



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

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1. Scope

1.1 This test method covers the determination of chromium oxide (Cr_2O_3) in chrome ores in the compositional range from 25 % to 60 %.

NOTE 1—As used in this test method, “%” refers to a mass fraction (wt/wt %) (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

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.

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.

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 HNO_3 and H_2SO_4 . Residual chromium is oxidized to chromate with silver nitrate, potassium permanganate, and peroxydisulfate. The excess of permanganate is destroyed by the addition of NaCl . After cooling, the chromate is reduced by the addition of a measured excess of a ferrous ammonium sulfate, and the excess is titrated with a 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 in chromium-bearing 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 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.

³ *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 the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.



7.2 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.

7.3 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.

7.4 Ferrous Ammonium Sulfate 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). Because the ferrous ammonium sulfate solution gradually weakens in reducing power, it is necessary to standardize the ferrous ammonium sulfate solution 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 (**7.8**) 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 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 $(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})$ prepared in **7.5**.

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

7.8 Potassium Permanganate Solution (0.2 N)—Dissolve 6.4 g of KMnO_4 in 1 L of water. Standardize against a National Institute of Standards and Technology Reference Material for sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) or equivalent.

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

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

7.11 Sodium Peroxide (Na_2O_2).

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 material 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 °C 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 2**) and add 8 g of dry Na_2O_2 (**Note 3**). Thoroughly mix the contents of the crucible and cover the mixture with an additional 1 g to 2 g of Na_2O_2 .

10.2 Cover the crucible with an iron or nickel cover and carefully fuse the contents at 600 °C 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 2—Ordinary iron crucibles that may contain significant amounts of chromium should be avoided. Crucibles made of ingot iron are satisfactory.

NOTE 3—Only about 5 g of Na_2O_2 is required if about 0.2 g of very fine pulverized sugar charcoal is mixed with the Na_2O_2 . 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 shortening the time for fusion and contact with the flux, the life of the crucible is extended.

10.3 Place the cool crucible and its cover into a 600-mL covered beaker, leach the melt with 150 mL of water, remove the crucible and cover, and rinse the crucible and cover into the beaker. Boil 10 min to destroy the residual peroxide.

10.4 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.

10.5 Add 15 mL of AgNO_3 solution, 2 drops of KMnO_4 solution (**7.7**), and 10 mL of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution and boil for 5 min.

10.6 Add 10 mL of NaCl solution and boil for 5 min to 10 min after the KMnO_4 or any MnO_2 has completely disappeared.

10.7 Cool, and if necessary, dilute with cold water to 350 mL, then add 3 mL to 5 mL of H_3PO_4 .

10.8 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 the 0.2 N prepared solution (**7.4**) or a weighed amount of the salt (**Note 4**). Add 2 drops of ortho-phenanthroline ferrous sulfate (ferroin) as an indicator.

10.9 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 (**7.8**). The end point is reached whenever the solution becomes clear green in color.

NOTE 4—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 (**7.4**) containing 5.5 g of the salt is required for a chrome ore containing 65 % Cr_2O_3 (**Note 1**).

11. Calculation

11.1 Calculate the chromium oxide content as follows:

$$\text{Chromium oxide } (\text{Cr}_2\text{O}_3), \% = \frac{[(A - B) \times C \times 2.534]}{D} \quad (1)$$

where:

- A** = millilitres of KMnO_4 solution (**7.8**) 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 KMnO_4 solution (**7.8**) 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 KMnO_4 solution, and
- D** = grams of sample used (**Note 1**).

12. Precision and Bias

12.1 Precision—The precision of this test method between laboratories is indicated in **Table 1**.



TABLE 1 Precision Data

Average Concentration, ^A %	Relative Standard Deviation, %	Number of Participating Laboratories
51.52	0.21	4
42.11	0.19	5

^A Each value represents a different kind of chrome ore (see Note 1).

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 employ accepted reference materials, if available, and to judge the bias of the method from the difference between the accepted value for the chromium oxide content and the mean value from interlaboratory testing of the reference material.

13. Keywords

13.1 chromium ores; chromium oxide content; permanganate titrimetry; titrimetry

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