



Designation: D6714 – 01 (Reapproved2010)^{ε1}

Standard Test Method for Chromic Oxide in Ashed Wet Blue (Perchloric Acid Oxidation)¹

This standard is issued under the fixed designation D6714; 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.

^{ε1} NOTE—The SI statement was added and the Subcommittee name in footnote 1 was corrected editorially in November 2010.

1. Scope

1.1 This test method covers the determination of chromic oxide in wet blue that has been partly or completely tanned with chromium compounds. In general the samples will contain chromium content between 1 and 5 %, calculated as chromic oxide expressed upon a dry basis otherwise referred to as moisture-free basis (mfb).

1.2 This test method is specific in that it applies to a sample or samples that are the resultant ash following the execution of Test Method D6716.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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. Specific hazards are given in Section 8.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D6658 Test Method for Volatile Matter (Moisture) of Wet Blue by Oven Drying

D6659 Practice for Sampling and Preparation of Wet Blue for Physical and Chemical Tests

D6716 Test Method for Total Ash in Wet Blue or Wet White

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Spe-

cialty Chemicals (Withdrawn 2009)³

3. Terminology

3.1 *Definitions*—The terms and definitions employed within this test method are commonly used in normal laboratory practice and require no special comment.

4. Summary of Test Method

4.1 The perchloric acid method may be applied to the ash obtained in Test Method D6716. The resultant ash is dissolved into acidic solution in a blend of nitric acid and a prepared oxidation mixture consisting of sulfuric and perchloric acids. Once completed, oxidation of all trivalent to hexavalent chromium is executed by controlled heating. Upon dilution, the chromium is indirectly (back) titrated volumetrically with standardized thiosulfate using released iodine as the titrate. The perchloric acid method requires less manipulation than procedures based on fusion of the ash. However care must be taken because of potential hazards in the use of perchloric acid. The perchloric acid method also tends to give low results.

5. Significance and Use

5.1 The procedure described is specific for chromium in wet blue. 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 wet blue itself, and the accuracy of previously performed test methods.

5.2 The chromium content of wet blue is related to the degree of tannage obtained, and hence may be a matter for specification in the purchase of wet blue. The procedure described provides adequate accuracy for this purpose.

6. Apparatus

6.1 *Analytical Balance*, accurate and calibrated to 0.001 g.

6.2 *Erlenmeyer Flasks*, 250 mL capacity or equivalent.

³ The last approved version of this historical standard is referenced on www.astm.org.

¹ This test method is under the jurisdiction of ASTM Committee D31 on Leather and is the direct responsibility of Subcommittee D31.02 on Wet Blue.

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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.

6.3 *Burette*, 50 mL capacity of suitable calibration grade, minimum calibration of 0.1 mL.

6.4 *Glass Anti-bumping Beads*, or equivalent.

6.5 *Measuring Cylinders*, 50 mL capacity or equivalent.

6.6 *Small Glass Filter Funnel*.

6.7 *Dessicator*, of suitable size and design and charged with fresh dessicant.

6.8 *Weighing Vessels*, of suitable size and design.

6.9 *Drying Oven*, with accurate variable temperature controls.

6.10 *Hot Plate*, with accurate variable temperature controls.

7. Reagents

7.1 *Purity of Reagents*—Analytical Reagent (AR) 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,⁴ where such specifications are available. 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, reference to water shall be understood to mean distilled water or water of equal purity.

7.3 *Commercial Reagents*—The use of commercially available pre-standardized analytical reagents and solutions is appropriate, providing those reagents and solutions have been prepared in accordance with and conforming to the previously mentioned specifications (see 7.1).

7.4 *Nitric Acid*—(HNO₃), 70 % w/w.

7.5 *Perchloric Acid*—(HClO₄), 60 to 62 % w/w. 70 or 72 % w/w perchloric acid may be substituted, however, storage is somewhat more hazardous.

7.6 *Sulfuric Acid*—(H₂SO₄), 96 to 98 % w/w.

7.7 *Potassium Iodide*—(KI), 99 to 100 % purity.

7.8 *Potassium Iodide Solution*—(KI) 10 % w/w. Dissolve 10 g (±0.1 g) of potassium iodide into 100 mL of water.

7.9 *Starch Indicator Solution*—2 % or equivalent, prepared according to accepted procedures available in analytical handbooks.

7.10 *Oxidizing Mixture*—Mix 1666 mL of concentrated sulfuric acid into an appropriate glass container that contains 2500 mL of perchloric acid, using extreme caution while adding. Cool the mixture to room temperature before use.

7.11 *Phosphoric Acid*—(H₃PO₄), 40 % v/v. Dilute 45 mL of 85 % phosphoric acid with water to 100 mL.

7.12 *Hydrochloric Acid*—(HCl), 1:1 dilution of 37 % HCl w/w. Used in standardization of thiosulfate solution.

7.13 *Potassium Dichromate*—(K₂Cr₂O₇). Used in standardization of thiosulfate solution.

7.14 *Sodium Carbonate*—(Na₂CO₃). Used in preparation of thiosulfate solution.

7.15 *Sodium Thiosulfate*—(Na₂S₂O₃ · 5H₂O). Used to prepare thiosulfate solution.

7.16 *Sodium Thiosulfate Standard Solution*—(Na₂S₂O₃), 0.1N (±0.0002). Dissolve 24.85 g of sodium thiosulfate (Na₂S₂O₃ · 5H₂O) in previously boiled water, add 1.00 g of sodium carbonate (Na₂CO₃) and dilute to 1000 mL.

7.16.1 *Standardization*—Dry potassium dichromate (K₂Cr₂O₇) in an oven at 130°C for 2 h and cool in a dessicator. Once cool, weigh about 0.2 g (±0.0001 g) of this dry potassium dichromate into a clean 250 mL, glass-stoppered Erlenmeyer flask. Dissolve in 50 mL of water; add 4 mL of hydrochloric acid (HCl, 1:1) and 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:

$$\text{Normality} = A \div (0.04903 \times B)$$

where:

A = K₂Cr₂O₇ used, g, and

B = amount required for titration, mL.

7.16.2 *Shelf Life*—The thiosulfate solution is relatively stable. However, it should be restandardized at least once a month.

7.17 Alternatively, a commercially available pre-standardized sodium thiosulfate analytical solution may be substituted.

8. Hazards

8.1 Chemicals used can be harmful, or explosive, or both.

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

8.3 The exact procedures given must be followed and the digestion, once started, should be kept from possible contact with other organic matter. The digestion should never be allowed to boil dry. The perchloric acid should never be used without accompanying use of nitric and sulfuric acids.

8.4 All spills involving perchloric acid should be flushed with water and a liquid acid neutralizer. Rags, sawdust, and other organic materials should never be used to mop up spilled acid.

8.5 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.

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D.C. For suggestions on the reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, DBH Ltd, Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.