**Designation: D2807 – 17**

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

This standard is issued under the fixed designation D2807; 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 U.S. 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 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.* See Section 7 for specific safety hazards.

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:*[2]

D2617 Test Method for Total Ash in Leather
D2813 Practice for Sampling Leather for Physical and Chemical Tests
D2868 Test Method for Nitrogen Content (Kjeldahl) and Hide Substance Content of Leather, Wet Blue and Wet White
D3495 Test Method for Hexane Extraction of Leather
D3790 Test Method for Volatile Matter (Moisture) of Leather by Oven Drying

## 3. Summary of Test Method

3.1 The perchloric acid method is applied to the ash obtained in Test Method D2617. 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.

## 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.[3] 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.

5.1.4 In carrying out the titration, the electrodes are immersed in the sample, the solution agitated by the stirrer, and

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

the potential balanced with the galvanometer or cathode-ray tube. Titrant is added dropwise until a sharp permanent change in potential occurs.

5.2 *Perchloric Acid Hood.*

## 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.[4] 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.

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

6.3 *Ferrous Ammonium Sulfate, Standard Solution (0.1 N)*—Dissolve 39.21 g of ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$) in water, add 25 mL of $H_2SO_4$, and dilute to 1 L.

6.3.1 *Standardization*—Dry potassium dichromate ($K_2Cr_2O_7$) 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 $K_2Cr_2O_7$ 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*,[5] 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:

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

where:

*A* = grams of $K_2Cr_2O_7$ 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 %)*—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).*[5]

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 ($Na_2S_2O_3{\cdot}5H_2O$) 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 ($K_2Cr_2O_7$) 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 $K_2Cr_2O_7$ 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:

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

where:

*A* = grams of $K_2Cr_2O_7$ 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.

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[4] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

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 Practice D2813, weighed and ashed according to Test Method D2617.

## 9. Procedure

9.1 Transfer the ash obtained from the determination of ash, Test Method D2617, to a 250-mL Erlenmeyer flask, or other appropriate glassware. Add, *in the order named*, 20 mL of $HNO_3$, 15 mL of $HClO_4$, and 10 mL of $H_2SO_4$. Add 3 to 5 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, or a watch glass over the mouth of a beaker, until all organic matter is destroyed and the color changes to a clear red-orange, indicating oxidation of chromium. Heat an additional 2 min, cool quickly, rinse and remove the acting condenser, and dilute to 125 mL with water. Heat to boiling and continue boiling for 7 min. Cool and titrate by the procedure given in 9.2 or 9.3.

NOTE 1—If the titration volume is less than 5 mL or more than 50 mL, adjust the size of the sample to give a titration volume between these limits and repeat the determination.

9.2 *Titration with $Na_2S_2O_3$ Solution*—Add 30 mL of $H_3PO_4$ and 20 mL of KI solution to the solution obtained in 9.1 and stopper the flask. Allow to stand 5 min in the dark. Titrate with 0.1 *N* sodium thiosulfate solution standardized as described in 6.9.1. When the color of the solution has faded to a brownish-green, add 2 mL of 2 % starch solution and continue the titration until the deep blue color changes to a clear green. Record the titration. Calculate the results in accordance with Section 9.

9.3 *Titration with Ferrous Ammonium Sulfate Solution*—Add 2 mL of $H_3PO_4$ and titrate with 0.1 *N* ferrous ammonium sulfate solution standardized as described in 6.3.1. When the color of the solution has changed from yellow through yellow-green to blue-green, add 5 drops of indicator[5] and continue titrating until the blue-green solution changes to a red-brown. Record titration. Calculate results as described in Section 10.

9.4 Alternatively, the titration may be done potentiometrically. After adding the $H_3PO_4$, transfer the solution to a 250-mL beaker and titrate with 0.1 *N* ferrous ammonium sulfate solution, using the potentiometric apparatus described in 5.1. The end point is signaled by a sudden large change in potential. Record the titration. Calculate results as described in Section 10.

9.5 It is preferable to use the same method of determining the end point in both the standardization of the ferrous ammonium sulfate solution and in the analysis of the sample.

## 10. Calculation

10.1 Calculate the chromium content as percentage of chromic oxide ($Cr_2O_3$) in the leather as follows:

$$Cr_2O_3, \% = A \times B \times 0.02533 \times (100/C) \quad (3)$$

where:

$A$ = millilitres of titrating solution used (either thiosulfate or ferrous ammonium sulfate),
$B$ = normality of titrating solution, and
$C$ = mass of leather. Use the mass of leather recorded as $C - B$ in Section 7 of Test Method D2617.

10.2 If the determination of $Cr_2O_3$ is performed on a leather that has been conditioned and weighed at constant temperature and humidity, the fact should be indicated in reporting the results.

10.3 The above calculations give the $Cr_2O_3$ content of the leather on an "as weighed" basis. If it is desired to express this on a moisture-free basis, a moisture determination should be run according to Test Method D3790 on a sample weighed from the same leather prepared at the same time according to Practice D2813. Unless otherwise specified, the chromium content on a moisture-free basis shall be considered the default calculation. If $D$ is the percentage moisture found in the sample, calculate the $Cr_2O_3$, moisture-free basis, % as follows:

$$Cr_2O_3, \% (\text{moisture-free basis}) = \frac{A \times B \times 0.02533 \times 100}{C \times \frac{100 - D}{100}} \quad (4)$$

where $A$, $B$, and $C$ have the same significance as above.

10.4 If it is desired to express the $Cr_2O_3$ content of the leather on a moisture-free and hexane-extractable basis, a moisture determination should be run according to Test Method D3790 and a hexane-extractable determination should be run according to Test Method D3495. Samples should be weighed from the same leather prepared at the same time according to Practice D2813. If $E$ is the percentage hexane-extractable material found in the sample, calculate the $Cr_2O_3$ moisture-free and hexane-extractable free basis, % as follows:

$$Cr_2CO_3, \ \% \ (\text{moisture-free and hexane-extractable-free basis}) = \frac{A \times B \times 0.02533 \times 100}{C \times \frac{(100 - D)}{100} \times \frac{(100 - E)}{100}} \quad (5)$$

where $A$, $B,C$, and $D$ have the same significance as above.

10.5 If it is desired to express the $Cr_2O_3$ content of the leather on a hide substance basis, a moisture determination should be run according to Test Method D3790 and a hide substance determination should be run according to Test Method D2868. Samples should be weighed from the same leather prepared at the same time according to Practice D2813. If $F$ is the $Cr_2O_3$ content on moisture-free basis and $G$ is the hide substance on a moisture-free basis, calculate the $Cr_2O_3$, hide substance basis, % as follows:

$$Cr_2O_3, \ \% \ (\text{hide substance basis}) = \frac{F}{G} \times 100 \quad (6)$$

## 11. Report

11.1 Report the following information.

11.1.1 Report the percentage of $Cr_2O_3$ to the nearest 0.1 %. Duplicate runs that agree within 0.09 % absolute are acceptable for averaging (95 % confidence level).

## 12. Precision and Bias[6]

12.1 *Reproducibility*—The average difference between two results (each the average of duplicate determination) obtained by analysts in different laboratories will approximate 0.06 % absolute. Two such values should be considered suspect (95 % confidence level) if they differ by more than 0.2 % absolute.

12.2 *Bias*—The test method yields results that average 1.75 % relative low when compared to a standard sample of NBS $K_2Cr_2O_7$. The 99 % confidence limits on this value are 1.50 to 2.00 % as determined by triplicate analyses in five laboratories.

NOTE 2—The estimates of checks for duplicates and reproducibility in 12.1 and 12.2 are based on an interlaboratory study of four leathers run in triplicate in each of eight laboratories.

## 13. Keywords

13.1 ash; chromic oxide; perchloric acid oxidation

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting RR:D31-1006

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