

Standard Test Method for Determination of Iron in Manganese Ores by Hydrogen Sulfide Reduction-Dichromate Titration¹

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1. Scope

1.1 This test method covers the determination of iron in manganese ore in the range from 2 to 20 %.

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:

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals²

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²

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

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E 135.

4. Summary of Test Method

4.1 The sample is decomposed by treatment with hydrochloric, hydrofluoric, and sulfuric acids. Any residue is treated for the recovery of insoluble iron. The iron is reduced with hydrogen sulfide, the insoluble sulfides are removed by filtration, and the excess hydrogen sulfide is expelled by boiling. After cooling, the reduced iron is titrated with a standard potassium dichromate solution using sodium diphenylamine sulfonate as the indicator.

5. Significance and Use

5.1 This test method is intended to be used for compliance with compositional specifications for iron content in manga-

nese ores. 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.

6. Interferences

6.1 None of the elements normally found in manganese ore interfere with this test method.

7. Reagents and Materials

7.1 *Purity and Concentration of Reagents*—The purity and concentration of the common chemical reagents used shall conform to Practices E 50. Special apparatus and reagents required are located in separate sections preceding the procedure.

7.2 *Ferrous Ammonium Sulfate Solution* (approx. 0.10 N)—Dissolve 40 g of ferrous ammonium sulfate ($\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) 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 $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ solution against the standard potassium dichromate solution (0.1000 N) as described in 11.1. Calculate the millilitres of standard potassium dichromate solution equivalent to 1 mL of the $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ solution.

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

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

7.5 *Hydrogen Sulfide* (H_2S).

7.6 *Hydrogen Sulfide Wash Solution*.

7.6.1 Saturate H_2SO_4 (1+99) with hydrogen sulfide (H_2S). Prepare fresh as needed.

7.7 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

7.8 *Phosphoric Acid* (85 %)—Concentrated phosphoric acid (H_3PO_4).

7.9 *Potassium Dichromate, Standard Solution* (0.1000 N)

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

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² *Annual Book of ASTM Standards*, Vol 03.05.

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

7.9.1 Dissolve 4.9035 g of Primary Standard Grade potassium dichromate ($K_2Cr_2O_4$) in water, transfer to a 1-L volumetric flask, dilute to volume, and mix.

7.10 *Sodium Diphenylamine Sulfonate Indicator Solution* (2 g/L).

7.10.1 Dissolve 0.20 g of sodium diphenylamine sulfonate in 100 mL of water. Store in a dark-colored bottle.

7.11 *Sodium Pyrosulfate* ($Na_2S_2O_7$).

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

7.13 *Sulfuric Acid* (1+1)—Mix 1 volume of concentrated H_2SO_4 (sp gr 1.84) with 1 volume of water.

7.14 *Sulfuric Acid* (1+19)—Mix 1 volume of concentrated H_2SO_4 (sp gr 1.84) with 19 volumes of water.

8. Hazards

8.1 For precautions to be observed in this method, refer to Practice E 50.

9. Sampling and Sample Preparation

9.1 The test unit shall be collected and prepared to maintain the representative iron content in the lot.

9.2 The laboratory sample shall be pulverized to pass a No. 100 (150- μ m) sieve.

9.3 Weigh approximately (within ± 25 mg) an amount of test sample specified as follows:

Content of Iron, %	Weight of Sample, g
2 to 10	2.0
10 to 20	1.0

10. Procedure

10.1 Transfer the test sample to a small, dry weighing bottle and place in a drying oven. After drying at 120°C for 1 h, cap the bottle and cool to room temperature in a desiccator. Momentarily release the cap to equalize pressure and weigh the capped bottle to the nearest 0.1 mg. Repeat the drying and weighing until there is no further weight loss. Transfer the test sample to a 400-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.

10.2 Moisten the sample with a few millilitres of water, add 15 mL of HCl, cover and heat gently until no further attack is apparent. Add 5 mL of HNO_3 and warm until the action subsides. Add 10 to 15 drops of HF and 15 mL of H_2SO_4 , and heat to copious fumes of SO_3 (do not prolong fuming). Cool, rinse the sides of the beaker with a few millilitres of water, and again heat to fumes of SO_3 . Cool, add 100 mL of water, and heat to boiling.

10.3 Filter off any residue through a medium texture paper into a 400-mL beaker and wash the paper and residue with hot water until the iron color is removed from the paper. Reserve the filtrate.

10.4 Ignite the paper and residue in a platinum crucible, cool, moisten with a few drops of water and add 3 to 4 drops of H_2SO_4 (1+1) and 5 mL of HF. Evaporate slowly to expel the silica and the excess H_2SO_4 . Add 3 g of $Na_2S_2O_7$ to the crucible and fuse over a burner until a clear melt is obtained. Dissolve the cool melt in a few millilitres of water and add this

solution and the washings of the crucible and cover to the reserved filtrate.

10.5 Dilute the solution with water to a volume of 250 mL and heat to boiling. Remove from the heat source and pass a rapid stream of H_2S through the solution for 15 min. Digest at 60°C for 15 min and filter through a medium texture paper with the aid of paper pulp into a 500-mL Erlenmeyer flask. Wash the precipitated sulfides thoroughly with the hydrogen sulfide wash solution. Add a few glass beads to the flask to prevent bumping, heat the solution to boiling, and boil for 15 to 20 min to completely expel the H_2S . (Check with lead acetate test paper.) Remove from the heat source, cover the flask with a small watch glass, and cool to 20°C in running water.

10.6 To the cool solution add 5 mL of H_3PO_4 and 5 drops of the sodium diphenylamine sulfonic indicator solution. Dilute with water to approximately 300 mL and titrate with the standard $K_2Cr_2O_7$ solution to a distinct purple end point.

11. Blank Determination

11.1 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 $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ solution. In another beaker place 350 mL of cold H_2SO_4 (1+19) and add an accurately measured 1 mL of the $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ solution. Add 5 mL of 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 1—In the absence of iron, the sodium diphenylamine sulfonate indicator does not react with the $K_2Cr_2O_7$ solution. The addition of the $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ 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.

12. Calculation

12.1 Calculate the percentage of iron as follows:

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

where:

A = millilitres of $K_2Cr_2O_7$ solution required for titration of sample,

B = millilitres of $K_2Cr_2O_7$ solution required for titration of blank,

C = iron value of $K_2Cr_2O_7$ in grams per millilitre, and

D = grams of sample used.

13. Precision and Bias

13.1 *Precision*—Table 1 indicates the precision of this test method between laboratories using standard samples as the unknowns.

13.2 *Bias*—No information on the bias of this test method is known. Accepted values for the reference materials used in the interlaboratory study are not available for evaluation. 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 iron content and the mean value of the reference material.

TABLE 1 Statistical Information

Average Concentration, ^A %	Relative Standard Deviation, ^B %	Number of Determinations	Number of Participating Laboratories
5.18	±0.7	17	8
5.57	±1.6	17	8

^A Each concentration represents a different kind of manganese ore.

^B Relative Standard Deviation, *RSD*, in this test method is calculated as follows:

$$RSD = (100/\bar{X})\sqrt{\sum d^2/(n-1)}$$

where:

\bar{X} = average concentration, %,

d = difference of the determination from the mean, and

n = number of determinations.

14. Keywords

14.1 iron content; manganese ore

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