Standard Test Method for
Total Iron in Iron Ores and Related Materials by Dichromate Titrimetry[1]

1. Scope

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

1.2 *This standard does not purport to address all of the safety problems, 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:*

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals[2]

E 877 Practice for Sampling and Sample Preparation of Iron Ores and Related Materials[3]

3. Summary of Test Method

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

3.2 *Decomposition by Fusion*—The sample is fused with a mixture of sodium carbonate and sodium peroxide or sintered with sodium peroxide at 400°C, and fused over a burner. The melt is leached with water and acidified with hydrochloric acid. For samples containing more than 0.1 % vanadium or 0.1 % molybdenum, or both, the melt is leached with water and filtered. The insoluble iron hydroxide is then dissolved in hydrochloric acid.

3.3 *Reduction of the Iron*—Most of the iron is reduced in a hot 6*M* hydrochloric acid medium with stannous chloride, followed by the addition of a slight excess of titanium (III) solution. The excess Ti (III) is oxidized in the hot solution with perchloric acid. The solution is rapidly cooled and the reduced iron is titrated with a standard dichromate solution using sodium diphenylamine sulfonate as indicator.

4. Significance and Use

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

4.2 This test method is intended to be a referee method for the determination of iron in iron ores. It is assummed that the user of this procedure 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.

5. Interferences

5.1 This test method is written for iron ores containing less than 0.1 % of copper. Other elements normally found in iron ores do not interfere with this test method.

6. Apparatus

6.1 *Zirconium*, vitreous carbon, or sintered alumina crucibles, 25 to 30-mL capacity.

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

7. Reagents

7.1 *Purity and Concentration of Reagents*—The purity and concentration of all reagents used shall conform to Practices E 50.

7.2 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

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

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

7.5 *Hydrochloric Acid* (1 + 2)—Mix 1 volume of concentrated hydrochloric acid (HCl) with 2 volumes of water.

7.6 *Hydrochloric Acid* (1 + 10)—Mix 1 volume of concentrated hydrochloric acid (HCl) with 10 volumes of water.

7.7 *Hydrochloric Acid* (1 + 50)—Mix 1 volume of concentrated hydrochloric acid (HCl) with 50 volumes of water.

7.8 *Hydrofluoric Acid* (sp gr 1.15)—Concentrated hydrofluoric acid (48 to 50 % HF).

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[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, Concentrates, and Related Metallurgical Materials.

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

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

7.9 *Ice Water*—Cool water to about 3 to 5°C by adding ice cubes, prepared from distilled water or water of equivalent purity.

7.10 *Iron (II) Ammonium Sulfate Solution* (approximately 0.1 *N*)—Dissolve 40 g of iron (II) ammonium sulfate, ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) in dilute sulfuric acid (7.22). Transfer to a 1-L volumetric flask, dilute to volume with the same acid, and mix. Standardize against the standard potassium dichromate solution (7.13) using diphenylamine sulfonate as indicator (9.6).

7.11 *Perchloric Acid* (1 + 1)—Mix 1 volume of perchloric acid (70 %) ($HClO_4$) with 1 volume of water.

7.12 *Phosphoric Acid* (sp gr 1.57)—Concentrated phosphoric acid (H_3PO_4).

7.13 *Potassium Dichromate, Standard Solution* (0.1 *N*)—Pulverize about 6 g of potassium dichromate ($K_2Cr_2O_7$) reagent in an agate mortar, dry in an air-bath at 140°C for 3 to 4 h, and cool to room temperature in a desiccator. Dissolve 4.9040 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.

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

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

7.16 *Sodium Carbonate Anhydrous Powder* (Na_2CO_3).

7.17 *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.

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

7.19 *Sodium Peroxide* (Na_2O_2), dry powder.

7.20 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

7.21 *Sulfuric Acid* (1+1)—Mix 1 volume of concentrated sulfuric acid (H_2SO_4) with 1 volume of water.

7.22 *Sulfuric Acid* (1 + 19)—Mix 1 volume of concentrated sulfuric acid (H_2SO_4) with 19 volumes of water.

7.23 *Sulfuric Phosphoric Acid Mixture*—Pour 150 mL of phosphoric acid (7.12) into about 400 mL of water. While stirring, add 150 mL of sulfuric acid (7.20). Cool in a water bath and dilute with water to 1 L.

7.24 *Tin (II) Chloride Solution* (100 g/L)—Dissolve 100 g of crystalline tin (II) chloride ($SnCl_2 \cdot 2H_2O$) in 200 mL of hydrochloric acid (7.3) by heating the solution on a water bath. Cool the solution and dilute with 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.

7.25 *Titanium (III) Chloride Solution* (2 %)—Dissolve 1 g of titanium sponge in about 30 mL of hydrochloric acid (7.3) 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 1 volume of commercial titanium (III) chloride solution (about 15 % w/v) with 7 volumes of hydrochloric acid (7.4)).

8. Sample Preparation

8.1 The final sample shall be pulverized to pass a No. 100 (150-µm) sieve in accordance with Practice E 877.

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

9. Hazards

9.1 For precautions to be observed in the use of certain reagents and equipment in this test method, refer to Practices E 50.

10. Procedure

NOTE 2—If the procedure is based on acid decomposition, use 10.1. 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 10.2. 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 10.3.

10.1 *Acid Decomposition*:

10.1.1 Weigh approximately 0.40 g of sample into a small weighing bottle previously dried at about 105°C (Note 3). 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 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 sample taken for analysis.

NOTE 3—For samples of iron content greater than 68 %, weigh approximately 0.38 g.

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

10.1.3 Add 30 mL of hydrochloric acid (7.3), 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 hydrochloric acid (7.7), until the yellow color of iron (III) chloride is no longer observed, then wash with warm water six to eight times. Collect the filtrate and washings in a 400-mL beaker. Start to evaporate this solution.

10.1.4 Place the filter paper and residue in a platinum crucible, dry, and ignite at 750 to 800°C. Allow the crucible to cool, moisten the residue with sulfuric acid (7.21), add about 5 mL of hydrofluoric acid (7.8), and heat gently to remove silica and sulfuric acid. Add to the cold crucible 2 g of potassium pyrosulfate (7.15), 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 hydrochloric acid (7.3), and warm to dissolve the melt. Remove and wash the crucible.

10.1.5 Adjust the solution to slight alkalinity with ammonia solution (7.2). Heat to coagulate the precipitate, filter on a coarse-texture paper, and wash several times with hot water. Discard the filtrate.

10.1.6 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 hydrochloric acid (7.5), wash the filter, first six to eight times with warm hydrochloric acid (7.7), then twice with hot water. Evaporate the combined filtrates at low heat to a volume of about 30 mL and continue with 10.4.

10.2 *Fusion Decomposition and Filtration of Leached Melt* (Note 2):

NOTE 4—For blank determination, see 10.1.2.

10.2.1 Dry the sample in accordance with 10.1.1 and transfer to crucible (6.2), add about 4 g of fusion mixture (1 + 2) mixture of sodium carbonate (7.16) and sodium peroxide (7.19). Mix thoroughly and place in a muffle furnace at 500 ± 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 to eight times with sodium hydroxide solution (7.18) and discard the filtrate and washings.

10.2.2 Wash the precipitate into the original beaker with water, add 10 mL of hydrochloric acid (7.3), and warm to dissolve the precipitate. Dissolve the iron in the reserved crucible in hot hydrochloric acid (7.4). Wash the crucible with hot hydrochloric acid (7.6) and add to the main solution. Wash the filter paper three times with warm hydrochloric acid (7.5), several times with warm hydrochloric acid (7.7), 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 10.4.

10.3 *Fusion Decomposition and Acidification of Leached Melt* (Note 2):

NOTE 5—For blank determination, see 10.1.2.

10.3.1 Dry the sample in accordance with 10.1.1 and transfer to a zirconium crucible (6.2). Add 3 g of sodium peroxide (7.19) and mix thoroughly. Place the crucible in a muffle furnace at 400°C. After 10 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.

10.3.2 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 hydrochloric acid (7.3) to the crucible and transfer to the beaker and rinse the crucible with water. Boil the solution for 2 to 3 min. Rinse the watch glass and the sides of the beaker with water. The volume of the solution should be between 40 and 50 mL. Continue with 10.4.

10.4 *Reduction*:

10.4.1 Heat the solution to just below the boiling point and add 3 to 5 drops of potassium permanganate solution (7.14). 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 hydrochloric acid (7.6). Immediately add tin (II) chloride solution (7.24), drop by drop, while swirling the liquid in the beaker, until only a light yellow color remains (Note 6).

10.4.2 Reduce the remaining iron (III) by adding titanium (III) chloride solution (7.25) until the yellow color has disappeared, then add an additional 3 to 5 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 perchloric acid (7.11). Mix well by swirling for 5 s. Dilute immediately with ice water (7.9) to 200 mL. Cool rapidly to below 15°C and proceed immediately to 10.5.1.

NOTE 6—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 (7.14).

10.5 *Titration*:

10.5.1 To the cold solution, add 30 mL of sulfuric acid-phosphoric acid mixture (7.23) and titrate with the standard potassium dichromate solution (7.13), using five drops of the sodium diphenylaminesulfonate solution (7.17) as indicator. The end point is reached when the green color of the solution changes to bluish green and a final drop of the titrant imparts a violet color.

10.5.2 Note the ambient temperature of the potassium dichromate 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 7—*Example:* The titre should be decreased when the ambient temperature during the titration is higher than the temperature during preparation of the standard solution.

10.6 *Blank Test*—Determine the blank value (10.1.2) 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 3 to 5 drops of Ti (III) solution. Immediately before titrating with the potassium dichromate solution (7.13), add 1.0 mL of the iron (II) ammonium sulfate solution (7.10) and make the appropriate correction.

NOTE 8—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 (7.13).

11. Calculation

11.1 Calculate the iron content as follows:

$$\text{Iron, \% (m/m)} = (V_1 - V_2)/m \times 0.0055847 \times 100 \qquad (1)$$

where:

V_1 = volume of potassium dichromate standard solution (7.13) used for the titration of the analytical sample, mL,

V_2 = volume of potassium dichromate standard solution (7.13) used for the titration of the blank test, mL, and

m = mass of the test portion, g.

12. Precision and Bias [4]

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

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[4] Supporting data are available from ASTM Headquarters. Request RR:E16-1008.

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

	Repeatability		Reproducibility	
Sample Designation	Standard Deviation,	R_1	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

12.2 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 of ISO Committee TC-102/SC2 using 5 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

12.3 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

12.4 *Absence of Bias*:

12.4.1 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 12.1 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

12.4.2 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.

12.4.3 Further evidence for the absence of any measurable bias is provided by a comparison of the ISO results reported in 12.2 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 E 1028					
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

13. Keywords

13.1 agglomerates; concentrates; iron content; iron ores