Standard Test Method for
Determination of Titanium in Iron Ores and Related Materials by Diantipyrylmethane Ultraviolet Spectrophotometry[1]

1. Scope

1.1 This test method covers the determination of titanium in iron ores, concentrates, and agglomerates in the compositional range from 0.01 % to 6.0 % titanium.

NOTE 1—As used in this test method (except as related to the term *relative standard deviation*), *percent* or "%" refers to mass fraction (wt/wt) of the form g/100g.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 This test method has been evaluated in accordance with Practice E1601 and Guide E1763. Unless otherwise noted in 13, the lower limit in the scope of each method specifies the lowest analyte content that may be analyzed with acceptable error (defined as a nominal 5 % risk of obtaining a 50 % or larger relative difference in results on the same test sample in two laboratories).

1.4 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E877 Practice for Sampling and Sample Preparation of Iron Ores and Related Materials for Determination of Chemical Composition

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology E135.

4. Summary of Test Method

4.1 The sample is decomposed by treatment with hydrochloric, nitric, and sulfuric acids, or by sintering with sodium peroxide, or by fusion with sodium tetraborate and sodium carbonate. Iron is reduced in an acid medium with ascorbic acid, the color is developed with diantipyrylmethane, and the absorbance is measured at approximately 385 nm.

5. Significance and Use

5.1 This test method is intended to be used for compliance with compositional specifications for titanium content. It is assumed that all who use these procedures 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 and that proper waste disposal procedures will be followed. Appropriate quality control practices must be followed such as those described in Guide E882.

6. Interferences

6.1 None of the elements normally found in iron ores interfere.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

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[1] This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.02 on Ores, Concentrates, and Related Metallurgical Materials.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type I or II of Specification D1193. Type III or IV may be used if they effect no measurable change in the blank or sample.

7.3 *Ascorbic Acid Solution* (10 g/100 mL) ($C_6H_8O_6$)—Dissolve 10 g of ascorbic acid ($C_6H_8O_6$) in water and dilute to 100 mL. Prepare fresh as needed.

7.4 *Diantipyrylmethane Solution* (15 g/L) $C_{23}H_{24}O_2N_4 \cdot H_2O$—Dissolve 15 g of the reagent in about 300 mL of water and 30 mL of (H_2SO_4) (1 + 1) and dilute to 1 L with water. If a residue remains, filter and store the filtrate in a brown bottle.

7.5 *Ferric Ammonium Sulfate (100 g/L)*—Dissolve 100 g of ferric ammonium sulfate $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4$ in 800 mL of water containing 5 mL of H_2SO_4 (1 + 1) and dilute to 1 L with water.

7.6 *Potassium Pyrosulfate* ($K_2S_2O_7$).

7.7 *Sodium Tetraborate (Anhydrous) ($Na_2B_4O_7$)*—Dry the commercial sodium tetraborate at 60 °C to 70 °C, then at 160 °C, and finally calcine at 400 °C.

7.8 *Sodium Tetraborate/Sodium Carbonate ($Na_2B_4O_7$/Na_2CO_3) Fusion Mixture*—Mix 1 part of $Na_2B_4O_7$ and 1 part of Na_2CO_3 and store in an airtight container.

7.9 *Standard Titanium Solution:*

7.9.1 *Solution A (1 mL = 0.1 mg Ti)*—Transfer 0.1670 g of TiO_2 (previously calcined at 900 °C) to a platinum crucible, add 3 g to 4 g of $K_2S_2O_7$, cover, and fuse at a temperature of 600 °C until a clear melt is obtained. Place the cooled crucible and cover into a 250-mL beaker, add 50 mL to 60 mL of H_2SO_4 (1 + 9), and heat to dissolve the melt. Wash crucible and cover with H_2SO_4 (1 + 9) and remove, adding the washings to the 250-mL beaker. Transfer the solution of a 1-L volumetric flask, dilute to volume with H_2SO_4 (1 + 9), and mix.

7.9.2 *Solution B (1 mL = 0.02 mg Ti)*—Transfer 50.0 mL of standard titanium Solution A to a 250-mL volumetric flask, dilute to volume with H_2SO_4 (1 + 9), and mix.

8. Hazards

8.1 For precautions to be observed in this test method, refer to Practices E50.

9. Sampling and Sample Preparation

9.1 *Sampling*—The gross sample shall be collected and prepared in accordance with Practice E877.

9.2 *Sample Preparation*—Pulverize the laboratory sample to pass a No. 100 (150-µm) sieve.

Note 2—To facilitate decomposition, some ores such as specular hematite require grinding to pass a No. 200 (75-µm) sieve.10.4.

10. Procedure

Note 3—If the procedure is based on acid decomposition, use steps in 10.1. If the procedure is based on alkaline sintering, use steps in 10.2. If the procedure is based on alkaline fusion, use steps in 10.3.

10.1 *Acid Decomposition:*

10.1.1 Weigh approximately the amount of the test sample specified in the table below into a small weighing bottle previously dried at 150 °C.

Ti content, %	Mass of test portion, g	Amount of H_2SO_4 to be added in 10.1.3, mL	Aliquot, mL
0.01–0.1	1.0	20	20
0.1–0.3	1.0	20	10
0.3–1.0	0.5	10	5
1.0–6.0	0.1	10	5

Dry the bottle and contents for 1 h at 105 °C to 110 °C. Cap the bottle and cool to room temperature in a desiccator. Momentarily release the cap to equalize the pressure and weigh the capped bottle and sample to the nearest 0.1 mg. Repeat the drying and weighing until there is no further loss of mass. Transfer the test sample to a 250-mL beaker and reweigh the capped bottle to the nearest 0.1 mg. The difference between the two masses is the mass of the test sample taken for analysis.

10.1.2 Carry a reagent blank through all steps of the procedure, starting with 10.1.3.

10.1.3 *Decomposition of Sample*—Moisten the test sample with a few milliliters of water, add 30 mL of HCl, cover, and digest below the boiling point until no further attack is apparent. Add 5 mL of HNO_3 and 10 mL to 20 mL of H_2SO_4 (see amounts specified in 10.1.1) evaporate slowly to fumes of H_2SO_4, then heat strongly for 10 min. Allow the solution to cool, add slowly 50 mL of water and 20 mL of HCl, and warm until soluble salts are in solution.

10.1.4 Filter on a fine-textured filter paper and collect the filtrate in a 250-mL beaker. Transfer the residue quantitatively to the filter paper and wash the filter paper two or three times with hot dilute H_2SO_4 (2 + 98) and two or three times with hot water. Reserve the filtrate.

10.1.5 *Treatment of Insoluble Matter*— Ignite the paper and residue in a platinum crucible. Cool, moisten with several drops of water, add 3 drops or 4 drops of dilute H_2SO_4 (1 + 1) and 10 mL of HF. Evaporate slowly to expel silica and excess of H_2SO_4. Cool, add to the residue about 2 g of potassium pyrosulfate, cover the crucible, and fuse over a burner (approximately 500 °C) until a clear melt is obtained.

10.1.6 Dissolve the cool melt in the reserved filtrate from 10.1.4, remove, and wash the crucible and cover, adding the washings to the 250-mL beaker. Transfer the solution to a 200-mL volumetric flask, dilute to volume, and mix. Continue in accordance with 10.4.

10.2 *Alkaline Sintering Decomposition:*

10.2.1 Transfer a sample weight in accordance with the table in 10.1.1 to a dried weighing bottle and dry the test

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[3] *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 the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

TABLE 1 Grand Means and Precision of Titanium Content of the Test Samples as Determined by the Method Described Using Various Decomposition Methods

Sample No.	Decomposition Methods	Grand Mean X, %	Repeatability r, %	Permissible Tolerance P, %	Standard Deviation	
					Within-Laboratories σ_r, %	Between-Laboratories σ_L, %
76-3	Acid	3.7944	0.0788	0.1706	0.0285	0.0582
76-3	Sintering	3.8137	0.0848	0.2765	0.0306	0.0974
76-3	Fusion	3.8122	0.0785	0.1995	0.0283	0.0692
76-16	Acid	0.0399	0.0023	0.0042	0.0008	0.0014
76-16	Sintering	0.0402	0.0026	0.0051	0.0009	0.0017
76-16	Fusion	0.0402	0.0015	0.0034	0.0005	0.0012
76-17	Acid	0.1602	0.0032	0.0102	0.0012	0.0036
76-17	Sintering	0.1625	0.0049	0.0133	0.0018	0.0046
76-17	Fusion	0.1608	0.0055	0.0129	0.0020	0.0044
76-18	Acid	0.1796	0.0049	0.0081	0.0018	0.0027
76-18	Sintering	...	...	...	...	...
76-18	Fusion	0.1856	0.0090	0.0159	0.0032	0.0053

TABLE 2 Regression Equations of the Precisions as Functions of Titanium Content in the Samples for Various Methods of Decomposition

(a) Acid Attack	(b) Sintering	(c) Fusion
$r = 0.0202 \times + 0.0035$	$r = 0.0219 \times + 0.0015$	$r = 0.0197 \times + 0.0040$
$P = 0.0438 \times + 0.0068$	$P = 0.0725 \times - 0.0017$	$P = 0.0508 \times + 0.0074$
$\sigma_r = 0.0072 \times + 0.0016$	$\sigma_r = 0.0079 \times + 0.0005$	$\sigma_r = 0.0071 \times + 0.0014$
$\sigma_L = 0.0150 \times + 0.0022$	$\sigma_L = 0.0256 \times - 0.0008$	$\sigma_L = 0.0176 \times + 0.0025$

sample as described in 10.1.1. Finally transfer the test sample to a 40-mL nickel crucible.

10.2.2 Carry a reagent blank through all steps of the procedure starting with 10.2.3.

10.2.3 Add 3 g of sodium peroxide and mix using a platinum or nickel spatula. Place the crucible for several minutes at the entrance of a muffle furnace set at 400 °C, then place the crucible inside the furnace for about 1 h, for sintering. Remove the crucible and allow to cool.

10.2.4 Transfer the sintered mass to a 250-mL beaker, cover, and add about 75 mL of water. Wash the crucible once with water and once with dilute HCl (1 + 4), adding the washings to the beaker. Acidify carefully with 30 mL of concentrated HCl, cover the beaker, and heat gently until a clear solution is obtained. Add 20 mL of dilute H_2SO_4 (1 + 1) and evaporate slowly to fumes of H_2SO_4; then heat strongly for 10 min. Allow the solution to cool, add slowly 50 mL of water and 20 mL of concentrated HCl, and warm until soluble salts are in solution.

10.2.5 Continue as described in 10.1.4-10.1.6. Finally carry out spectrophotometric measurements as described in 10.4.

10.3 *Alkaline Fusion Decomposition:*

10.3.1 Transfer a test sample weight in accordance with the table in 10.1.1 to a dried weighing bottle and dry the sample portion as described in 10.1.1. Finally transfer the sample to a platinum crucible.

10.3.2 Carry a reagent blank through all steps of the procedure starting with 10.3.3.

10.3.3 Add 5 g of fusion mixture (7.8) and mix, using a platinum or nickel spatula. Cover the crucible and heat in a muffle furnace, first gently at 600 °C and finally for 10 min at 1000 °C to 1050 °C. Remove the crucible and swirl cautiously to cause the cooling melt to solidify in a thin layer on the walls of the crucible.

10.3.4 Place the cooled crucible and cover into a 250-mL beaker and add 100 mL of dilute HCl (1 + 4). Heat gently to dissolve the melt, remove, and wash the crucible, cover, and police adding the washing to the 250-mL beaker.

10.3.5 Transfer the solution to a 200-mL volumetric flask, dilute to volume, and mix. Continue in accordance with 10.4.

10.4 *Preparation of Test Solution for Spectrophotometric Measurements*—Transfer with the help of pipet, an aliquot of the test solution and the blank solution in accordance with the table in 10.1 and transfer into 100-mL volumetric flasks. Add 5 mL of ferric ammonium sulfate solution (7.5), and 10 mL of ascorbic acid solution (7.3), and mix. Add 15 mL of dilute HCl (1 + 1) and 30 mL of diantipyrylmethane solution (7.4), dilute to volume, and mix. Allow the solution to stand for at least 10 min.

10.5 *Preparation of Calibration Solutions for Spectrophotometric Measurements*—Transfer with the help of a pipet (0.0, 1.0, 3.0, 5.0, 7.0, and 10.0 mL) of the titanium standard Solution B (7.9.2) to six 100-mL volumetric flasks, add 5 mL of ferric ammonium sulfate solution (7.5) and 10 mL of ascorbic acid solution (7.3), and mix. Add 15 mL of dilute HCl (1 + 1) and 30 mL of diantipyrylmethane solution (7.4), dilute to volume, and mix. Allow the solution to stand for at least 10 min.

11. Spectrophotometry

11.1 Adjust the spectrophotometer to the initial setting, using water as the reference solution. While maintaining this setting, take spectrophotometric readings of the blank, standard, and test solutions, using a light band centered at approximately 385 nm in a 1-cm cell (see Note 2).

11.2 *Preparation of Calibration Curve*— Subtract the average absorbance of the 0-mL titanium standard solution from the average absorbance of each standard solution and plot the net absorbance against milligrams of titanium per 100 mL of solution.

11.3 *Photometric Range*—The recommended concentration range is from 0.03 mg to 0.2 mg in 100 mL using a cell depth of 1 cm.

NOTE 4—Cells having other dimensions may be used, provided suitable adjustments can be made in the amount of sample and reagent used.

12. Calculation

12.1 Subtract the average absorbance of the reagent blank solution from the average absorbances of each of the test solutions. Convert the net absorbance of the test solutions to milligrams of titanium by means of the calibration curve. Calculate the titanium content as follows:

$$\text{Titanium, \%} = \frac{0.1A}{B} \tag{1}$$

where:

A = titanium found in the aliquot used, mg, and
B = test sample weight in the aliquot, g.

13. Precision[4]

13.1 *Precision*—Statistical data are based on a comparison of results of international tests carried out between 1976 and 1978 involving four iron ore samples. Twenty-four laboratories representing eight ISO member countries including the United States participated in the test program. The grand means and precision of the test samples using various decomposition methods are presented in Table 1. The regression equations of the precisions as functions of titanium content in the samples are shown in Table 2.

13.2 *Bias*—No information on the bias of this test method is known. Accepted reference materials may have not been included in the materials used in the interlaboratory study. Users of the method are encouraged to employ accepted reference materials, if available, and to judge the bias of the method from the difference between the accepted value for the copper content and the mean value from interlaboratory testing of the reference material.

14. Keywords

14.1 diantipyrylmethane; iron ore; photometric titanium; spectrophotometry; titanium

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[4] Supporting data are available from ASTM International Headquarters. Request RR:E16-1006.