Designation: D7967 – 16

Standard Test Method for Analysis of Chrome Content (as Cr_2O_3) in Wet Blue using Atomic Absorption[1]

This standard is issued under the fixed designation D7967; 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.

1. Scope

1.1 This test method covers the Atomic Absorption procedure, using nitrous oxide-acetylene flame, to analyze the chrome content of Wet Blue on a moisture-free basis.

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.* Some specific hazards statements are given in Section 9 on Hazards and in 12.5.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1517 Terminology Relating to Leather

D6656 Test Method for Determination of Chromic Oxide in Wet Blue (Perchloric Acid Oxidation)

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

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

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions:* For Definitions of general leather and tanning terms used in this test method refer to Terminology D1517.

4. Summary of Test Method

4.1 The chromium content measured as Cr_2O_3 is determined in Wet Blue using Atomic Absorption (AA). The Wet Blue is digested using oxalic acid, hydrochloric acid, and potassium chloride. The chromium content in Wet Blue is measured at a wavelength of 429 nanometers with a 0.7 slit using Atomic Absorption with a nitrous oxide/acetylene flame. After the AA reading the chromium content is determined on a moisture-free basis.

5. Significance and Use

5.1 The procedure described is for chromium in Wet Blue using Atomic Absorption. This method may be used to determine the chromium content in Wet Blue as an alternate to Test Method D6656.

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. Interferences

6.1 The nitrous oxide/acetylene flame reduces or eliminates many chemical or compound interferences that can occur if just an air/acetylene flame is used, however, sensitivity may be reduced.

7. Apparatus

7.1 Atomic Absorption analyzer using a nitrous oxide-acetylene flame measuring at a wavelength of 429 nanometers with a slit of 0.7 mm.

NOTE 1—Follow manufacturer's recommendations for using nitrous oxide-acetylene flame conditions.

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

7.3 *Leather Cutting Tool,* (such as scissors or razor blade).

7.4 *Beaker,* 250 mL capacity or equivalent.

7.5 *Beaker,* 1000 mL capacity or equivalent.

7.6 *Volumetric Flask,* 200 mL capacity or equivalent.

7.7 *Volumetric Flask,* 1000 mL capacity or equivalent.

7.8 *Erlenmeyer Flask,* 1 L capacity, or equivalent.

[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.

7.9 *Watch Glass.*

7.10 *Hot Plate,* to be placed inside exhaust or fume hood.

7.11 *Desiccator.*

8. Reagents and Materials

8.1 *Purity of Reagents*—Analytical Reagent (AR) Grade 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 (ACS), where such specifications are available.[3] 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.

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

8.3 *Commercial Reagents*—The use of commercially available pre-standardized analytical reagents and solutions is appropriate, providing those reagents and solutions have been prepared according to and conform to the previously mentioned specifications (see 8.1).

8.4 *Oxalic Acid ($H_2C_2O_4$).*

8.5 *Hydrochloric Acid (HCl).*

8.6 *Potassium Chloride (KCl).*

8.7 *Potassium Dichromate ($K_2Cr_2O_7$)*—Used in standard Cr_2O_3 solution.

8.8 *Sulfuric Acid (H_2SO_4), 96-98 % w/w*—Used to prepare standard Cr_2O_3 solution.

8.9 *Sodium Bisulfite ($NaHSO_3$).*

8.10 *Wet Blue Digestion Mixture*.

NOTE 2—Wet Blue Digestion Mixture must be prepared in a Fume or Exhaust Hood.

8.10.1 Add approximately 400 mL of water to a 500 mL (or larger) container.

8.10.2 Place container on stirrer with stir bar in water. Turn stirrer on.

8.10.3 Add 16 g oxalic acid to container and stir until fully dissolved.

8.10.4 Slowly add 56 mL concentrated hydrochloric acid (HCl).

8.10.5 Allow solution to stir at least 5 min.

8.10.6 Add 13.0 g potassium chloride (KCl).

8.10.7 Dilute to 500 mL with water.

8.10.8 Allow solution to stir until the potassium chloride (KCl) has visually dissolved. if the KCl does not dissolve, slightly heat the solution. Once dissolved, remove from heat and cool to room temperature before use.

8.11 *Commercial Cr Standard, 1000 ppm:*

8.11.1 Using a commercially available 1000 ppm Cr Standard solution, make a 10 ppm Cr solution which will be used to verify the concentration of the prepared Cr_2O_3 standard in 8.12. To convert from Cr to Cr_2O_3, multiply by a factor of 1.462 (A 10 ppm Cr solution equates to a 14.62 ppm Cr_2O_3 solution).

8.12 *Standard Cr_2O_3 solution (1000 ppm):*

8.12.1 Dry approximately 5.0 g potassium dichromate ($K_2Cr_2O_7$) at 100°C overnight. Then cool the dried potassium dichromate ($K_2Cr_2O_7$) to room temperature in a desiccator.

8.12.2 Weight exactly 1.9356 g of oven dried $K_2Cr_2O_7$ and put in a 1000 mL beaker.

8.12.3 Add 500 mL water and stir until dissolved.

8.12.4 Carefully add 5 mL of concentrated sulfuric acid (H_2SO_4) while stirring.

NOTE 3—Perform in fume hood or exhaust hood, especially when adding acids.

8.12.5 Slowly add 5 g of sodium bisulfite ($NaHSO_3$) while stirring.

8.12.6 Place beaker with stirring rod in it on the hot plate.

8.12.7 Add 50 g oxalic acid while stirring.

8.12.8 Bring solution to boiling (or near boiling) for 15 min.

8.12.9 Remove from the hot plate and add 300 mL of water while stirring. When cooled to room temperature, transfer solution to a 1000 mL volumetric flask, rinsing beaker completely and into the flask with water.

8.12.10 Bring to volume, 1000 mL, with water and mix well. Verify Cr_2O_3 content according to 8.13. Store according to good laboratory practices.

8.12.11 Pipet 1 mL of the 1000 ppm Cr_2O_3 solution into a volumetric flask and dilute to 100 mL with water. Invert and mix well. Use this as a 10 ppm Cr_2O_3 standard solution.

8.12.12 Pipet 5 mL of the 1000 ppm Cr_2O_3 solution into a volumetric flask and dilute to 200 mL with water. Invert and mix well. Use this as a 25 ppm Cr_2O_3 standard solution.

NOTE 4—Prepare the 10 ppm and 25 ppm Cr_2O_3 standard solution fresh daily (on day of use).

8.13 *Calibration and Standardization:*

8.13.1 Using water to zero the AA, create a calibration curve with the 10 ppm and the 25 ppm Cr_2O_3 standards from 8.12.11 and 8.12.12. respectively.

8.13.2 Obtain a reading from the AA for the 10 ppm commercial Cr solution. This should be 14.6 ppm (±0.3 ppm) Cr_2O_3, if the standard solution prepared in 8.12 is accurate. If not, the solution will need to be discarded and remade. Once the 1000 ppm Cr_2O_3 standard solution is deemed acceptable, retain this standard stock solution for future use. Verify 8.12 every 6 months with commercial standard (8.11) to ensure standard stock solution is still viable. If the results after 6 months are not within ±0.3 ppm of the commercial standard, remake your standard stock solution according to 8.12.

9. Hazards

9.1 Chemicals used can be harmful.

[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 *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.