



Standard Test Method for Iron in Iron Ores and Related Materials by Hydrogen Sulfide Reduction and Dichromate Titration¹

This standard is issued under the fixed designation E 246; 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 total iron in iron ores, concentrates, and agglomerates in the concentration range from 30 to 75 %.

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 276 Test Methods for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Finer for Metal Bearing Ores and Related Materials³

E 877 Practice for Sampling and Sample Preparation of Iron Ores and Related Materials⁴

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory⁴

3. Summary of Test Method

3.1 The sample is dissolved in hydrochloric acid. The insoluble residue is removed by filtration, ignited, and treated for the recovery of iron, and added to the main solution. To this solution containing all the iron, sulfuric acid is added and the solution evaporated to fumes to expel chlorides. The salts are dissolved in water, the solution heated to boiling, and the iron reduced by a rapid stream of hydrogen sulfide. The precipitated sulfides are filtered and washed with an acid-sulfide wash solution until free of iron. The filtrate is then boiled to expel the hydrogen sulfide, cooled, and titrated with potassium dichro-

mate solution using sodium diphenylamine sulfonate as the indicator.

4. Significance and Use

4.1 This test method is intended to be used for compliance with compositional specifications for iron 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.

5. Interferences

5.1 None of the elements normally found in iron ores interfere with this test method. These include vanadium, copper, and small amounts of molybdenum, which occasionally occur in iron ores.

6. Apparatus

6.1 *Analytical Balance and Weights*—The balance used to weigh the sample shall be sensitive to 0.05 mg and shall have a precision of 0.1 mg. Analytical weights shall be of precision grade or calibrated against a set of certified standard weights.

6.2 *Buret*—The buret used to titrate the reduced solution shall be of precision grade, calibrated to tenths of a millilitre, and shall be read to 0.05 mL.

6.3 *Hydrogen Sulfide Generator*—Hydrogen sulfide shall be obtained from a cylinder of the compressed gas or from a Kipp generator. A consistent flow of 1 L/min shall be maintained and the gas passed through a water trap to remove any salts.

6.4 *Glassware*—Beakers or flasks used in the analysis of the sample shall be of chemical-resistant glass and free of etched surfaces. Before using, all glassware shall be cleaned in hot, dilute hydrochloric acid and thoroughly rinsed in water.

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

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 03.05.

⁴ *Annual Book of ASTM Standards*, Vol 03.06.

TABLE 1 Precision Data

Sample	Number of Laboratories	Iron Found %	Repeatability		Reproducibility	
			s_r	R_1 ($2.8 s_r$)	s_R	R_2 ($2.8 s_R$)
Seine River Ore	9	57.52	0.125	0.35	0.126	0.35
Knob Lake Ore	9	58.45	0.097	0.27	0.136	0.38
NBS 27d (64.96 % Fe)	6	65.01	0.057	0.16	0.085	0.24
Chilean Iron Ore	9	66.11	0.102	0.29	0.172	0.48
Pooled standard deviations ^A			0.101		0.137	

^A Weighted by degrees of freedom, n for s_r and $(n - 1)$ for s_R where n = number of laboratories.

all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently 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 Specification D 1193.

7.3 Ferrous Ammonium Sulfate Solution (approximately 0.10 *N*)—Dissolve 40 g of ferrous ammonium sulfate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) in sulfuric acid (1 + 19). Transfer to a 1-L flask and dilute to volume with the same acid. When the sample solution is ready for titration, standardize the $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ solution against the standard potassium dichromate (0.1000 *N*), as described in 9.5. Calculate the millilitres of standard potassium dichromate equivalent to 1 mL of the $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ solution.

7.4 Hydrochloric Acid (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

7.5 Hydrochloric Acid (1 + 50)—Mix 1 volume of HCl (sp gr 1.19) with 50 volumes of water.

7.6 Hydrofluoric Acid (48 %)—Concentrated hydrofluoric acid (HF).

7.7 Hydrogen Sulfide (H_2S).

7.8 Nitric Acid (85 %)—Concentrated nitric acid (HNO_3).

7.9 Phosphoric Acid (sp gr 1.69)—Concentrated phosphoric acid (H_3PO_4).

7.10 Potassium Dichromate, Standard Solution (0.1000 *N*)—Transfer 4.9035 g of primary standard grade potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), previously ground in an agate mortar, and dried at 105 to 110°C, to a 1-L volumetric flask. Dissolve in water and dilute to 1 L. If preferred, this solution may be prepared from reagent grade $\text{K}_2\text{Cr}_2\text{O}_7$, by purifying the salt twice by recrystallizing from water, drying at 110°C, pulverizing in an agate mortar, and drying at 180°C to constant weight. The titer of this solution shall be confirmed by means of standard sample similar in type and composition to the test sample.

7.11 Potassium Permanganate Solution (25 g/L)—Dissolve 25 g of potassium permanganate (KMnO_4) in water and dilute to 1 L.

⁵ *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.

7.12 Sodium Diphenylamine Sulfonate Indicator Solution—Dissolve 0.3 g of sodium diphenylamine sulfonate in 100 mL of water. Store in a dark-colored bottle.

7.13 Sodium Pyrosulfate ($\text{Na}_2\text{S}_2\text{O}_7$).

7.14 Sulfuric Acid (1 + 1)—Carefully mix 1 volume of concentrated sulfuric acid (H_2SO_4 , sp gr 1.84) with 1 volume of water.

7.15 Sulfuric Acid (1 + 19)—Carefully mix 1 volume of concentrated sulfuric acid (H_2SO_4 , sp gr 1.84) with 19 volumes of water.

7.16 Sulfuric Acid-Hydrogen Sulfide Wash Solution—Add 20 mL of concentrated sulfuric acid (H_2SO_4 , sp gr 1.84) to 900 mL of water, cool, dilute to 1 L, and pass a rapid stream of H_2S through it for at least 10 min.

8. Sampling, Test Specimen, and Test Unit

8.1 The test unit shall be collected and prepared in accordance with Practice E 877.

8.2 The test unit shall be pulverized or ground so that at least 95 % passes a No. 100 (150 $\mu\text{-m}$) sieve in accordance with Test Method E 276.

NOTE 1—Some ores, such as specular hematites, may require finer grinding to pass a No. 200 (75- μm) sieve.

9. Procedure

9.1 Transfer approximately 0.50 g of the test specimen to a small weighing bottle previously dried at about 105°C. Dry the bottle and contents for 1 h at 105 to 110°C (Note 2). 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 specimen 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 sample taken for analysis.

NOTE 2—Most ores yield their hygroscopic moisture at this temperature. If a drying temperature other than that specified is required, this shall be determined by mutual agreement between manufacturer and purchaser.

9.2 *Decomposition of the Sample*—Moisten the sample with a few millilitres of water and add 25 mL of HCl. Cover the beaker and heat, maintaining a temperature below boiling until most of the dark particles are dissolved and no further attack is apparent. Add 5 mL of HNO_3 and digest for another 15 min. Remove from the source of heat, wash the sides and cover of the beaker, and dilute to 50 mL with warm water. Filter the insoluble residue on a fine-texture paper. Wash the residue with warm HCl (1 + 50) until the yellow color of ferric chloride is no longer observed and then with warm water six to eight

times. Collect the filtrate and washings in a 600-mL beaker and reserve as the main solution (Note 3). Place the paper and residue in a platinum crucible. Char the paper at a low temperature, then ignite at 950°C. Allow the crucible to cool, moisten the residue with H₂SO₄ (1 + 1), add about 5 mL of HF, and heat gently to remove silica and H₂SO₄ (Note 4). Cool the crucible, add 3 g of Na₂S₂O₇, and heat until a clear melt is obtained. Cool, place the crucible in a 250-mL beaker, add about 25 mL of water and 5 mL of HCl, and warm to dissolve the melt. Rinse and remove the crucible. Add the solution and washings to the main solution.

NOTE 3—If the residue is small in amount and perfectly white, the filtration, and treatment of the residue may be omitted without causing significant error.

NOTE 4—The treatment of the residue depends upon the nature of the minerals present. Many ores require only an H₂SO₄-HF treatment to decompose the residue.

9.3 *Reduction*—To the combined solution add 10 mL of H₂SO₄ (1 + 1) and evaporate to copious fumes of SO₃ (Note 5). Cool, dilute to approximately 100 mL with water, and heat to boiling. Add dropwise KMnO₄ solution until the permanganate color persists. Dilute the solution to 250 mL and again heat to boiling for several minutes. Remove from the source of heat and pass a rapid stream of H₂S through the solution for 15 min. Digest at 60°C for 15 min and filter through a medium-texture paper, collecting the filtrate in a 500-mL Erlenmeyer flask. Wash the precipitated sulfides thoroughly with the H₂SO₄-H₂S wash solution. Add 10 mL of H₂SO₄ (1 + 1) to the solution in the flask and add glass beads to prevent bumping. Boil for 10 min to expel H₂S (lead acetate test paper) and continue boiling for an additional 10 min (Note 6). Remove from the source of heat, cover the flask with a small watch glass, and cool in running water to 20°C.

NOTE 5—If the sample contains much calcium, prolonged fuming with H₂SO₄ may lead to the formation of salts that are difficult to dissolve. Therefore, in the presence of considerable calcium, fume just long enough to expel the chlorides and nitrates. Cool, wash the sides of the beaker with water, and again evaporate to light fumes.

NOTE 6—If the sample contains an appreciable amount of molybdenum, further precipitation may occur in the filtrate when boiling out the H₂S. The effect of residual molybdenum is not significant and may be neglected.

9.4 *Titration*—Add to the cooled solution 5 mL of H₃PO₄ and 5 drops of the sodium diphenylamine sulfonate indicator solution. Dilute to 350 mL and titrate with the standard K₂Cr₂O₇ solution to a distinct purple end point.

9.5 *Determination of Blank*—Determine the blank value of the reagents concurrently with the test determination, using the same amount of all reagents and following all the steps of the procedure. Immediately before titrating with the K₂Cr₂O₇

solution add 1.0 mL, accurately measured, of the FeSO₄·(NH₄)₂SO₄·6H₂O solution. In another beaker place 350 mL of cold H₂SO₄ (1 + 19) and add an accurately measured 1 mL of the FeSO₄·(NH₄)₂SO₄·6H₂O solution. Add 5 mL of H₃PO₄ and 5 drops of the sodium diphenylamine sulfonate indicator solution and titrate with the K₂Cr₂O₇ solution. Record this titration and subtract from the titration of the blank solution to obtain the corrected blank.

NOTE 7—In the absence of iron, the diphenylamine sulfonate indicator does not react with the K₂Cr₂O₇ solution. The addition of the FeSO₄·(NH₄)₂SO₄·6H₂O is, therefore, necessary to promote indicator response in the blank solution. A correction must be made in terms of its equivalent in millilitres of K₂Cr₂O₇ solution.

10. Calculation

10.1 Calculate the percentage of iron as follows:

$$\text{Iron, \%} = [(A - B) \times C/D] \times 100 \quad (1)$$

where:

A = millilitres of K₂Cr₂O₇ required for titration of the sample,

B = millilitres of K₂Cr₂O₇ required for titration of the blank,

C = iron equivalent of the K₂Cr₂O₇, g/mL, and

D = grams of sample used.

11. Precision and Bias

11.1 From six to nine laboratories analyzed four iron ore samples to determine iron. The replication made by the different laboratories ranged from 2 to 4, averaging 3 replicates. The data was studied by the interlaboratory test procedure of Practice E 691-87 modified by weighting certain sums to accommodate the unequal replication.⁶ Table 1 shows a summary of these results. From pooled standard deviations, the overall between-laboratory reproducibility coefficient, *R*, was calculated as being 0.38.

11.2 The agreement of the determination of iron in the NBS Standard Reference Material with the certified value shows no evidence of bias, well within a 95 % confidence level (*R*₂ = 0.24).


12. Keywords

12.1 agglomerates and related materials; concentrates; iron content; iron ores

⁶ Supporting data giving the results of cooperative testing are available from ASTM Headquarters. Request RR: E 16-63, dated April 23, 1968 with an amendment, dated July 27, 1993.

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