



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

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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 % when calculated as chromic oxide expressed upon a dry basis otherwise referred to as moisture-free basis (mfb).

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 test method does not apply to Wet White.

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.* See Section 9 for specific safety hazards.

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 and Wet White for Physical and Chemical Tests](#)

[E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals \(Withdrawn 2009\)](#)³

[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](#)

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.

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

3. Terminology

3.1 *Definitions*—The terms and definitions employed within this 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 Wet Blue. Accurately weighed Wet Blue samples are digested in a blend of concentrated nitric acid and a prepared “oxidation mixture” consisting of sulfuric and perchloric acids. Once completed, oxidation of all tri-valent to hexavalent chrome 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 upon fusion of the ash. However, care must be taken because of potential hazards in the use of this reagent.

5. Significance and Use

5.1 The procedure described is specific for chromium in Wet Blue. Vanadium is the only common interfering element and is rarely present in quantity. The precision and accuracy of the methods are usually, at least, as good as the sampling of Wet Blue itself.

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.

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*—of 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.

7. Reagents and Materials

7.1 *Purity of Reagents*—Analytical Reagent (AR) grade 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.

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 according to and conform to the previously mentioned specifications (see 7.1).

7.4 *Nitric Acid*—(HNO₃), 70 % w/w.

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

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

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

NOTE 1—The reagents may be added individually according to 11.3.1.

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

7.12 *Hydrochloric Acid*—(HCl, 1:1 dilution of 37 %, 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.

8. Standardization

8.1 Dry potassium dichromate (K₂Cr₂O₇) in an oven at 130 °C for 2 h and cool in a desiccator. 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 water; add 4 ml of hydrochloric acid (HCl, 1:1) and 20 ml of KI solution. Stopper the flask and allow to stand for 5 min. in the dark. Titrate with the thiosulfate solution that is to be standardized. When the solution color has faded to brownish-green, add 2 ml of 2 % starch solution and continue titrating until the deep blue color changes to a clear green. Record the volume of titrant used. Calculate the Normality of the thiosulfate solution as follows:

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

where:

A = grams of K₂Cr₂O₇ used, and

B = ml required for titration.

8.2 *Shelf Life*—The thiosulfate solution is relatively stable. However, it should be re-standardized at least once every month. Alternatively, a commercially available pre-standardized analytical solution may be substituted.

9. Hazards

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

9.2 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.

9.3 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 the accompanying use of nitric and sulfuric acids.

9.4 Any spills involving perchloric acid should be flushed with water and a liquid acid neutralizer.

9.5 The use of a perchloric acid hood, reserved for perchloric acid digestion, equipped with wash-down facilities and constructed entirely of non-porous inorganic material is required.

9.6 Perchloric acid bottles should be stored on a ceramic or non-porous tray or shelf and never on a wooden or pervious shelf.

9.7 Perchloric acid must not be permitted to go dry in the presence of organics, metals or metal salts.

9.8 It is advisable to keep only a one pound (0.45 kg) bottle of acid in a working area.

10. Test Specimens

10.1 The test specimen shall be 3-5 g of Wet Blue from a composite sample prepared according to Practice D6659 and weighed to an accuracy of 0.001 g.

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, UK and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

11. Procedure

11.1 Accurately weigh between 3 and 5 g (± 0.001 g) of the prepared Wet Blue sample into a 250 mL Erlenmeyer flask. Record the weight to the nearest 0.001 g.

11.2 Using extreme care, add 20 mL of nitric acid (HNO₃) to the flask.

11.3 Next, carefully and slowly add 25 mL of the Oxidizing Mixture to the flask.

11.3.1 Alternatively, add in this order: 20 mL HNO₃, 15 mL HClO₄, and 10 mL H₂SO₄.

11.4 Add a few glass anti-bumping beads (these will allow the solution to boil evenly), then place the filter funnel into the neck of the flask.

11.5 Under the perchloric hood, heat the solution gently under reflux conditions (using the funnel as a condenser in the neck of the flask) until all organic matter is destroyed and the solution color changes to a clear red-orange, indicating oxidation of the chromium. Do not allow the sample to boil to dryness.

11.6 Heat the solution for an additional 2 min to ensure complete oxidation; then rapidly cool the solution, rinse and remove the funnel, then dilute to 125 mL with water. Rapid cooling can be achieved with the use of a cold water bath.

11.7 Re-heat the solution to boiling and continue for 7 to 10 min in order to expel and any chlorine or oxides of nitrogen.

11.8 Remove the flask from the heat and allow the solution to cool to room temperature.

11.9 Once cool, add 30 mL of phosphoric acid and 25 mL of the 10 % potassium iodide solution, then stopper the flask.

11.10 Place the flask in the dark and allow to stand for 5 min to allow complete release of iodine (dark brown color).

11.11 Titrate volumetrically with 0.1 N, standardized sodium thiosulfate.

11.12 When the solution color has faded to a pale yellow-brown, add approximately 2 ml of the starch indicator solution. Continue the titration until the deep blue color changes to a clear blue-green.

11.13 Record the titration volume.

11.14 If the titration volume is less than 5 mL or more than 50 ml, repeat the entire procedure, after adjusting the sample weight so that the titration volume is toward the middle of the burette.

11.15 Calculate the results in accordance with Section 12.

12. Calculation

12.1 Calculate the chromium content as the percentage of chromic oxide (Cr₂O₃) in the leather as follows:

$$\text{Chromic Oxide (Cr}_2\text{O}_3\text{), \%} = T \times N \times E \times (100 \div W)$$

where:

T = titration volume of sodium thiosulfate solution used in milliliters (ml),

N = Normality of the sodium thiosulfate solution,

E = 0.025332 = chromic oxide (Cr₂O₃) equivalence weight per milliliter (g/mL),

W = weight of original Wet Blue specimen (as received) in grams (g), and

100 = conversion to percent.

12.2 The above calculation provides the Cr₂O₃ content of the Wet Blue on an “as received” basis. Since the chromium content of Wet Blue is expressed upon a dry (moisture-free) basis, a moisture determination must be run in accordance with Test Method **D6658**. If D is found to be the moisture content in the Wet Blue sample, then calculate the Cr₂O₃ upon a dry basis (mfb) as follows:

$$\text{Chromic Oxide (Cr}_2\text{O}_3\text{), \%} = T \times N \times E \times (100 \div W) \times (1 \div [1 - (D \div 100)])$$

where:

T , N , E and W = the same significance as in the previous calculation.

13. Report

13.1 Report the percentage of Cr₂O₃ to the nearest 0.01 % for each and all values.

13.2 Duplicate runs that agree within 0.09 % absolute are acceptable for averaging (95 % confidence level).

14. Precision and Bias

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

14.2 *Bias*—The test method yields results that average 1.75 % lower in relation to the standard sample of NBS K₂Cr₂O₇. 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 **14.1** and **14.2** are based on an interlaboratory study of four leather samples run in triplicate in each of laboratories. The precision statements were developed⁵ using Practice **E180**.

14.3 A real world precision statement was determined through statistical examination⁶ of 139 results from 9 laboratories, on 16 materials over nearly 2 years. Practice **E691** was followed for the design and analysis of the data. The terms below (repeatability and reproducibility) are used as specified in Practice **E177**.

14.3.1 *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

⁵ The actual data upon which the results are based are reported in *Journal*, American Leather Chemists' Assn. JALCA, Vol. 54, 1959, p. 2.

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D31-1020. Contact ASTM Customer Service at service@astm.org.

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.

14.3.2 *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.

Repeatability (<i>r</i>) 0.14	Reproducibility (<i>R</i>) 0.70
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14.4 The precision of this test method is based on an intralaboratory study of ASTM WK40322, New Standard Test Method for the Determination of Chromic Oxide in Wet Blue and Wet White, conducted between 2011 and 2013. Nine laboratories participated in this study, testing 16 Wet Blue samples. Every “test result” represents an individual determination. The laboratories were asked to report a single test result for 13 materials and duplicate test results for 3 materials. Except for the absence of replicate test results from all of the study materials, Practice E691 was followed for the design and analysis of the data; the details are given in an ASTM research report.⁶

14.4.1 *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.

14.4.1.1 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.

14.4.1.2 Repeatability limits are listed in Table 1.

14.4.2 *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.

14.4.2.1 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.

14.4.2.2 Reproducibility limits are listed in Table 1.

TABLE 1 Chromic Oxide

Material	Average ^A \bar{x}	Repeatability Standard Deviation S_r	Reproducibility Standard Deviation S_R	Repeatability Limit r	Reproducibility Limit R
Wet Blue 1–24–12	3.75		0.18		0.50
Wet Blue 1–31–12	3.72		0.25		0.70
Wet Blue 11–9–12	3.74		0.34		0.95
Wet Blue 12–22–11	3.52		0.61		1.71
Wet Blue 2–21–12	3.47		0.14		0.40
Wet Blue 2–5–13	3.71		0.09		0.26
Wet Blue 3–13–12	3.27		0.42		1.19
Wet Blue 4–18–12	3.81		0.19		0.53
Wet Blue 5–16–12	3.86		0.17		0.47
Wet Blue 6–28–12	3.24		0.28		0.78
Wet Blue 8–15–12	3.45		0.22		0.62
Wet Blue 9–24–12	3.87		0.46		1.28
Wet Blue 4–13–13	3.84		0.11		0.31
Wet Blue 6–13–13	3.67	0.05	0.22	0.13	0.62
Wet Blue 8–7–13	4.03	0.03	0.09	0.09	0.24
Wet Blue 9–25–13	3.99	0.06	0.22	0.18	0.61
Average	3.68	0.05	0.25	0.14	0.70

^AThe average of the laboratories' calculated averages.

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

14.4.4 Any judgment in accordance with 14.2 would normally have an approximate 95 % probability of being correct, however the precision statistics obtained in this ILS must not be treated as exact mathematical quantities which are applicable to all circumstances and uses. The limited number of laboratories, and the absence of replicate results essentially guarantees that there will be times when differences greater than predicted by the ILS results will arise, sometimes with considerably greater or smaller frequency than the 95 % probability limit would imply. Consider the reproducibility limit as a general guide, and the associated probability of 95 % as only a rough indicator of what can be expected.

14.5 *Bias*—No information can be presented on the bias of the procedure in Test Method D6656 for measuring chromic oxide because no material having an accepted reference value was included in the analysis.

14.6 The precision statement was determined through statistical examination of 139 results, from 9 laboratories, on 16 materials over nearly 2 years.

15. Keywords

15.1 blue stock; chrome content; chromic oxide; perchloric acid oxidation; Wet Blue

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