**Designation: E316 – 11**

# Standard Test Method for
# Determination of Iron in Manganese Ores by Hydrogen Sulfide Reduction-Dichromate Titrimetry[1]

This standard is issued under the fixed designation E316; 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 ($\varepsilon$) indicates an editorial change since the last revision or reapproval.

## 1. Scope

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

NOTE 1—As used in this test method (except as related to the term *relative standard deviation*), "percent" or "%" refers to mass fraction (wt/wt) of the form g/100g.

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

1.3 *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:*[2]

D1193 Specification for Reagent Water

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E135.

## 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 manganese 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 E882.

## 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 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[3]. 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

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[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] 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] *Reagent Chemical, 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

to Type I or II of Specification D1193. Type III or IV may be used if they effect no measurable change in the blank or sample.

7.3 *Ferrous Ammonium Sulfate Solution* (approx. 0.10 *N*)—Dissolve 40 g of ferrous ammonium sulfate ($FeSO_4(NH_4)_2SO_4·6H_2O$) in sulfuric acid (1 + 19). Transfer to a 1-L flask and dilute to volume with sulfuric acid (1 + 19). When the sample solution is ready for titration, standardize the $FeSO_4(NH_4)_2SO_4·6H_2O$ solution against the standard potassium dichromate solution (0.1000 *N*) (7.7) as described in 11.1. Calculate the millilitres of standard potassium dichromate solution equivalent to 1 mL of the $FeSO_4(NH_4)_2SO_4·6H_2O$ solution.

7.4 *Hydrogen Sulfide*—($H_2S$).

7.5 *Hydrogen Sulfide Wash Solution.*

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

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

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

7.7.1 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.

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

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

7.9 *Sodium Pyrosulfate* ($Na_2S_2O_7$).

## 8. Hazards

8.1 For precautions to be observed in this method, refer to Practices E50.

## 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-µm) 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 into 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 masses is the mass 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 drops 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 drops 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 min 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 $FeSO_4(NH_4)_2SO_4·6H_2O$ solution. In another beaker place 350 mL of cold $H_2SO_4$ (1 + 19) and add an accurately measured 1 mL of the $FeSO_4(NH_4)_2SO_4·6H_2O$ 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 2—In the absence of iron, the sodium diphenylamine sulfonate indicator does not react with the $K_2Cr_2O_7$ solution. The addition of the $FeSO_4(NH_4)_2SO_4·6H_2O$ 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 iron content as follows:

TABLE 1 Statistical Information

| Average Iron Content,[A] % | Relative Standard Deviation, % | Number of Determinations | Number of Participating Laboratories |
|---|---|---|---|
| 5.18 | ± 0.7 | 17 | 8 |
| 5.57 | ± 1.6 | 17 | 8 |

[A] Each average iron content represents a different kind of manganese ore.

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

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.

## 14. Keywords

14.1 dichromate titrimetry; iron content; manganese ore

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