



Designation: E342 – 04

Standard Test Method for Determination of Chromium Oxide in Chrome Ores by Permanganate Titrimetry¹

This standard is issued under the fixed designation E342; 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 This test method covers the determination of chromium oxide (Cr_2O_3) in chrome ores in the concentration range from 25 to 60 %.

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:*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

E276 Test Method for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Finer for Metal-Bearing 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 fusion with sodium peroxide. After leaching in water and boiling to decompose peroxides, the solution is acidified with nitric and sulfuric acids. Residual chromium is oxidized to chromate with silver

nitrate, potassium permanganate, and peroxydisulfate. The excess of permanganate is destroyed by the addition of sodium chloride. After cooling, the chromate is reduced by the addition of a measured excess of a ferrous ammonium sulfate, and the excess titrated with a standard permanganate solution.

5. Significance and Use

5.1 This test method is intended to be used for compliance with compositional specifications for chromium oxide content. 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 chrome ores 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 available³. 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 as defined by Type I of Specification **D1193**.

7.3 *Ammonium Peroxydisulfate Solution (250 g/L)*—Dissolve 25 g of ammonium persulfate (ammonium peroxydisulfate) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in water, and dilute to 100 mL. Prepare fresh as needed.

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 *Anal. 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.

7.4 Ferrous Ammonium Sulfate, Standard Solution (0.2 N)—Dissolve 78.4 g of ferrous ammonium sulfate ($\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) in 1 L of cool H_2SO_4 (5+95). As the ferrous ammonium sulfate solution gradually weakens in reducing power, it is necessary to standardize it daily, or at the same time that the chrome ore is analyzed. To standardize, transfer 100 mL of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ to a 600-mL beaker, dilute to 300 mL with cold H_2SO_4 (5+95), add 2 mL of H_3PO_4 and 2 drops of ortho-phenanthroline ferrous sulfate (Ferroin). Titrate immediately with 0.2 N KMnO_4 solution to a faint, permanent pink color.

7.5 Ferrous Sulfate Solution (0.025 M)—Dissolve 6.95 g of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in 500 mL of water and dilute to 1 L.

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

7.7 Ortho-Phenanthroline Ferrous Sulfate Indicator Solution (0.025 M)—Dissolve 1.485 g of 1,10-phenanthroline monohydrate in 100 mL of ferrous sulfate solution ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

7.8 Phosphoric Acid (sp gr 1.69)—Concentrated phosphoric acid (H_3PO_4).

7.9 Potassium Permanganate Solution (20 g/L)—Dissolve 20 g of potassium permanganate (KMnO_4) in water and dilute to 1 L.

7.10 Potassium Permanganate, Standard Solution (0.2 N)—Dissolve 6.4 g of KMnO_4 in 1 L of water. Standardize against the National Institute of Standards and Technology Standard sodium oxalate or equivalent.

7.11 Silver Nitrate Solution (8 g/L)—Dissolve 8 g of silver nitrate (AgNO_3) in water and dilute to 1 L.

7.12 Sodium Chloride Solution (100 g/L)—Dissolve 10 g of sodium chloride (NaCl) in water and dilute to 100 mL.

7.13 Sodium Peroxide (Na_2O_2).

7.14 Sulfuric Acid (1+1)—Carefully pour 1 volume of concentrated sulfuric acid (H_2SO_4 , sp gr 1.84) into 1 volume of water.

7.15 Sulfuric Acid (5+95)—Carefully pour 5 volumes of concentrated H_2SO_4 (sp gr 1.84) into 95 volumes of water.

8. Hazards

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

9. Sampling, Test Specimens, and Test Units

9.1 The test unit shall be pulverized so that at least 95 % passes a No. 100 (150- μm) sieve in accordance with Test Method E276 and shall be dried at 105 to 110°C for a minimum of 1 h.

10. Procedure

10.1 Transfer 0.50 g of the previously dried sample, weighed to the nearest 0.1 mg to a 30-mL iron crucible (Note 1) and add 8 g of dry Na_2O_2 (Note 2). Thoroughly mix the contents of the crucible and cover the mixture with an additional 1 to 2 g of Na_2O_2 . Cover the crucible with an iron or nickel cover and carefully fuse the contents at 600 to 700°C, preferably in an electric muffle furnace. After the mix has

melted, fuse for several minutes at a low red heat while giving a slight rotary motion to the crucible to ensure complete decomposition.

NOTE 1—Ordinary iron crucibles which may contain significant amounts of chromium should be avoided. Crucibles made of ingot iron are satisfactory.

NOTE 2—If about 0.2 g of very fine pulverized sugar charcoal is mixed with the Na_2O_2 , only about 5 g of the peroxide is required. After heating for about 30 s, ignition of the charcoal takes place, and the crucible will suddenly become a dull red on the outside. The total time required to complete the fusion is about 2 min. By thus shortening the time for fusion and contact with the flux, the life of the crucible is extended.

10.2 Place the cool crucible and cover in a 600-mL covered beaker, leach the melt with 150 mL of water, remove the crucible and cover, and rinse. Boil 10 min to destroy the residual peroxide. Add to the cooled solution 60 mL of H_2SO_4 (1+1) and 5 mL of HNO_3 and boil for several minutes until any iron scale from the crucible is dissolved. Add 15 mL of AgNO_3 solution, 2 drops of KMnO_4 solution (7.9), and 10 mL of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution and boil for 5 min. Add 10 mL of NaCl solution and boil for 5 to 10 min after the KMnO_4 or any MnO_2 has completely disappeared.

10.3 Cool, and if necessary, dilute with cold water to 350 mL, then add 3 to 5 mL of H_3PO_4 (7.8). Add a measured excess of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. The point at which reduction is complete can be detected by the development of deep green color. The $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ may be added either as 0.2 N solution (7.4) or a weighed amount of the salt (Note 3). Add 2 drops of orthophenanthroline ferrous sulfate (Ferroin) as an indicator. Titrate the excess $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ with 0.2 N KMnO_4 solution. The end point is reached when the solution becomes clear green in color.

NOTE 3—Approximately 70 mL of 0.2 N $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ solution of 5.5 g of the salt is required for a chrome ore containing 65 % Cr_2O_3 .

11. Calculation

11.1 Calculate the percentage of chromium oxide as follows:

$$\text{Chromium oxide } (\text{Cr}_2\text{O}_3), \% = [(A - B) \times C \times 0.02534/D] \times 100 \quad (1)$$

where:

A = millilitres of standard KMnO_4 solution equivalent to the total amount of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ added to the sample solution,

B = millilitres of standard KMnO_4 solution required to titrate the excess $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$,

C = normality of standard KMnO_4 solution, and

D = grams of sample used.

12. Precision and Bias

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

12.2 *Bias*—No information on the bias of this test method is known. Accepted reference materials may not have been included in the materials used in the interlaboratory study. Users of this test method are encouraged to compare accepted