream of water from a wash bottle after forming a partial drop. Continue the titration until the color changes from blue to green Notes 4 and 5. Record the buret reading to the nearest 0.05 mL.

NOTE 3—An excess of a few millilitres in this preliminary reduction is of no consequence. Do not record the volume used.

NOTE 4—Titration on a white surface with a light in back of the beaker makes the end point easier to detect.

NOTE 5—The color change, while fairly sharp, is from dark blue through light blue to clear green.

14. Calculation

14.1 Calculate the percentage of vanadium as follows:

$$\text{Vanadium, \%} = [A \times B \times 0.050942]/C \times 100 \quad (2)$$

where:

A = millilitres of ferrous ammonium sulfate solution,
B = normality of the ferrous ammonium sulfate solution, and
C = grams of sample used.

15. Precision and Bias [8]

15.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the data summarized in Table 1.

15.2 *Bias*—No information on the accuracy of this test method is available. The user is cautioned to verify, by the use of reference materials, if available, that the precision and bias of this method is adequate for the contemplated use.

16. Keywords

16.1 chemical analysis; ferrovanadium; vanadium alloying additives

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[8] Supporting data are available from ASTM Headquarters. Request RR: E03-1000.

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