



Standard Test Method for Determination of Titanium in Iron Ores and Related Materials by Diantipyrylmethane Ultraviolet Spectrometry¹

This standard is issued under the fixed designation E 878; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

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

1.2 *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:*

D 1193 Specification for Reagent Water²

E 877 Practice for Sampling and Sample Preparation of Iron Ores³

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory³

3. Summary of Test Method

3.1 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.

4. Significance and Use

4.1 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 E 882.

¹ This test method is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.02 on Ores, Slags, Refractories, Cement, and Related Oxide Materials.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 03.06.

5. Interferences

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

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁴ 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.

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

6.3 *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.

6.4 *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) (7.10) and dilute to 1 L with water. If a residue remains, filter and store the filtrate in a brown bottle.

6.5 *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) (6.11) and dilute to 1 L with water.

6.6 *Hydrochloric Acid* (1 + 1)—Mix 1 volume of concentrated hydrochloric acid (HCl) with 1 volume of water.

6.7 *Hydrochloric Acid* (1 + 4)—Mix 1 volume HCl with 4 volumes of water.

6.8 *Potassium Pyrosulfate* ($K_2S_2O_7$).

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

6.10 *Sodium Tetraborate/Sodium Carbonate* ($Na_2B_4O_7/Na_2CO_3$) *Fusion Mixture*—Mix 1 part of $Na_2B_4O_7$ and 1 part

⁴ *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 Pharmacopoeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

of Na₂CO₃ and store in an airtight container.

6.11 *Sulfuric Acid* (1 + 1)—Carefully pour 1 volume of concentrated sulfuric acid (H₂SO₄) into 1 volume of water.

6.12 *Sulfuric Acid* (1 + 9)—Carefully pour 1 volume of H₂SO₄ into 9 volumes of water.

6.13 *Sulfuric Acid* (2 + 98)—Carefully pour 2 volumes of H₂SO₄ into 98 volumes of water.

6.14 *Standard Titanium Solution:*

6.14.1 *Solution A* (1 mL = 0.1 mg Ti)—Transfer 0.1670 g of TiO₂ (previously calcined at 900°C) to a platinum crucible, add 3 to 4 g of K₂S₂O₇, cover, and fuse at a temperature of 600°C until a clear melt is obtained. Place the cooled crucible and cover in a 250-mL beaker, add 50 to 60 mL of H₂SO₄ (1 + 9) (6.12), and heat to dissolve the melt. Wash crucible and cover with H₂SO₄ (1 + 9) (6.12) and remove, adding the washings to the 250-mL beaker. Transfer the solution of a 1-L volumetric flask, dilute to volume with H₂SO₄ (1 + 9) (6.12), and mix.

6.14.2 *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 H₂SO₄ (1 + 9) (6.12), and mix.

7. Sampling and Sample Preparation

7.1 *Sampling*—The gross sample shall be collected and prepared in accordance with Practice E 877.

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

NOTE 1—To facilitate decomposition, some ores such as specular hematite require grinding to pass a No. 200 (75-μm) sieve.

8. Procedure

NOTE 2—If the procedure is based on acid decomposition, use steps in 8.1. If the procedure is based on alkaline sintering, use steps in 8.2. If the procedure is based on alkaline fusion, use steps in 8.3.

8.1 *Acid Decomposition:*

8.1.1 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, %	Weight of test portion, g	Amount of sulfuric acid to be added in 9.1, 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 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 weight loss. 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 weights is the weight of the test sample taken for analysis.

8.1.2 Carry a reagent blank through all steps of the procedure, starting with 8.1.3.

8.1.3 *Decomposition of Sample*—Moisten the test sample with a few millilitres of water, add 30 mL of hydrochloric acid, cover, and digest below the boiling point until no further attack is apparent. Add 5 mL of nitric acid and 10 to 20 mL of sulfuric acid (see amounts specified in 8.1.1) evaporate slowly to fumes of H₂SO₄, then heat strongly for 10 min. Allow the solution to cool, add slowly 50 mL of water and 20 mL of hydrochloric acid, and warm until soluble salts are in solution.

8.1.4 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 it two or three times with hot dilute sulfuric acid (2+98) (6.13) and two or three times with hot water. Reserve the filtrate.

8.1.5 *Treatment of Insoluble Matter*—Ignite the paper and residue in a platinum crucible. Cool, moisten with several drops of water, add 3 or 4 drops of dilute sulfuric acid (1+1) (6.11) and 10 mL of hydrofluoric acid. Evaporate slowly to expel silica and excess of sulfuric acid. 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.

8.1.6 Dissolve the cool melt in the reserved filtrate from 8.1.4, remove, and wash the crucible and cover, adding the

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 _w , %	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

washings to the 250-mL beaker. Transfer the solution to a 200-mL volumetric flask, dilute to volume, and mix. Continue in accordance with 8.4.

8.2 Alkaline Sintering Decomposition:

8.2.1 Transfer a sample weight in accordance with the table in 8.1.1 to a dried weighing bottle and dry the test sample as described in 8.1.1. Finally transfer the test sample to a 40-mL nickel crucible.

8.2.2 Carry a reagent blank through all steps of the procedure starting with 8.2.3.

8.2.3 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 it inside the furnace for about 1 h, for sintering. Remove the crucible and allow to cool.

8.2.4 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) (6.7), 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 H₂SO₄ (1 + 1) (6.11) and evaporate slowly to fumes of H₂SO₄; 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.

8.2.5 Continue as described in 8.1.4-8.1.6. Finally carry out spectrophotometric measurements as described in 8.4.

8.3 Alkaline Fusion Decomposition:

8.3.1 Transfer a test sample weight in accordance with the table in 8.1.1 to a dried weighing bottle and dry the sample portion as described in 8.1.1. Finally transfer the sample to a platinum crucible.

8.3.2 Carry a reagent blank through all steps of the procedure starting with 8.3.3.

8.3.3 Add 5 g of fusion mixture (7.9) 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 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.

8.3.4 Place the cooled crucible and cover in a 250-mL beaker and add 100 mL of dilute hydrochloric acid (1 + 4) (6.7). Heat gently to dissolve the melt, remove, and wash the crucible, cover, and police adding the washing to the 250-mL beaker.

8.3.5 Transfer the solution to a 200-mL volumetric flask, dilute to volume, and mix. Continue in accordance with 8.4.

8.4 *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 8.1 and transfer into 100-mL volumetric flasks. Add 5 mL of ferric ammonium sulfate solution (6.5), and 10 mL of ascorbic acid solution (6.3), and mix. Add 15 mL of dilute hydrochloric acid (1 + 1) (6.6) and 30 mL of diantipyrylmethane solution (6.4), dilute to volume, and mix. Allow the solution to stand for at least 10 min.

8.5 *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 (6.14.2) to six 100-mL volumetric flasks, add 5 mL of ferric ammonium sulfate solution (6.5) and 10 mL of ascorbic acid solution (6.3), and mix. Add 15 mL of dilute hydrochloric acid (1+1) (6.6) and 30 mL of diantipyrylmethane solution (6.4), dilute to volume, and mix. Allow the solution to stand for at least 10 min.

9. Photometry

9.1 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 1).

9.2 *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.

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

NOTE 3—Cells having other dimensions may be used, provided suitable adjustments can be made in the amount of sample and reagent used.

10. Calculation

10.1 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 percentage of titanium as follows:

$$\text{Titanium, \%} = A/(B \times 10) \quad (1)$$

where:

A = titanium found in the aliquot used, mg, and

B = test sample weight in the aliquot, g.

11. Precision⁵

11.1 *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.

11.2 *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.

⁵ Supporting data are available from ASTM Headquarters. Request RR:E16-1006.

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
$r = 0.0202 \times + 0.0035$	$r = 0.0219 \times + 0.0015$	$r = 0.0197 \times + 0.0040$
$P = 0.0438 \times + 0.0068$	$P = 0.0725 \times - 0.0017$	$P = 0.0508 \times + 0.0074$
$\sigma_r = 0.0072 \times + 0.0016$	$\sigma_r = 0.0079 \times + 0.0005$	$\sigma_r = 0.0071 \times + 0.0014$
$\sigma_L = 0.0150 \times + 0.0022$	$\sigma_L = 0.0256 \times - 0.0008$	$\sigma_L = 0.0176 \times + 0.0025$

12. Keywords

12.1 Diantiprylmethane; iron ore; photometric titanium; titanium

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