



Designation: D7967 – 21

Standard Test Method for Analysis of Chrome Content (as Cr₂O₃) in Wet Blue using Atomic Absorption or ICP¹

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, 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 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:*²

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

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.

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 Cr₂O₃ is determined in Wet Blue using Atomic Absorption (AA) or ICP. The Wet Blue is digested using oxalic acid, hydrochloric acid, and potassium 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; 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 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*, 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, 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.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).

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

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* ($NaHSO_3$).

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.

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 Cr₂O₃ 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) Cr₂O₃, 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 Cr₂O₃ 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.

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 (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. 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 Cr₂O₃ 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 Cr₂O₃ 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 HNO₃.

12.18 Add 10 mL H₂SO₄.

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 AA Nitrous oxide-acetylene flame:

13.1.1 Obtain the percent Cr₂O₃ (MFB) as follows:

$$\frac{\text{ppm Cr}_2\text{O}_3}{10\,000} = \% \text{Cr}_2\text{O}_3 \quad (1)$$

13.1.2 Simplified:

$$\frac{A \times 0.02}{W} = \% \text{Cr}_2\text{O}_3 \quad (2)$$

$$\frac{\% \text{Cr}_2\text{O}_3}{(100 - \% \text{Moisture})} = \% \text{Cr}_2\text{O}_3(\text{MFB}) \quad (3)$$

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 Cr₂O₃ (MFB) as follows:

$$\text{Cr}_2\text{O}_3, \text{ppm} = B \times d.f. \times 1.462 \quad (4)$$

where:

- B = concentration of Cr in the diluted sample,
- d.f. = dilution factor,
- Cr₂O₃, % = Cr₂O₃, ppm ÷ 10 000
- Cr₂O₃, % (MFB) = Cr₂O₃, % ÷ [(100 – % Moisture) ÷ 100]

14. Report

14.1 Report the percentage of Cr₂O₃ 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 Cr₂O₃) 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.⁴

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.

15.1.1.1 Repeatability can be interpreted as maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

15.1.1.2 Repeatability limits are listed in Table 1.

15.1.2 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material 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.

15.1.2.1 Reproducibility can be interpreted as maximum difference between two results, obtained under reproducibility conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

15.1.2.2 Reproducibility limits are listed in Table 1 and Table 2.

15.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

15.1.4 Any judgment in accordance with 15.1.1 and 15.1.2 would have an approximate 95 % probability of being correct.

15.2 *Bias*—No reference materials were tested as part of this study, therefore no statement on bias can be made at this time.

15.3 The precision statement was determined through statistical examination of 26 test results, submitted by three laboratories, measuring a single material.

15.4 The following results, Table 3, were obtained when the same laboratory tested the same sample using an existing ASTM standard, D6656, and the atomic absorption method:

15.5 Another intralaboratory study of ASTM D7967, Standard Test Method for Analysis of Chrome Content (as Cr₂O₃) in Wet Blue using Atomic Absorption, was conducted between May and July of 2019. Four laboratories participated in this study, testing eight materials (Wet Blue and “chrome crust”

⁴ 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.

TABLE 1 Chrome Content as Cr₂O₃(%)

Material Average ^A	Repeatability Standard Deviation <i>S_r</i>	Reproducibility Standard Deviation <i>S_R</i>	Repeatability Limit <i>r</i>	Reproducibility Limit <i>R</i>
Wet Blue	3.115	0.058	0.135	0.161

^A The average of the laboratories’ calculated average.