



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 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:

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals²

E 276 Test Method for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Finer for Metal-Bearing Ores and Related Materials²

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory³

3. Summary of Test Method

3.1 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.

4. Significance and Use

4.1 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 E 882.

5. Interferences

5.1 None of the elements normally found in chrome ores interfere with this test method.

6. Reagents and Materials

6.1 *Purity and Concentration of Reagents*—The purity and concentration of the common chemical reagents used shall conform to Practices E 50. Special apparatus and reagents required are located in separate sections preceding the procedure.

6.2 *Ammonium Peroxydisulfate Solution (250 g/L)*—Reagent No. 106 (see Practices E 50).

6.3 *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 (Ferroun).⁴ Titrate immediately with 0.2 N KMnO_4 solution to a faint, permanent pink color.

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

6.5 *Ortho-Phenanthroline Ferrous Sulfate Indicator Solution (0.025 M)*—Reagent No. 122 (see Practices E 50).

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

6.7 *Potassium Permanganate Solution (20 g/L)*—Reagent No. 134.

6.8 *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.

¹ This test method is under the jurisdiction of ASTM Committee E-1 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 *Annual Book of ASTM Standards*, Vol 03.05.

³ *Annual Book of ASTM Standards*, Vol 03.06.

⁴ Ferroun indicator distributed by G. F. Smith Chemical Co. has been found to be acceptable.

6.9 *Silver Nitrate Solution* (8 g/L)—Reagent No. 133 (see Practices E 50).

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

6.11 *Sodium Peroxide* (Na₂O₂).

6.12 *Sulfuric Acid* (1+1)—Carefully pour 1 volume of concentrated sulfuric acid (H₂SO₄, sp gr 1.84) into 1 volume of water.

6.13 *Sulfuric Acid* (5+95)—Carefully pour 5 volumes of concentrated H₂SO₄ (sp gr 1.84) into 95 volumes of water.

7. Sampling, Test Specimens, and Test Units

7.1 The test unit shall be pulverized so that at least 95 % passes a No. 100 (150-μm) sieve in accordance with Test Method E 276 and shall be dried at 105 to 110°C for a minimum of 1 h.

8. Procedure

8.1 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 Na₂O₂ (Note 2). Thoroughly mix the contents of the crucible and cover the mixture with an additional 1 to 2 g of Na₂O₂. 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 Na₂O₂, 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.

8.2 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 H₂SO₄ (1+1) and 5 mL of HNO₃ and boil for several minutes until any iron scale from the crucible is dissolved. Add 15 mL of AgNO₃ solution, 2 drops of KMnO₄ solution (Reagent No. 134), and 10 mL of (NH₄)₂S₂O₈ solution and boil for 5 min. Add 10 mL of NaCl solution and boil for 5 to 10 min after the KMnO₄ or any MnO₂ has completely disappeared.

8.3 Cool, and if necessary, dilute with cold water to 350 mL, then add 3 to 5 mL of H₃PO₄. Add a measured excess of FeSO₄(NH₄)₂SO₄·6H₂O. The point at which reduction is complete can be detected by the development of deep green color. The FeSO₄(NH₄)₂SO₄·6H₂O may be added either as 1.2

N solution or a weighed amount of the salt (Note 3). Add 2 drops of orthophenanthroline ferrous sulfate (Ferroin) as an indicator. Titrate the excess FeSO₄(NH₄)₂SO₄·6H₂O with 0.2 N KMnO₄ solution. The end point is reached when the solution becomes clear green in color.

NOTE 3—Approximately 70 mL of 0.2 N FeSO₄(NH₄)₂SO₄·6H₂O solution of 5.5 g of the salt is required for a chrome ore containing 65 % Cr₂O₃.

9. Calculation

9.1 Calculate the percentage of chromium oxide as follows:

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

where:

A = millilitres of standard KMnO₄ solution equivalent to the total amount of FeSO₄(NH₄)₂SO₄·6H₂O added to the sample solution,

B = millilitres of standard KMnO₄ solution required to titrate the excess FeSO₄(NH₄)₂SO₄·6H₂O,

C = normality of standard KMnO₄ solution, and

D = grams of sample used.

10. Precision and Bias

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

10.2 *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.

11. Keywords

11.1 chromium ores; chromium oxide content

TABLE 1 Precision Data

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

^A Each concentration represents a different kind of chrome ore.

^B Relative Standard Deviation, RSD, in this test method is calculated as follows:

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

where:

\bar{X} = average concentration, %

d = difference of the determination from the mean, and

n = number of determinations.

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