



Designation: E465 – 23

# Standard Test Methods for Determination of Manganese (IV) in Manganese Ores by Redox Titrimetry<sup>1</sup>

This standard is issued under the fixed designation E465; 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 ( $\epsilon$ ) 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:

### Sections

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|--------------------------------------------|---------|
| Test Method A (Ferrous Ammonium Sulfate)   | 9 – 13  |
| Test Method B (Periodate (Sodium Oxalate)) | 14 – 18 |

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D1193 Specification for Reagent Water
- E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- 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

<sup>1</sup> 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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

erations 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. 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 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 E882.

## 5. Interferences

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

## 6. Reagents and Materials

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.<sup>3</sup> 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.

<sup>3</sup> *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming 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. Hazards

7.1 For precautions to be observed in these methods, refer to Practice E50.

## 8. Sampling and Sample Preparation

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

### TEST METHOD A—FERROUS AMMONIUM SULFATE METHOD

## 9. Summary of Test Method

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.

## 10. Reagents and Materials

10.1 *Ferrous Ammonium Sulfate Solution* (45 g/L)—Dissolve 45 g of ferrous ammonium sulfate  $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$  in 1 L of  $\text{H}_2\text{SO}_4$  (1 + 7).

10.2 *Potassium Dichromate, Standard Solution* (0.1 N)

10.2.1 Dissolve 4.9035 g of Primary Standard Grade potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) in water, transfer to a 1-L volumetric flask, dilute to volume, and mix.

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

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

## 11. Procedure

11.1 Transfer approximately 0.4 g of test sample to a small, dry weighing bottle and place into 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 mass 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 mass of the test sample.

11.2 Add 50.0 mL of the ferrous ammonium sulfate solution, plus an additional 10.0 mL for each 0.1 g of  $\text{MnO}_2$  present, to the flask. Close the flask with a stopper equipped with inlet and outlet tubes. Pass carbon dioxide ( $\text{CO}_2$ ) through the flask.

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

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

11.5 Open the flask, add 2 mL of sodium diphenylamine sulfonate indicator solution, and 10 mL of  $\text{H}_3\text{PO}_4$ . Dilute to

150 mL with cold water (from which the air was removed by boiling) and titrate the excess ferrous ammonium sulfate with standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution to a permanent purple end point.

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

## 12. Calculation

12.1 Calculate the manganese dioxide content as follows:

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

where:

A = millilitres of standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution used to establish the correlation in 11.6,

B = millilitres of standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution required to titrate the excess of ferrous ammonium sulfate in the sample solution,

C = the normality of standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, and

D = grams of test sample used.

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.

12.2 Rounding of test results obtained using this test method shall be performed in accordance with Practice E29, Rounding Method, unless an alternative rounding method is specified by the customer or applicable material specification.

## 13. Precision and Bias

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

13.2 *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

## 14. Summary of Test Method

14.1 The test sample is dissolved in  $\text{H}_2\text{SO}_4$  in the presence of sodium oxalate. The manganese dioxide reacts with an

TABLE 1 Statistical Information

| Sample | Method | Average Manganese Dioxide Content, % | Relative Standard Deviation, % | 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                                    |