



Designation: ~~D7967~~—16 D7967 – 21

## Standard Test Method for Analysis of Chrome Content (as $\text{Cr}_2\text{O}_3$ ) in Wet Blue using Atomic Absorption or ICP<sup>1</sup>

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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

### 1. Scope

1.1 This test method covers the Atomic Absorption procedure, using nitrous oxide-acetylene flame, air-acetylene flame or ICP (Inductively coupled plasma) to analyze the chrome content of Wet Blue (and leather) 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, health, and ~~health~~environmental 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 and 12.20.

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:<sup>2</sup>

- [D1517 Terminology Relating to Leather](#)
- [D2813 Practice for Sampling Leather for Physical and Chemical Tests](#)
- [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—Definitions~~—For ~~Definitions~~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  $\text{Cr}_2\text{O}_3$  is determined in Wet Blue using Atomic Absorption (AA). ~~(AA)~~ or ICP. The Wet

<sup>1</sup> 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. Current edition approved ~~Sept. 1, 2016~~Sept. 1, 2021. Published ~~October 2016~~October 2021. Originally approved in 2016. Last previous edition approved in 2016 as [D7967–16](#). DOI: ~~10.1520/D7967-16~~10.1520/D7967-21.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Blue is digested using oxalic acid, hydrochloric acid, and potassium ~~chloride~~-chloride (Option A); or digested using nitric acid and sulfuric acid (Option B). 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~~-flame; or at a wavelength of 357.9 nm with a 0.7 slit for the air-acetylene flame; or standard operating settings for the ICP. 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~~-Absorption or ICP. 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. Use of the ionization suppressant solution is recommended when the iron content of the sample is expected to be high.

## 7. Apparatus

7.1 Atomic Absorption Analyzer, Atomic Absorption analyzer using a nitrous oxide-acetylene flame measuring at a wavelength of 429 nanometers with a slit of 0.7 mm; or air-acetylene flame measuring at a wavelength of 357.9 nanometers with a slit of 0.7 mm.

NOTE 1—Follow manufacturer's recommendations for using nitrous oxide-acetylene flame ~~conditions~~-conditions, air-acetylene flame conditions, or ICP.

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, 500 mL, 250 mL capacity or equivalent.

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

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.<sup>3</sup> 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<sub>2</sub>C<sub>2</sub>O<sub>4</sub>)*.

8.5 *Hydrochloric Acid (HCl)*.

8.6 *Potassium Chloride (KCl)*.

8.6.1 *Ionization Suppressant Solution*—Use 95 g KCl in 1L of water.

8.7 *Potassium Dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>)*—Used in standard Cr<sub>2</sub>O<sub>3</sub> solution.

8.8 *Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>)*, 96-98 % w/w—Used to prepare standard Cr<sub>2</sub>O<sub>3</sub> solution.

8.9 *Sodium Bisulfite (NaHSO<sub>3</sub>)*.

8.10 *Wet Blue Digestion Mixture*.

NOTE 2—Wet Blue Digestion Mixture digestion mixture must be prepared in a Fumehood or Exhaust Hood-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<sub>2</sub>O<sub>3</sub> standard in 8.12. To convert from Cr to Cr<sub>2</sub>O<sub>3</sub>, multiply by a factor of 1.462 (A 10 ppm Cr solution equates to a 14.62 ppm Cr<sub>2</sub>O<sub>3</sub> solution).

<sup>3</sup> *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.

### 8.12 *Standard Cr<sub>2</sub>O<sub>3</sub> solution (1000 ppm):*

8.12.1 Dry approximately 5.0 g potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) at ~~100°C~~ 100 °C overnight. Then cool the dried potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) to room temperature in a desiccator.

8.12.2 Weight exactly 1.9356 g of oven dried K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 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<sub>2</sub>SO<sub>4</sub>) 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<sub>3</sub>) 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<sub>2</sub>O<sub>3</sub> content according to 8.13. Store according to good laboratory practices.

8.12.11 Pipet 1 mL of the 1000 ppm Cr<sub>2</sub>O<sub>3</sub> solution into a volumetric flask and dilute to 100 mL with water. Invert and mix well. Use this as a 10 ppm Cr<sub>2</sub>O<sub>3</sub> standard solution.

8.12.12 Pipet 5 mL of the 1000 ppm Cr<sub>2</sub>O<sub>3</sub> solution into a volumetric flask and dilute to 200 mL with water. Invert and mix well. Use this as a 25 ppm Cr<sub>2</sub>O<sub>3</sub> standard solution.

NOTE 4—Prepare the 10 ppm and 25 ppm Cr<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> 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 ( $\pm 0.3$  ppm) Cr<sub>2</sub>O<sub>3</sub>, 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<sub>2</sub>O<sub>3</sub> 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  $\pm 0.3$  ppm of the commercial standard, remake your standard stock solution according to 8.12.

## 9. Hazards

9.1 Chemicals used can be harmful.

9.2 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.

## 10. Sampling, Test Specimens, and Test Units

10.1 The test specimen shall be 0.2 to 0.3 g of Wet Blue from a composite sample prepared according to Practice [D6659](#), Method A, weighed to an accuracy of 0.001 g and performed in duplicate, or

10.2 The test specimen shall be 0.1 to 0.15 g of Wet Blue from a composite sample prepared according to Practice [D6659](#), ~~Method B~~, Method B (or Practice [D2813](#) for leather), weighed to an accuracy of 0.001 g and performed in duplicate.

## 11. Preparation of Apparatus

11.1 Turn on Atomic absorption machine. ~~Using~~ When using a nitrous oxide-acetylene flame, optimize the AA at a wavelength of 429 nanometers with a 0.7 mm slit. When using an air-acetylene flame, optimize the AA at a wavelength of 357.9 nanometers with a 0.7 mm slit, and reducing flame (fuel-rich, yellow).

11.2 Turn on ICP and optimize as normal for metal analysis.

## 12. Procedure

NOTE 5—High concentration of iron can be a spectral interference in the analysis of chromium by AA and ICP. When the sample's iron concentration is high, the interference is overcome by using a sample matrix modifier (KCl) and matrix matching all standards. When the sample's iron concentration is low, the interference is overcome simply by dilution of the test portion without any suppressant.

NOTE 6—Digestion step Option A incorporates KCl in the digestion mixture (8.10) as an iron suppressant. When using Digestion step Option B, and the sample contains high iron content, add 2 mL of the ionization suppressant solution (8.6.1) per 100 mL of sample dilution and standard.

NOTE 7—Although the iron content of most commercially available Wet Blue is low, the analyst should be aware of the possibility of spectral interference at high iron concentration and how to control that interference when needed and as explained in [Note 6](#).

### **OPTION A (AA Nitrous oxide-acetylene flame)**

12.1 Weigh a sample according to Test Method [D6658](#) to determine the percent moisture in the specimen. This must be done concurrently with the other sample weights to eliminate moisture loss between samples. The percent moisture value will be used for the calculation (see Section [13](#)) for percent  $\text{Cr}_2\text{O}_3$  on a moisture-free basis (MFB).

12.2 Cut and weigh the test specimen (see [10.1](#)) or weigh the dry specimen (see [10.2](#)) to the nearest 0.001 g, and record the weight as "W."

12.3 Place sample in a labeled 250 mL beaker.

12.4 Add 25 mL of Wet Blue digestion mixture, from [8.10](#).

12.4.1 Place a watch glass over the beaker.

12.5 Boil sample on a hot plate in a fume hood until sample has completely digested (approximately 10 to 15 min, some insoluble residue may remain). (**Warning**—DO NOT BOIL DRY.)

12.6 Remove from hot plate and allow to cool.

12.7 Rinse watch glass and sides of beaker with water into the beaker.

12.8 Dilute to 200 mL in a volumetric flask with water and mix well.

12.9 Using a nitrous oxide-acetylene flame, optimize the AA at a wavelength of 429 nanometers with a 0.7 mm slit.

12.10 Using water as a blank, obtain a calibration curve as in [8.13.1](#).

12.11 Run sample through AA and record reading as “A.”

12.12 Calculate chrome content on a moisture-free basis as explained in [13.1.1](#) and [13.1.2](#).

**OPTION B (ICP or AA Air-acetylene flame)**

12.13 Weigh a sample according to Test Method [D6658](#) to determine the percent moisture in the specimen. This must be done concurrently with the other sample weights to eliminate moisture loss between samples. The percent moisture value will be used for the calculation (see Section [14](#)) for percent  $Cr_2O_3$  on a moisture-free basis (MFB).

12.14 Cut and weigh the test specimen (see [10.1](#)) or weigh the dry specimen (see [10.2](#)) to the nearest 0.001 g, and record the weight as “W.”

12.15 Place sample in a labeled 250 mL (or other appropriately sized, for example, 125 mL, 500 mL) beaker.

12.16 Add 3-5 glass beads.

12.17 Add 10 mL  $HNO_3$ .

12.18 Add 10 mL  $H_2SO_4$ .

12.19 Place the flask(s) on the hot plate(s) pre-heated to 200 – 210 °C in a fume hood.

12.20 Leave the flask(s) on the pre-heated hot plate(s) for approximately 10 min (or until the flask contents stop boiling and the flask fills with a dense smoke. **(Warning – DO NOT BOIL DRY.)**)

12.21 Remove all flasks from the hot plate(s), and leave them in the hood to cool for 5 min.

12.22 After all flasks have cooled, slowly add DI water to each flask, then transfer the contents to a 500 mL volumetric flask (or other appropriate volumetric flask). Dilute to volume and mix the contents until homogeneous.

NOTE 8—When the digest ([12.22](#)) is diluted in a 500 mL volumetric flask, the chromium concentration is typically in the range of 10–20 ppm.

12.23 Prepare appropriate dilutions, if needed (see [Note 1](#)) to get within the instrument’s operating range.

12.24 Analyze for ppm Cr content using ICP or AA and record reading as “B.”

12.25 Calculate chrome content on a moisture-free basis as explained in [13.2](#).

**13. Calculation or Interpretation of Results**

13.1 Obtain the percent  $Cr_2O_3$  (MFB) as follows:

$$\frac{ppm Cr_2O_3}{10\,000} = \%Cr_2O_3 \quad (1)$$

13.1 Simplified:

$$\frac{A \times 0.02}{W} = \%Cr_2O_3 \quad (2)$$

$$\frac{\%Cr_2O_3}{(100 - \%Moisture)} = \%Cr_2O_3(MFB) \quad (3)$$

where:

- $A$  = ppm reading from AA (12.11);
- $W$  = weight of sample in grams (12.2);
- $ppm$  = parts per million, and
- $MFB$  = moisture-free basis (12.1).

AA Nitrous oxide-acetylene flame:

13.1.1 Obtain the percent  $Cr_2O_3$  (MFB) as follows:

$$\frac{\text{ppm } Cr_2O_3}{10\,000} = \% Cr_2O_3 \quad (1)$$

13.1.2 Simplified:

$$\frac{A \times 0.02}{W} = \% Cr_2O_3 \quad (2)$$

$$\frac{\%Cr_2O_3}{(100 - \% Moisture)} = \%Cr_2O_3(MFB) \quad (3)$$

where:

- $A$  = ppm reading from AA (12.11);
- $W$  = weight of sample in grams (12.2);
- $ppm$  = parts per million, and
- $MFB$  = moisture-free basis (12.1).

13.2 ICP or AA Air-acetylene:

13.2.1 Obtain the percent  $Cr_2O_3$  (MFB) as follows:

$$Cr_2O_3, ppm = B \times d.f. \times 1.462 \quad (4)$$

where:

- $B$  = concentration of Cr in the diluted sample,
- $d.f.$  = dilution factor,
- $Cr_2O_3, \%$  =  $Cr_2O_3, ppm \div 10\,000$
- $Cr_2O_3, \% (MFB)$  =  $Cr_2O_3, \% \div [(100 - \% Moisture) \div 100]$

## 14. Report

14.1 Report the percentage of  $Cr_2O_3$  on a moisture-free basis for each replicate and the average of the replicates.

## 15. Precision and Bias

15.1 The precision of this test method is based on an interlaboratory study of ASTM WK39120, New Standard Test Method for Analysis of Chrome Content (as  $Cr_2O_3$ ) in Wet Blue Using Atomic Absorption, conducted in 2011. A total of three laboratories participated in this study, testing a single Wet Blue material. Each “test result” reported represents an individual determination. All participants were asked to report duplicate test results, as well as an average. Practice E691 was followed for the design and analysis of the data; the details are given in an ASTM Research Report.<sup>4</sup>

15.1.1 *Repeatability (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

<sup>4</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D31-1023. Contact ASTM Customer Service at service@astm.org.