Standard Test Methods for Determination of Iron in Iron Ores and Related Materials by Dichromate Titrimetry[1]

1. Scope

1.1 These test methods cover the determination of total iron in iron ores, concentrates, and agglomerates in the concentration range 30 % to 95 % iron.

1.2 The test methods in this standard are contained in the sections indicated as follows:

Test Method A— Iron by the Hydrogen Sulfide Reduction Dichromate Titration Method (30 % to 75 % Fe)

Test Method B—Iron by the Stannous Chloride Reduction Dichromate Titration Method (35 % to 95 % Fe)

Test Method C—Iron by the Silver Reduction Dichromate Titration Method (35 % to 95 % Fe)

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

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.* Specific hazards statements are given in Section 5 and in special "Warning" paragraphs throughout these test methods.

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
E276 Test Method for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Finer for Metal-Bearing Ores and Related Materials
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E877 Practice for Sampling and Sample Preparation of Iron Ores and Related Materials for Determination of Chemical Composition and Physical Properties
E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
E1028 Test Method for Total Iron in Iron Ores and Related Materials by Dichromate Titrimetry (Withdrawn 2003)[3]

3. Significance and Use

3.1 The determination of the total iron content is the primary means for establishing the commercial value of iron ores used in international trade.

3.2 These test methods are intended as referee methods for the determination of iron in iron ores. It is assumed that all who use these test 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 and that proper waste disposal procedures will be followed. Appropriate quality control practices must be followed, such as those described in Guide E882.

4. Apparatus, Reagents, and Instrumental Practices

4.1 *Apparatus*—Specialized apparatus requirements are listed in the "Apparatus" Section in each test method.

4.2 *Reagents:*

4.2.1 *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.[4] Other grades may be used provided it is first ascertained that they are of sufficient purity to permit their use without adversely affecting the expected performance of the determination, as

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[1] These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC, www.chemistry.org. For suggestions on the testing of reagents not listed by the American Chemical Society, see the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD, http://www.usp.org.

indicated in the "Precision and Bias" Section. Reagent water shall conform to Type II as described in Specification D1193.

5. Hazards

5.1 For precautions to be observed in the use of certain reagents and equipment in this test method refer to Practices E50.

6. Sampling and Sample Preparation

6.1 Collect and prepare the test sample in accordance with Practice E877.

6.2 The test sample shall be pulverized to pass a No. 100 (150-µm) sieve in accordance with Test Method E276. To facilitate decomposition some ores, such as specular hematite, require grinding to pass a No. 200 (75-µm) sieve.

TEST METHOD A—IRON BY THE HYDROGEN SULFIDE REDUCTION DICHROMATE TITRATION METHOD

7. Scope

7.1 This test method covers the determination of total iron in iron ores, concentrates, and agglomerates in the concentration range from 30 % to 75 %.

8. Summary of Test Method

8.1 The sample is dissolved in HCl. The insoluble residue is removed by filtration, ignited, treated for the recovery of iron, and added to the main solution. To this solution containing all of the iron, H_2SO_4 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 (H_2S). 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 H_2S, cooled, and titrated with $K_2Cr_2O_7$ solution, using sodium diphenylamine sulfonate as the indicator.

9. Interferences

9.1 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.

10. Apparatus

10.1 *Hydrogen Sulfide Generator*—H_2S 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.

10.1.1 **Warning—**H_2S is extremely toxic. All procedures involving its use must be performed in an efficient fume hood. Refer to Hazards section in Practices E50.

10.2 *Crucibles,* platinum, 25-mL capacity.

11. Reagents and Materials

11.1 *Ferrous Ammonium Sulfate Solution* (approximately 0.10 *N*) —Dissolve 40 g of ferrous ammonium sulfate ($FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$) in H_2SO_4 (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 $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ solution against the standard $K_2Cr_2O_7$ (0.1000 *N*), as described in 12.5. Calculate the millilitres of standard $K_2Cr_2O_7$ equivalent to 1 mL of the $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ solution.

11.2 *Potassium Dichromate, Standard Solution* (0.1000 *N*)—Transfer 4.9031 g of primary standard grade potassium dichromate ($K_2Cr_2O_7$); previously ground in an agate mortar, and dried at 105 °C 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 $K_2Cr_2O_7$, 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.

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

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

11.5 *Sodium Pyrosulfate* ($Na_2S_2O_7$).

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

12. Procedure

12.1 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 °C to 110 °C (Note 1). 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 1—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.

12.2 *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 times to eight times. Collect the filtrate and washings in a 600-mL beaker and reserve as the main solution (Note 2). Place the paper and residue in a platinum crucible. Char the paper at

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.

a low temperature, then ignite at 950 °C. Allow the crucible to cool, moisten the residue with H_2SO_4 (1 + 1), add about 5 mL of HF, and heat gently to remove silica and H_2SO_4 (Note 3). Cool the crucible, add 3 g of $Na_2S_2O_7$, 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 2—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 3—The treatment of the residue depends upon the nature of the minerals present. Many ores require only an H_2SO_4–HF treatment to decompose the residue.

12.3 *Reduction*—To the combined solution add 10 mL of H_2SO_4 (1 + 1) and evaporate to copious fumes of sulfur trioxide (SO_3) (Note 4). Cool, dilute to approximately 100 mL with water, and heat to boiling. Add dropwise $KMnO_4$ 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 H_2S through the solution for 15 min. (**Warning—**Hydrogen sulfide is extremely toxic. All procedures involving its use must be performed in an efficient fume hood. Refer to Hazards section in Practices E50.) 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 H_2SO_4–H_2S wash solution. Add 10 mL of H_2SO_4 (1 + 1) to the solution in the flask and add glass beads to prevent bumping. Boil for 10 min to expel H_2S (lead acetate test paper) and continue boiling for an additional 10 min (Note 5). Remove from the source of heat, cover the flask with a small watch glass, and cool in running water to 20 °C.

NOTE 4—If the sample contains much calcium, prolonged fuming with H_2SO_4 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 5—If the sample contains an appreciable amount of molybdenum, further precipitation may occur in the filtrate when boiling out the H_2S. The effect of residual molybdenum is not significant and may be neglected.

12.4 *Titration*—Add to the cooled solution 5 mL of phosphoric acid (H_3PO_4) and five drops of the sodium diphenylamine sulfonate indicator solution. Dilute to 350 mL and titrate with the standard $K_2Cr_2O_7$ solution to a distinct purple endpoint.

12.5 *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 $K_2Cr_2O_7$ solution, add 1.0 mL, accurately measured, of the $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ solution. In another beaker place 350 mL of cold H_2SO_4 (1 + 9) and add an accurately measured 1 mL of the $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ solution. Add 5 mL of H_3PO_4 and five drops of the sodium diphenylamine sulfonate indicator solution and titrate with the $K_2Cr_2O_7$ solution. Record this titration and subtract from the titration of the blank solution to obtain the corrected blank.

NOTE 6—In the absence of iron, the diphenylamine sulfonate indicator does not react with the $K_2Cr_2O_7$ solution. The addition of the $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ is, therefore, necessary to promote indicator response in the blank solution. A correction must be made in terms of its equivalent in millilitres of $K_2Cr_2O_7$ solution.

13. Calculation

13.1 Calculate the percentage of iron as follows:

$$\text{iron, \%} = \left[(A - B) \times C/D \right] \times 100 \qquad (1)$$

where:

A = millilitres of $K_2Cr_2O_7$ required for titration of the sample,
B = millilitres of $K_2Cr_2O_7$ required for titration of the blank,
C = iron equivalent of the $K_2Cr_2O_7$, g/mL, and
D = grams of sample used.

14. Precision and Bias

14.1 *Precision*—From six to nine laboratories analyzed four iron ore samples to determine iron. The replication made by the different laboratories ranged from two to four, averaging three replicates. The data was studied by the interlaboratory test procedure of Practice E691 – 87 modified by weighting certain sums to accommodate the unequal replication.[5] 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.

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[5] Supporting data giving the results of cooperative testing have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E16-63, dated April 23, 1968, with an amendment, dated July 27, 1993.

14.2 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:

$$(R_2 = 0.24)$$

TEST METHOD B—IRON BY THE STANNOUS CHLORIDE REDUCTION DICHROMATE TITRATION METHOD

15. Scope

15.1 This test method covers the determination of total iron in iron ores, concentrates, and agglomerates in the concentration range from 35 % to 95 %.

16. Summary of Test Method

16.1 This test method provides two alternative dissolution procedures.

16.2 *Acid Decomposition*—The sample is dissolved in HCl. The insoluble residue is removed by filtration, ignited, treated for the recovery of iron, and added to the main solution.

16.3 *Decomposition by Fusion*—The sample is fused with a mixture of sodium carbonate and sodium peroxide (Na_2O_2). The melt is leached with water. For samples containing more than 0.1 % of vanadium or molybdenum, or both, the solution is filtered and the insoluble residue is dissolved in HCl. For other samples the leachate is acidified with HCl.

16.4 *Reduction of the Iron*—Most of the iron is reduced with stannous chloride, followed by the addition of a slight excess of titanium (III) chloride solution. The excess titanium (III) is then oxidized in the hot solution with $HClO_4$. The solution is cooled and the reduced iron is titrated with a standard $K_2Cr_2O_7$ solution using sodium diphenylamine sulfonate as the visual endpoint indicator.

17. Interferences

17.1 This test method covers the analysis of iron ores containing less than 0.1 % copper. In the case of iron ores containing molybdenum or vanadium, or both, these elements are removed by water leach and filtration of the cooled sodium carbonate/sodium peroxide fusion melt. Other elements normally found in iron ores do not interfere.

18. Apparatus

18.1 *Crucibles,* platinum, 25-mL to 30-mL capacity.

18.2 *Crucibles,* zirconium, 25-mL to 30-mL capacity.

18.3 *Weighing Spatula,* of a nonmagnetic material or demagnetized stainless steel.

19. Reagents

19.1 *Iron (III) Ammonium Sulfate (approximately 0.1 N)*—Dissolve 40 g of iron (II) ammonium sulfate [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$] in H_2SO_4 (1 + 19). Transfer to a 1-L volumetric flask, dilute to volume with the same acid, and mix. Standardize against standard $K_2Cr_2O_7$ solution using diphenylamine sulfonate as indicator.

19.2 *Potassium Dichromate, Standard Solution (0.1 N)*—Pulverize about 6 g of $K_2Cr_2O_7$ reagent in an agate mortar, dry in an air-bath at 140 °C for 3 h to 4 h, and cool to room temperature in a desiccator. Dissolve 4.9031 g of the dry reagent in water and dilute the solution with water to exactly 1 L in a volumetric flask. Record the temperature at which this dilution was made.

19.3 *Potassium Permanganate Solution* ($KMnO_4$), 25 g/L.

19.4 *Potassium Pyrosulfate Fine Powder* ($K_2S_2O_7$).

19.5 *Sodium Carbonate Anhydrous Powder* (Na_2CO_3).

19.6 *Sodium Diphenylaminesulfonate Solution*—Dissolve 0.2 g of the reagent ($C_6H_5NC_6H_4 \cdot SO_3Na$) in water and dilute to 100 mL. Store the solution in a brown glass bottle.

19.7 *Sodium Hydroxide Solution* (NaOH), 20 g/L.

19.8 *Sodium Peroxide* (Na_2O_2), dry powder. (**Warning—**Use proper safety practices and equipment when performing Na_2O_2 fusions.)

19.9 *Sulfuric Acid-Phosphoric Acid Mixture*—Pour 150 mL of H_3PO_4 (6.12) into about 400 mL of water. While stirring, add 150 mL of H_2SO_4 (6.20). Cool in a water bath and dilute with water to 1 L.

19.10 *Tin (II) Chloride Solution (100 g/L)*—Dissolve 100 g of crystalline tin (II) chloride ($SnCl_2 \cdot 2H_2O$) in 200 mL of HCl by heating the solution in a water bath. Cool the solution and dilute the water to 1 L. This solution should be stored in a brown glass bottle with the addition of a small quantity of granular or mossy tin metal.

19.11 *Titanium (III) Chloride Solution (2 %)*—Dissolve 1 g of titanium sponge (99.5 % minimum purity) in about 30 mL of HCl in a covered beaker by heating on a steam bath. Cool the solution and dilute with water to 50 mL. Prepare fresh as needed. (If preferred, dilute one volume of commercial titanium (III) chloride solution (about 15 % w/v) with seven volumes of HCl (1 + 1).)

20. Procedure

NOTE 7—If the procedure is based on acid decomposition, use 20.1. If the procedure is based on an alkaline fusion followed by the filtration of the leached melt, (samples containing more than 0.1 % vanadium or molybdenum, or both), use 20.2. If the procedure is based on an alkaline fusion, followed by acidification of the leached melt (samples containing less than 0.1 % of molybdenum or vanadium, or both), use 20.3. (**Warning—**Use proper safety practices and equipment when performing Na_2O_2 fusions.)

20.1 *Acid Decomposition:*

20.1.1 Weigh approximately 0.40 g of sample into a small weighing bottle previously dried at about 105 °C (Note 8). 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 weight loss. Transfer the samples 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 8—For samples of iron content greater than 68 %, weigh approximately 0.38 g.

20.1.2 Carry a reagent blank through all steps of the procedure.

20.1.3 Add 30 mL of HCl, cover the beaker with a watch glass, and heat the solution gently without boiling until no further attack is apparent. Wash the watch glass and dilute to 50 mL with warm water. Filter the insoluble residue on a close-texture paper. Wash the residue with warm HCl (1 + 50), until the yellow color or iron (III) chloride is no longer observed, then wash with warm water six times to eight times. Collect the filtrate and washings in a 400-mL beaker. Start to evaporate this solution.

20.1.4 Place the filter paper and residue in a platinum crucible, dry, and ignite at 750 °C to 800 °C. Allow the crucible to cool, moisten the residue with H_2SO_4 (1 + 1), add about 5 mL of HF, and heat gently to remove silica and H_2SO_4. Add to the cold crucible 2 g of potassium pyrosulfate, heat gently at first, then strongly until a clear melt is obtained. Cool, place the crucible in a 250-mL beaker, add about 25 mL of water and about 5 mL of HCl, and warm to dissolve the melt. Remove and wash the crucible.

20.1.5 Adjust the solution to slight alkalinity with ammonia solution. Heat to coagulate the precipitate, filter on a coarse-texture paper, and wash several times with hot water. Discard the filtrate.

20.1.6 Place the beaker containing the main solution under the funnel and dissolve the precipitate on the filter paper by pouring over it 10 mL of hot HCl (1 + 2), wash the filter, first six times to eight times with warm HCl (1 + 50), then twice with hot water. Evaporate the combined filtrates at low heat to a volume of about 30 mL and continue with 20.4.

20.2 *Fusion Decomposition and Filtration of Leached Melt* (Note 7)*:*

NOTE 9—For blank determination, see 20.1.2.

20.2.1 Dry the sample in accordance with 20.1.1 and transfer to a zirconium crucible, add about 4 g of a (1 + 2) mixture of sodium carbonate and Na_2O_2. Mix thoroughly and place in a muffle furnace at 500 °C ± 10 °C for 30 min. Remove from the furnace and heat over a burner until melted. Continue heating just above the melting point for approximately 1.5 min. Allow the melt to cool, place the crucible in a 400-mL beaker, add about 100 mL of warm water, and heat to leach the melt. Remove the crucible and wash. Reserve the crucible. Cool the solution and filter through a filter paper of dense texture. Wash the paper six times to eight times with NaOH solution (20 g/L) and discard the filtrate and washings.

20.2.2 Wash the precipitate into the original beaker with water, add 10 mL of HCl, and warm to dissolve the precipitate. Dissolve the iron in the reserved crucible in hot HCl (1 + 1). Wash the crucible with hot HCl (1 + 10) and add to the main solution. Wash the filter paper three times with warm HCl (1 + 2), several times with warm HCl (1 + 50), and finally with warm water until the washings are no longer acid, adding the washings to the main solution. Evaporate with low heat to a volume of about 30 mL and continue with 20.4.

20.3 *Fusion-Decomposition and Acidification of Leached Melt* (Note 7) *:*

NOTE 10—For blank determination, see 20.1.2.

20.3.1 Dry the sample in accordance with 20.1.1 and transfer to a zirconium crucible. Add 3 g of Na_2O_2 and mix thoroughly. Place the crucible in a muffle furnace at 400 °C. After 10 min to 15 min remove from the furnace and heat over a burner to the melting point. Fuse, swirling the crucible, until the melt is cherry red and clear.

20.3.2 Allow the melt to cool and place in a 400-mL beaker. Add about 10 mL of water to the crucible and cover the beaker immediately with a watch glass. After the reaction has ceased, empty the contents of the crucible into the beaker, and wash the crucible with about 20 mL of water. Add 20 mL of HCl to the crucible, transfer to the beaker, and rinse the crucible with water. Boil the solution for 2 min to 3 min. Rinse the watch glass and the sides of the beaker with water. The volume of the solution should be between 40 mL and 50 mL. Continue with 20.4.

20.4 *Reduction:*

20.4.1 Heat the solution to just below the boiling point and add three drops to five drops of $KMnO_4$ solution (25 g/L). Maintain at this temperature for 5 min to oxidize any arsenic and organic matter. Wash the cover and inside wall of the beaker with a small amount of hot HCl (1 + 10). Immediately add tin (II) chloride solution (100 g/L), drop by drop, while swirling the liquid in the beaker, until only a light yellow color remains (Note 11).

20.4.2 Reduce the remaining iron (III) by adding titanium (III) chloride solution (2 %) until the yellow color has disappeared, then add an additional three drops to five drops. Wash the inside wall of the beaker with a small amount of water and heat to an incipient boil. Remove from the source of heat and without delay, add all at once 5 mL, dilute $HClO_4$ (35 %). Mix well by swirling for 5 s. Dilute immediately with ice cold water to 200 mL. Cool rapidly to below 15 °C and proceed immediately to 20.5.1.

NOTE 11—It is essential that some iron (III) is left unreduced by the stannous chloride. If all the iron is inadvertently reduced, reoxidize a little iron with a drop of the permanganate solution.

20.5 *Titration:*

20.5.1 To the cold solution, add 30 mL of H_2SO_4–H_3PO_4 mixture and titrate with the standard $K_2Cr_2O_7$ solution, using five drops of the sodium diphenylaminesulfonate solution as indicator. The endpoint is reached when the green color of the solution changes to bluish green and a final drop of the titrant imparts a violet color.

20.5.2 Note the ambient temperature of the $K_2Cr_2O_7$ solution. If this differs by more than 3 °C from the temperature at which it was prepared, make the appropriate volumetric correction: 0.06 % relative to each 3 °C of difference.

NOTE 12—*Example:* The titer should be decreased when the ambient temperature during the titration is higher than the temperature during preparation of the standard solution.

20.6 *Blank Test*—Determine the blank value of the reagents concurrently with the test determination using the same amounts of all reagents and following all the steps of the procedure. In the reduction step, omit the addition of tin (II) chloride solution. Add only three drops to five drops of titanium (III) solution. Immediately before titrating with the

$K_2Cr_2O_7$ solution, add 1.0 mL of the iron (II) ammonium sulfate solution and make the appropriate correction.

NOTE 13—In the absence of iron (II) the diphenylaminesulfonate indicator does not react with dichromate solution. The addition of iron (II) ammonium sulfate therefore is necessary to promote indicator response in the blank solution, and thus allows a suitable correction for the blank in terms of its equivalent in millilitres of the standard dichromate solution.

21. Calculation

21.1 Calculate the iron content as follows:

$$\text{Iron, \% } (m/m) = (V_1 - V_2)/m \times 0.0055847 \times 100 \quad (2)$$

where:

V_1 = volume of $K_2Cr_2O_7$ standard solution used for the titration of the analytical sample, mL,
V_2 = volume of $K_2Cr_2O_7$ standard solution used for the titration of the blank test, mL, and
m = mass of the test portion, g.

22. Precision and Bias[6]

22.1 Seven laboratories analyzed five iron ores of varying composition by this test method. The results are summarized as follows:

Sample Designation	Standard or Assumed Fe Content, %	Average Fe Content Reported
USS QCM-3	65.29	65.195
NBS-27d	64.96	64.949
BCS-302	35.51	35.491
632-1	60.78	60.774
NBS-691	90.8	90.854

Sample Designation	Repeatability Standard Deviation,	R_1	Reproducibility Standard Deviation,	R_2
USS QCM-3	0.117	0.330	0.104	0.441
NBS-27d	0.109	0.309	0.110	0.438
BCS-302	0.132	0.373	0.149	0.563
632-1	0.094	0.266	0.076	0.342
NBS-691	0.195	0.552	0.127	0.658

22.2 Thirty-four laboratories from ten countries including four laboratories in the United States, participated in a concurrent testing program of this test method, under the auspices of WG-23A if ISO Committee TC-102/SC2 using five samples of varying compositions. A summary of the statistical data are given as follows:

Sample	Mean (X)	Repeatability
1	67.1816	0.2196
2	66.7471	0.1699
3	60.6684	0.2831
4	59.5675	0.1942
5	45.8620	0.1739

Sample	Permissible Tolerance	Sigma- R	Sigma- L
1	0.5029	0.07759	0.16902
2	0.2944	0.06002	0.09497
3	0.2680	0.10004	0.06297
4	0.2983	0.06860	0.09357
5	0.3167	0.06145	0.10313

22.3 The regression equations are as follows:

	Correlation Coefficient
$R = 0.0012\ X + 0.1348$	0.2276
$P = 0.0039\ X + 0.1019$	0.3548
Sigma $R = 0.0004\ X + 0.0476$	0.2277
Sigma $L = 0.0013\ X + 0.0250$	0.2935

22.4 *Absence of Bias:*

22.4.1 The cooperative ASTM program, examined for precision, included two NBS and one BCS Standards. The average iron results obtained in the cooperative test program and reported in 22.1 agree within narrow limits with the assigned iron content of the certified reference samples as is indicated as follows:

	Fe Content Found in Test Program	Fe Content Assigned Value
NBS 27d	64.949	64.96
NBS 691	90.854	90.8
BCS-302	35.491	35.51

22.4.2 The deviation of the test results from the assigned iron content of the reference samples is significantly smaller than the R_1 and R_2 precision figures. This test method therefore is shown to be free from any measurable bias.

22.4.3 Further evidence for the absence of any measurable bias is provided by a comparison of the ISO results reported in 22.2 by this test method with the results obtained on the same samples by two other test methods. These test methods have been accepted in the meantime as ISO Standards.

Method and Year of International Test	Sample No.	95 % Confidence Interval			Relative, % of the Mean
Test Method E1028					
WG-23A 1983	76-17	67.115	67.1816	67.2467	100
$TiCl_3$ reduction		67.0440	67.1076	67.1712	99.89
WG-16B 1982					
Ag reduction		67.0395	67.0836	67.1277	99.85
WG-17B 1982					
WG-23A 1983	81-2	59.5310	59.5675	59.6039	100.00
WG-16B 1982		59.5664	59.6058	59.6453	100.06
WG-17B 1982		59.5773	59.6128	59.6483	100.08
WG-23A	76-12	60.6385	60.6683	60.6982	100.00
WG-16B		60.6226	60.6738	60.7249	100.01
WG-17B		60.6022	60.6477	60.6932	99.97

TEST METHOD C—IRON BY THE SILVER REDUCTION DICHROMATE TITRATION METHOD

23. Scope

23.1 This test method covers the determination of total iron in iron ores, concentrates, and agglomerates in the concentration range from 35 % to 95 %.

24. Summary of Test Method

24.1 *Acid Decomposition*—The test sample is dissolved in HCl. The insoluble residue is removed by filtration, ignited, treated for recovery of iron, and added to the main solution.

24.2 *Decomposition of Fusion*—The test sample is fused with Na_2O_2 or sintered with Na_2O_2 at 400 °C, and fused over a burner. The melt is leached with water and acidified with HCl.

24.3 *Reduction of Iron*—The test sample is passed through a silver reductor. After addition of H_2SO_4–H_3PO_4 mixture and

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E16-1008.

diphenylamine sulfonate indicator, the total iron is determined by titration with a standard solution of $K_2Cr_2O_7$.

25. Interferences

25.1 This test method covers the analysis of iron ores containing less than 0.1 % copper. Other elements, particularly vanadium, normally found in iron ores do not interfere.

26. Apparatus

26.1 *Silver Reductor.*

26.1.1 *Preparation of Silver Reductor*—Use a glass column (2 cm in diameter and 25 cm in length) fitted with a stopcock and a reservoir cup (about 100 mL in capacity, 4 cm in diameter, and 9 cm in length).

26.1.1.1 Place glass wool *very lightly* above the stopper. Fill column with HCl (1 + 11). Place silver powder into a 150-mL beaker. Add HCl (1 + 11) and transfer the silver powder into the column using HCl (1 + 11), avoiding the entrapment of air. Pass about 100 mL of HCl (1 + 11) through the column.

NOTE 14—Care must be taken not to let the column dry. Always maintain about 1 mL of HCl (1 + 11) above the silver powder.

NOTE 15—The height of silver in the column is about 17 cm and is adequate for about 18 samples prior to regeneration. The flow rate is from 35 mL/min to 40 mL/min. Alternatively silver can be prepared by reducing silver nitrate with zinc as follows: Dissolve 50 g of $AgNO_3$ in 400 mL of water in a 600-mL beaker. Add 10 mL of HNO_3. Place two zinc metal rods, 15 cm in length, crosswise and leave 4 h or overnight. Wash the precipitated silver thoroughly by decantation using H_2SO_4 (1 + 99). A glass column (2 cm in diameter and 15 cm in length) fitted with a stopcock and reservoir cup (about 100 mL in capacity, 4 cm in diameter, and 9 cm in length) is used. Pack glass wool lightly above the stopper. Transfer the washed, precipitated silver into the column using H_2SO_4 (1 + 99) and avoiding any trapped air. Wash the column with HCl (1 + 99) several times (150 mL are sufficient) at a flow rate of 30 mL/min to 35 mL/min. (Length of the silver column is about 9 cm.) The silver reductor is now ready. Always maintain about 1 mL of HCl (1 + 11) above the column.

26.1.2 *Regeneration of Silver Reductor*—With the passage of iron (III) the silver in the reductor darkens at the very top, forming a greyish ring which extends down. When this ring extends down to about 10 cm, the column should be regenerated as follows: Drain the solution (leaving about 1 cm on the top and wash with 150 mL of H_2SO_4 (1 + 99). Finally keep the level of H_2SO_4 (1 + 99) in the column about 1 cm above the silver. Gently rest two zinc rods in contact with the silver in the column. Leave overnight. The dark color changes to silvery white indicating complete regeneration to metallic silver.

NOTE 16—Passing 50 mL of H_2SO_4 (1 + 99) through the column accelerates the regeneration. Then wash the column several times by passing HCl (1 + 11). The column is ready for re-use. The regeneration can also be done by emptying the contents into a beaker, placing zinc-rods, and repacking as in Note 15.

NOTE 17—If the flow is slow, remove the silver and the glass wool from the column and repack as in 26.1.1. Ensure that the new glass wool is placed very lightly for restoring the flow rate at 30 mL/min to 35 mL/min.

26.2 *Weighing Spatula* of a nonmagnetic material or demagnetized stainless steel.

26.3 *Zirconium (Metal) Crucibles,* 50 mL capacity.

26.4 *Platinum Crucibles,* 25 mL capacity.

27. Reagents and Materials

27.1 *Potassium Dichromate, Standard Solution (0.1 N)*—Pulverize about 6 g of $K_2Cr_2O_7$ reagent in an agate mortar, dry in an air-bath at 140 °C for 3 h to 4 h, and cool to room temperature in a desiccator. Dissolve 4.9031 g of the dry reagent in water and dilute the solution with water to exactly 1 L in a volumetric flask.

27.2 *Potassium Pyrosulfate* ($K_2S_2O_7$) *Fine Powder.*

27.3 *Silver Nitrate* ($AgNO_3$).

27.4 *Silver Powder*—40 mesh to 60 mesh is suitable.

27.5 *Sodium Diphenylaminesulfonate Solution(2 g/L)*—Dissolve 0.2 g of the reagent ($C_6H_5NC_6H_4{\cdot}SO_3Na$) in water and dilute to 100 mL. Store the solution in a brown glass bottle.

27.6 *Sodium Peroxide* (Na_2O_2) dry powder. (**Warning—** Use proper safety practices and equipment when performing Na_2O_2 fusions.)

27.7 *Sulfuric Acid-Phosphoric Acid Mixture*—Pour 150 mL of H_3PO_4 into about 400 mL of water. While stirring, add 150 mL of H_2SO_4. Cool in a water bath and dilute with water to 1 L.

27.8 *Zinc Metal Rods,* about 8 mm in diameter and about 150 mm in length.

NOTE 18—If the procedure is based on acid decomposition, use steps in 28.1. If the procedure is based on fusion, use steps in 28.2. (**Warning—** Use proper safety practices and equipment when performing Na_2O_2 fusions.)

28. Procedure

28.1 *Acid Decomposition:*

28.1.1 Weigh approximately 0.3 g of prepared sample into a small weighing bottle previously dried at about 105 °C. 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 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.

28.1.2 Add 20 mL of HCl, cover the beaker with a watch glass, and heat the solution gently without boiling, to decompose the ore. Wash the watch glass with a jet of water and dilute to 50 mL with warm water. Filter the insoluble residue on a close texture paper. Wash the residue with warm HCl (1 + 50), until the yellow color of iron (III) chloride is no longer observed. Then wash with warm water six times to eight times. Collect the filtrate and washings in a 400-mL beaker.

28.1.3 Place the filter paper and residue in a platinum crucible, dry, and ignite at 750 °C to 800 °C. Allow the crucible to cool, moisten the residue with H_2SO_4 (1 + 1), add about 5 mL of HF, and heat gently to remove silica and H_2SO_4. Add to the cold crucible 2 g of $K_2S_2O_7$ and heat gently at first then strongly until a clear melt is obtained. Cool, place the crucible in a 250-mL beaker, add about 25 mL of water and about 5 mL of HCl, and warm to dissolve the melt. Remove and wash the crucible. Adjust the solution to a slight alkalinity with NH_4OH.

Heat to coagulate the precipitate, filter on a coarse-texture paper, and wash several times with hot water. Discard the filtrate. Place the beaker containing the main solution under the funnel and dissolve the precipitate on the filter paper by pouring over it 5 mL of hot HCl (1 + 2) wash the filter, first six times to eight times with warm HCl (1 + 50) then twice with hot water. Dilute to about 180 mL with water and follow the procedure given under 28.3 – 28.5.

28.2 *Fusion Decomposition (Note 18):*

28.2.1 Dry and weigh the test sample in accordance with 28.1.1 and transfer to a dry zirconium crucible containing 2 g of Na_2O_2. Mix the contents with a dry spatula.

28.2.1.1 Fuse over a Meker burner (low heat) swirling the crucible until the melt is cherry red and clear. Remove the crucible from the heat and swirl it until the melt solidifies on the crucible wall.

NOTE 19—In case of high humidity, place the crucible on a hot plate for 10 min to 15 min to dry the contents.

NOTE 20—If desired, place the crucible in a muffle furnace at 400 °C (prior to fusion) for 10 min to 15 min.

28.2.2 Allow the crucible to cool in air for 1 min to 2 min and place it in a dry 250-mL beaker. Add about 10 mL of water into the crucible, while covering the beaker with a watch glass. After effervescence has ceased, empty the crucible contents into the beaker and wash the crucible with 15 mL to 20 mL of water. Introduce 10 mL of HCl, by means of the crucible, into the beaker and rinse the crucible with water. Boil the solution in the beaker for 3 min to 4 min. Wash the sides of the beaker and watch glass with water and continue boiling for about 30 s. Cool and dilute the solution to about 60 mL with water.

28.3 Place a 600-mL beaker under the silver reductor. Pass the solution through the silver reductor at a rate of 35 mL/min, retaining about 1 cm over the silver top. Rinse the reservoir and column two times to three times with HCl (1 + 11) and drain the rinsings. Finally pass 150 mL of HCl (1 + 11) at a rate of 35 mL/min to elute the reduced iron completely from the silver reductor, leaving 1 cm of the acid over the silver top (Note 14).

28.4 To the reduced iron and washings in the 600-mL beaker, add 30 mL of H_2SO_4–H_3PO_4 mixture and add five drops to six drops of sodium diphenylamine-sulphonate indicator solutions (2 g/L).

28.5 Titrate immediately with standard $K_2Cr_2O_7$ solution to a permanent purple endpoint. The endpoint is discernible within 0.02 mL (Note 21).

NOTE 21—The procedure blank has been established to be 0.02 mL, the same volume required to discern the endpoint.

TABLE 2 Statistical Information

Sample	Mean Iron, %	Repeatability, *r* (2.8 σ *r*)		Reproducibility, *R* (2.8 σ*L*)	
		Fusion	Acid Decomposition	Fusion	Acid Decomposition
76-17	67.18	0.22	0.18	1.54	0.21
81-2	59.57	0.21	0.21	1.47	0.23
76-12	60.67	0.21	0.20	1.47	0.23

TABLE 3 Bias Fusion Decomposition

Sample Designation	Standard Fe Content, %	Average Fe Content Reported
JSS-852 Savage River pellets	67.23	67.084
JSS-850-1 Marcona Pellets	66.78	66.781
NBS-692 Labrador	59.58	59.613
SCH-1 Canadian Standard	60.73	60.648

TABLE 4 Bias Acid Decomposition

Sample Designation	Standard or Assumed Fe Content, %	Average Fe Content Reported
JSS-850-3 Marcona Pellets	66.78	66.814
SCH-1 Canadian Standard	60.73	60.669
NBS-692 Labrador	59.58	59.636
LM-07 Brazilian Ore	45.96	45.928

29. Calculation

29.1 Calculate the iron content as follows:

$$\text{Iron, \% } (m/m) = \frac{T \times 0.0055847 \times 100}{m} = \frac{T \times 0.55847}{m} \qquad (3)$$

where:

T = the volume in millilitres of $K_2Cr_2O_7$ standard solution used for the titration (Note 21), and

m = the mass, in grams of the test portion.

30. Precision and Bias[7]

30.1 *Precision*—Thirty-three laboratories in nine countries, including laboratories from the United States, participated in the international testing of the fusion decomposition procedure of this test method using four iron ore samples of varying composition. Also 17 laboratories in 5 countries analyzed 4 iron ore samples of varying composition by the acid decomposition procedure of this test method.

30.1.1 The test results were conducted under the auspices of WG17B of ISO Committee TC-102/SC2. The precision of this test method is expressed by the following regression formulae:

Fusion Decomposition	Acid Decomposition
$r = 0.0012\ X + 0.1484$	$r = -0.0032\ X + 0.3944$
$p = 0.0085\ X + 0.8789$	$p = -0.0025\ X + 0.4309$
$sigma\ r = 0.0004\ X + 0.0525$	$sigma\ r = -0.0011\ X + 0.1393$
$sigma\ L = 0.0034\ X + 0.3208$	$sigma\ L = -0.0006\ X + 0.1170$

where:

X = the iron content in percent (*m/m*), of the test sample,

r = the permissible tolerance within laboratory (repeatability),

p = the permissible tolerance between laboratories,

sigma r = the within laboratory standard deviation, and

sigma L = the between laboratory standard deviation.

30.1.2 Precision results are shown in Table 2.

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E16-1010.

30.2 *Bias*—Evidence for the absence of any measurable bias is provided by a comparison of the ISO results reported in 30.1 by this test method with the results obtained on the same samples by two other test methods WG16B and WG23A (similar to Test Method B). These test methods have been accepted in the meantime as ISO (DIS) Standards, the comparison is tabulated in Tables 3 and 4.

31. Keywords

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

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