INTERNATIONAL

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Standard Test Methods for Determination of Manganese (IV) in Manganese Ores by Redox Titration[1]

This standard is issued under the fixed designation E 465; 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 These test methods cover the determination of manganese dioxide in amounts commonly found in manganese ore. The determination measures the amount of manganese (IV) present in the sample. The result may be expressed as available oxygen or as manganese dioxide. The following test methods are included and may be used interchangeably:

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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 Water[2]

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[1] These test methods are under the jurisdiction of ASTM Committee ~~E-1~~ 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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E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals[3]
E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[3]
E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory[4]

3. ~~Significance and Use~~

~~3.1 This test method is intended to be~~Terminology

3.1 *Definitions*—For definitions of terms used ~~for compliance with compositional specifications for manganese dioxide 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 shall be followed, such as those described in Guide E 882.~~ this test method, refer to Terminology E 135.

4. ~~Interferences~~

~~4.1 The elements ordinarily present~~Significance and Use

4.1 This test method is intended to be used for compliance with compositional specifications for manganese dioxide content in manganese ores. It is assumed that all who~~n~~ 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. Appropriat~~me~~ quality control practices shall be followed, such as those described in Guide E 882.

5. Interferences

5.1 The elements ordinarily present in manganese ores do not interfere in either test method.

6. Reagents and Materials

~~5~~6.1 *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.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

~~5~~6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D 1193.

~~6~~7. Hazards

7.1 For precautions to be observed in these methods, refer to Practice E 50.

8. Sampling and Sample Preparation

~~6~~8.1 The sample shall pass a No. 100 (150-µm) sieve.

TEST METHOD A—FERROUS AMMONIUM SULFATE METHOD

~~7~~9. Summary of Test Method

~~7~~9.1 The test sample is dissolved in an excess of ferrous ammonium sulfate solution. The manganese dioxide reacts with an equivalent amount of ferrous iron. The excess ferrous iron is titrated with standard potassium dichromate solution using sodium diphenylamine sulfonate as an indicator.

~~8~~10. Reagents and Materials

~~8~~10.1 *Ferrous Ammonium Sulfate Solution* (45 g/L)—Dissolve 45 g of ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$] in 1 L of sulfuric acid (H_2SO_4, 1 + 7).

~~8~~10.2 *Potassium Dichromate, Standard Solution* (0.1 *N*~~)—Reagent No. 10 (see Practices E 50).~~
~~8.2.1 Dissolve~~)

10.2.1 Dissolve 4.9035 g of Primary Standard Grade potassium dichromate ($K_2Cr_2O_7$) in water, transfer to a 1-L volumetric flask, dilute to volume, and mix.

~~8~~10.3 *Sodium Diphenylamine Sulfonate Indicator Solution* (2 g/L)~~—Reagent No. 121 (Practices E 50).~~
~~8.3.1 Dissolve~~

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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.
[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 "Reagent Chemicals and Standards," by Joseph Rosin, D. Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

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

~~9~~11. Procedure

~~9~~11.1 Transfer approximately 0.4 g of test sample to a small, dry weighing bottle and place in a drying oven. Dry at 120°C for 1 h, cap the bottle, and cool to room temperature in a desiccator. Momentarily release the cap to equalize the 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 dry 300-mL Erlenmeyer flask and reweigh the capped bottle to the nearest 0.1 mg. The difference is the weight of the test sample.

~~9~~11.2 Add 50.0 mL of the ferrous ammonium sulfate solution, plus an additional 10.0 mL for each 0.1 g of MnO_2 present, to the flask. Close the flask with a stopper equipped with inlet and outlet tubes. Pass carbon dioxide through the flask.

~~9~~11.3 Heat the flask moderately and shake intermittently until the ore is decomposed.

~~9~~11.4 Cool the contents of the flask while maintaining the flow of carbon dioxide.

~~9~~11.5 Unstopper the flask, add 2 mL of sodium diphenylamine sulfonate indicator solution, and 10 mL of H_3PO_4. Dilute to 150 mL with cold water (from which the air was removed by boiling) and titrate the excess ferrous ammonium sulfate with standard $K_2Cr_2O_7$ solution to a permanent purple end point.

~~9~~11.6 The correlation between the solutions of ferrous ammonium sulfate and potassium dichromate is established under test conditions. For this purpose, pour into a flask the same amount of ferrous ammonium sulfate solution used to dissolve the ore, and proceed as directed in ~~9~~ 11.3.

1~~0~~2. Calculation

1~~0~~2.1 Calculate the percentage of manganese dioxide as follows:

$$\text{Manganese dioxide, \%} = [(A - B) \times C \times 4.3465]/D \quad (1)$$

where:

A = millilitres of standard $K_2Cr_2O_7$ solution used to establish the correlation in ~~9~~ 11.6,
B = millilitres of standard $K_2Cr_2O_7$ solution required to titrate the excess of ferrous ammonium sulfate in the sample solution,
C = the normality of standard $K_2Cr_2O_7$ solution, and
D = grams of test sample used.

1~~1~~3. Precision and Bias

1~~1~~3.1 *Precision*—Table 1 indicates the precision of the test method between laboratories.

1~~1~~3.2 *Bias*—No information on the bias of this test method is known. Accepted reference materials may have not been included in the materials used in the interlaboratory study. 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 manganese dioxide content and the mean value from interlaboratory testing of the reference material.

TEST METHOD B—SODIUM OXALATE METHOD

1~~2~~4. Summary of Test Method

1~~2~~4.1 The test sample is dissolved in sulfuric acid in the presence of sodium oxalate. The manganese dioxide reacts with an equivalent amount of oxalate. The excess sodium oxalate is titrated with a standard solution of potassium permanganate.

1~~3~~5. Reagents and Materials

1~~3~~5.1 *1,10 Phenanthroline Indicator Solution* (0.025 *M*)~~—Reagent No. 122 (see Practices E 50).~~

TABLE 1 Statistical Information

Sample	Method	Average Concentration, %	Relative Standard Deviation,[A] %	Number of Determinations	Number of Participating Laboratories
1	A	40.87	0.54	35	7
2	A	70.23	0.47	29	6
1	B	40.90	0.46	29	8
2	B	70.32	0.38	29	8

[A] Relative Standard Deviation, RSD, in this test method is calculated as follows:

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

where:

$\bar{X}$ = average concentration, %,
d = difference of the determination from the mean, and
n = number of determinations.

13.1.1 Dissolve)

15.1.1 Dissolve 1.485 g of 1,10-phenanthroline mononydrate and 0.695 g of ferrousulfate (Fe $SO_4 \cdot 7\ H_2O$) in 50 mL of water. Dilute to 100 mL.

135.2 *Potassium Permanganate, Standard Solution* (0.1 *N*)—Reagent No. 13 (see Practices E 50).

13.2.1)

15.2.1 *Preparation*—Dissolve 3.2 g of potassium permanganate ($KMnO_4$) in 1 L of water. Let stand in the dark for two weeks. Filter, without washing, through a Gooch crucible or a fine porosity fritted-glass crucible. Avoid contact with rubber or other organic material. Store in a dark-colored glass-stoppered bottle.

135.2.2 *Standardization*—Dry a portion of the primary standard sodium oxalate at 105°C. Transfer 0.3000 g of the sodium oxalate to a 600-mL beaker. Add 250 mL of H_2SO_4 (5 + 95), previously boiled for 10 to 15 min and then cooled to 27 ± 3°C, and stir until the oxalate has dissolved. Add 39 to 40 mL (Note 1) of the $KMnO_4$ solution, at a rate of 25 to 35 mL/min, while stirring slowly. Let stand until the pink color disappears (about 45 s) (Note 2). Heat to 55 to 60°C and complete the titration by adding $KMnO_4$ solution until a faint pink color persists for 30 s. Add the last 0.5 to 1 mL dropwise, allowing each drop to become decolorized before adding the next drop. To determine the blank: Titrate 250 mL of H_2SO_4(5 + 95), treated as above, with $KMnO_4$ solution to a faint pink color. The blank correction is usually equivalent to 0.03 × 0.05 mL.

NOTE 1—A 0.3000-g portion of sodium oxalate requires 44.77 mL of $KMnO_4$ solution (0.1 *N*).

NOTE 2—If the $KMnO_4$ solution is too strong, the pink color will fade at this point; begin again, adding a few millilitres less of the InO_4 solution.

135.3 *Sodium Oxalate*—Dry the reagent for 2 h at 105°C prior to use.

146. Procedure

146.1 Transfer approximately 0.4 g of test sample to a small, dry weighing bottle and place in a drying oven. Dry 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 dry 300-mL Erlenmeyer flask and reweigh the capped bottle to the nearest 0.1 mg. The difference is the weight of the sample.

146.2 Add 100 mL of H_2SO_4(1 + 9) and 0.8000 g of sodium oxalate to the flask.

146.3 Cover the flask with a small cover glass and heat on a steam bath to decompose the ore. Swirl the flask occasionally and continue heating until all dark colored particles have disappeared.

146.4 When decomposition is complete, rinse the contents of the flask into a 600-mL beaker and adjust the volume to about 200 mL with hot water. Add 2 to 3 drops of the 1,10 phenanthroline indicator solution and titrate the hot solution (60 to 70°C) with the standard $KMnO_4$ solution (Note 3). At the end point, the color will change from pink to green.

NOTE 3—The titration may be performed without using the indicator by observing a pink end point due to excess potassium permanganate.

146.5 The correlation between the sodium oxalate and the standard permanganate solution is established under test conditions. For this purpose, transfer 0.8000 g of sodium oxalate and 100 mL of H_2SO_4(1 + 9) to a 300-mL Erlenmeyer flask. Proceed as directed in 146.3.

157. Calculation

157.1 Calculate the percentage of manganese dioxide as follows:

$$\text{Manganese dioxide, \%} = [(A - B) \times C \times 4.3465]/D \qquad (2)$$

where:

A = millilitres of standard $KMnO_4$ solution used to titrate 0.8000 g of sodium oxalate,
B = millilitres of standard $KMnO_4$ solution used to titrate the excess of sodium oxalate in the sample solution,
C = normality of the standard $KMnO_4$ solution, and
D = grams of sample used.

168. Precision and Bias

168.1 *Precision*—Table 1 indicates the precision of the test method between laboratories.

168.2 *Bias*—No information on the bias of this test method is known. Accepted reference materials may have not been included in the materials used in the interlaboratory study. 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 manganese dioxide content of the reference material and the mean value from interlaboratory testing of the reference material.

179. Keywords

179.1 manganese dioxide content; manganese ores