



Designation: D 2807 – 93 (Reapproved 2003)

Standard Test Method for Chromic Oxide in Leather (Perchloric Acid Oxidation)¹

This standard is issued under the fixed designation D 2807; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers the determination of chromic oxide in leathers that have been partly or completely tanned with chromium compounds. In general the samples will contain between 1 and 5 % chromium, calculated as chromic oxide.

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.* See Section 7 for specific safety hazards.

2. Referenced Documents

2.1 *ASTM Standards:*

D 2617 Test Method for Total Ash in Leather²

D 2813 Practice for Sampling Leather for Physical and Chemical Tests²

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Specialty Chemicals³

3. Summary of Test Method

3.1 The perchloric acid method is applied to the ash obtained in Test Method **D 2617**. In the acid digestion, any remaining organic matter is destroyed and the chromium oxidized to the hexavalent state. On dilution, the chromium is titrated volumetrically with thiosulfate or ferrous salt. The perchloric acid method requires less manipulation than procedures based on fusion of the ash, but care must be taken because of potential hazards in the use of this reagent. The perchloric acid method also tends to give low results.

¹ This test method is under the jurisdiction of ASTM Committee D31 on Leather and is the direct responsibility of Subcommittee D31.06 on Chemical Analysis. This test method was developed in cooperation with the American Leather Chemists Assn.

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² *Annual Book of ASTM Standards*, Vol 15.04.

³ *Annual Book of ASTM Standards*, Vol 15.05.

4. Significance and Use

4.1 The procedure described is specific for chromium in leather. Vanadium is the only common interfering element and this is rarely present in quantity. The precision and accuracy of the methods are usually at least as good as the sampling of the leather itself.

4.2 The chromium content of leather relates to the degree of tannage obtained, and hence may be a matter for specification in the purchase of leather. The procedure described provides adequate accuracy for this purpose.

5. Apparatus

5.1 *Potentiometric Titration Equipment*—This is required in an alternative method for titrating chromium (Cr^{6+}) with ferrous ammonium sulfate solution. The equipment consists of:

5.1.1 *Stirrer.*

5.1.2 *Calomel and Platinum Electrodes.*

5.1.3 *Potentiometer*—A variety of instruments is satisfactory.⁴ The most convenient common feature of these instruments is a null-point device (either a cathode-ray electron tube or galvanometer) that will signal the abrupt change occurring in the potential when the end point is reached.

5.2 In carrying out the titration, the electrodes are immersed in the sample, the solution agitated by the stirrer, and the potential balanced with the galvanometer or cathode-ray tube. Titrant is added dropwise until a sharp permanent change in potential occurs.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to 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 sufficiently high purity to permit its use without lessening the accuracy of the determination.

⁴ Satisfactory equipment include, among others the following: the Kelley, Serfass, and Fisher tritrimeters, Leeds & Northrup potentiometers, and Beckman pH meters.

6.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean distilled water or water of equal purity.

6.3 *Ferrous Ammonium Sulfate, Standard Solution (0.1 N)*—Dissolve 39.21 g of ferrous ammonium sulfate ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) in water, add 25 mL of H_2SO_4 , and dilute to 1 L.

6.3.1 *Standardization*—Dry potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in an oven at 130°C for 2 h and cool in a desiccator. Weigh into a 250-mL glass-stoppered Erlenmeyer flask about 0.200 g of $\text{K}_2\text{Cr}_2\text{O}_7$ to an accuracy of 0.0001 g. A beaker is preferred if potentiometric titration is used. Dissolve in 75 to 100 mL of water, add 20 mL of sulfuric acid (H_2SO_4 , 1+1) and titrate with the ferrous ammonium sulfate solution to be standardized. Determine the end point either potentiometrically, or with 1,10-phenanthroline ferrous sulfate solution, 0.025 M,⁶ as indicator. The potentiometric end point is marked by a sharp decrease in oxidation potential. The indicator end point is from blue-green to a red-brown. It is preferable not to add the indicator until the end point is approaching, as evidenced by the disappearance of a yellowish-green color and a gradual change to blue-green.

6.3.2 The titer of the ferrous ammonium sulfate solution decreases slowly because of oxidation of ferrous iron. This change may be retarded by storing the solution in a dark bottle and by adding a few pieces of mossy tin to the solution. However, the solution should be standardized daily whenever samples are being analyzed. Calculate the normality of the ferrous ammonium sulfate solutions as follows:

$$\text{Normality} = A/(0.04903 \times B) \quad (1)$$

where:

A = grams of $\text{K}_2\text{Cr}_2\text{O}_7$ used, and
 B = millilitres required for titration.

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

6.5 *Perchloric Acid (60 percent)*—70 or 72 % perchloric acid (HClO_4) may be substituted but storage is somewhat more hazardous.

6.6 *1,10-Phenanthroline-Ferrous Sulfate Solution (0.025 M)*.⁶

6.7 *Phosphoric Acid (40 %)*—Dilute 45 mL of 85 % phosphoric acid (H_3PO_4) with water to 100 mL.

6.8 *Potassium Iodide Solution (10 %)*—Dissolve 10 g of potassium iodide (KI) in 100 mL of water.

6.9 *Sodium Thiosulfate, Standard Solution (0.1 N)*—Dissolve 24.85 g of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in previously boiled water, add 1 g of sodium carbonate (Na_2CO_3), and dilute to 1 L.

6.9.1 *Standardization*—Dry potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in an oven at 130°C for 2 h and cool in a desiccator. Weigh into a 250-mL glass-stoppered Erlenmeyer flask about 0.200 g of $\text{K}_2\text{Cr}_2\text{O}_7$ to an accuracy of 0.0001 g. Dissolve in 50 mL of water; add 4 mL of hydrochloric acid (HCl, 1+1) 20 mL of KI solution, stopper the flask, and allow to stand 5 min in the dark. Titrate with the thiosulfate solution to be standardized. When the color of the solution has faded to a brownish-green, add 2 mL of 2 % starch solution and continue titrating until the deep blue color changes to a clear green. Record the titration. Calculate the normality of the thiosulfate solution as follows:

$$\text{Normality} = A/(0.04903 \times B) \quad (2)$$

where:

A = grams of $\text{K}_2\text{Cr}_2\text{O}_7$ used, and
 B = millilitres required for titration.

6.9.2 The thiosulfate solution is quite stable but should be restandardized at least once a month.

6.10 *Starch Indicator Solution*, prepared according to accepted procedures available in analytical handbooks.

6.11 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (H_2SO_4).

7. Hazards

7.1 The improper use of HClO_4 can lead to violent and serious explosions. In general, these can be traced to situations where concentrated HClO_4 has come in contact with organic or easily oxidized materials.

7.2 The exact procedures given must be followed and the digestions, once started, should be kept from possible contact with other organic matter. The digestions should never be allowed to boil dry. HClO_4 should never be used without accompanying use of HNO_3 and H_2SO_4 .

7.3 All spills involving HClO_4 should be flushed with water. Rags, sawdust, and other organic materials should never be used to mop up spilled acid.

7.4 The use of a perchloric acid hood, reserved for perchloric acid digestions, equipped with wash-down facilities and constructed entirely of nonporous inorganic material is required.

7.5 Perchloric acid bottles should be stored on a ceramic tray or shelf and never on a wooden or pervious shelf. It is advisable to keep only one 1-lb (0.45-kg) bottle of acid in the working area.

8. Test Specimen

8.1 The specimen shall be 2 g leather from the composite sample prepared in accordance with an accepted procedure, weighed and ashed according to Test Method **D 2617**.

9. Procedure

9.1 Transfer the ash obtained from the determination of ash, Test Method **D 2617**, to a 250-mL Erlenmeyer flask. Add, *in the order named*, 20 mL of HNO_3 , 15 mL of HClO_4 , and 10 mL of H_2SO_4 . Add a few glass beads. In the perchloric acid hood, heat gently under reflux conditions, using a small funnel as a condenser in the neck of the flask, until all organic matter is

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 *Analar 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.

⁶ A satisfactory reagent, Ferroin, is manufactured by the G. Frederick Smith Chemical Co., Columbus, Ohio.