



Test Method for Determination of Chromic Oxide in Basic Chromium Tanning Liquors (Ammonium Persulfate Oxidation)¹

This standard is issued under the fixed designation D6019; 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 determination of chromic oxide in chrome tanning liquors, either simple, with added aluminum or zirconium, or with the usual masking complexing agents.

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.*

2. Summary of Test Method

2.1 The solution is oxidized with ammonium persulfate until the chromium is completely converted to the chromate ion. The solution is boiled to complete oxidation of organic materials and to destroy excess ammonium persulfate; it is then cooled and acidified. Potassium iodide is added, and the liberated iodine is titrated with standardized sodium thiosulfate.

3. Significance and Use

3.1 The procedure described is for the quality control for manufacturing liquors and specifications for the purchase of such liquors.

3.2 The chromium content of the liquors determines the amount to be used to obtain the desired degree of tannage, and hence may be a matter for specification in the purchase of leather.

4. Reagents and Materials

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Commit-

tee on Analytical Reagents of The American Chemical Society, where such specifications are available.² 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.

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

4.3 *Ammonium Persulfate*—20 % solution 100 g of persulfate into 500 mL water.

4.3.1 Alternatively, ammonium persulfate may be added in 5.5 as solid form using plastic scoopula.

4.4 *Starch Indicator, 2 %*—Make a paste of 2 g of soluble starch in about 10 mL of water, add 90 mL water, and boil for 1 min with stirring. Cool. Refrigerate after use. The solution is subject to decomposition and should be renewed if a deep blue color is not obtained on addition of one drop of indicator to a solution of 1 drop tincture of iodine in 100 mL of water.

4.5 *Sodium Thiosulfate Solution, 0.1 N*—Dissolve 24.85 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in water, add 1 g Na_2CO_3 , and dilute to 1 L.

4.5.1 *Standardization*—Dry potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in an oven at 130°C for 2 h and cool in a desiccator. Weigh into a glass stoppered Erlenmeyer flask (500 mL) about 0.2 g of potassium dichromate to an accuracy of 0.1 mg. Dissolve in 250 mL water, add 15 mL 1:4 hydrochloric acid, 20 mL of 10 % potassium iodide solution, stopper the flask, and allow to stand 5 min in the dark. Titrate with the sodium thiosulfate 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.

$$\text{normality of sodium thiosulfate} = \frac{\text{weight potassium dichromate}}{0.04903 \times \text{mL titration}} \quad (1)$$

¹ This test method is under the jurisdiction of ASTM Committee D31 on Leather and is the direct responsibility of Subcommittee D31.06 on Chemical Analysis.

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² *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.

The thiosulfate solution is quite stable but should be restandardized at least once a month.

4.6 *Potassium Dichromate*, $K_2Cr_2O_7$, primary standard grade.

4.7 *Potassium Iodide*, 10 %—Dissolve 10 g KI in 100 mL water.

4.8 *Hydrochloric Acid*, 1:1—Dilute 250 mL concentrated hydrochloric acid (sp gr 1.19) in 250 mL water.

4.9 *Silver Nitrate*, 1 %—Dissolve 1 g of $AgNO_3$ in 100 mL water.

4.10 *Potassium Permanganate*, 1 %—Dissolve 1 g of $KMnO_3$ in 100 mL water.

5. Procedure

5.1 Weigh 11 to 12 g, to the nearest 0.1 mg, of the chrome tanning material to be analyzed.

5.2 Quantitatively transfer to a 500 mL volumetric flask. Dilute to the mark and mix thoroughly.

5.3 Pipet 25 mL aliquots into each of 500 mL Erlenmeyer flasks. Run in triplicate.

5.4 Dilute to the 200 mL mark of the flask with water.

5.5 Add the following chemicals in this order (**Warning**—This should be done in a hood. Heat and fumes will be generated):

10 mL concentrated sulfuric acid

50 mL of 20 % ammonium persulfate solution or 10 g of ammonium persulfate

8 mL of 1 % silver nitrate solution

1 mL of 1 % potassium permanganate solution

5.6 Add boiling chips or glass beads and bring to a medium boil. At this stage the solution changes to an orange to red-brown color. If the orange to red-brown color fails to develop, or fades on boiling, remove the heat and carefully add 5-10 mL of additional 20 % ammonium persulfate solution or 1-2 g of ammonium persulfate. If necessary, continue addition of ammonium persulfate (5-10 mL of 20 % ammonium persulfate solution or 1-2 g of ammonium persulfate, at a time) until the orange to red-brown color is permanent. This color will not be permanent until all of the chromium is oxidized.

5.6.1 Continue the medium boil for 1-1.5 h.

NOTE 1—Additional water may be added to keep final volume at least 200 mL.

5.7 Add 25 mL of 1:1 hydrochloric acid and continue boiling for 5 min. This is to destroy the permanganate. After addition of the 1:1 HCl the color will change from orange to opaque yellow and precipitated silver chloride will be present. Continue boiling for an additional 15-30 min. The color will become more translucent (less turbid).

5.8 Remove from heat and cool to room temperature (60 to 80°F). A warm sample will result in low recovery.

5.9 Add 25 mL of 10 % potassium iodide solution.

NOTE 2—This will produce a purple color.

5.9.1 Stopper the flask and place it in a dark location. Let the stoppered flask stand in the dark location for 5 min to allow for complete release of iodine.

5.10 Titrate with 0.1 N sodium thiosulfate solution.

5.10.1 Continue titrating until the yellow/brownish-orange color of the liberated iodine is almost discharged (the solution turns pale yellow/green to yellowish-orange).

5.10.2 Add 2 mL of 2 % starch indicator solution. The color will turn dark blue to gray-black at this stage. Continue titrating, drop-wise, until the dark blue to gray-black color changes to a green endpoint. Record the titration volume.

6. Calculation

6.1 Calculate the chromic oxide in the liquor as follows:

$$Cr_2O_3 \% = \frac{A \times N \times 0.02533}{W} \times \frac{V}{25} \times 100 \quad (2)$$

where:

A = the number of millilitres of standard thiosulfate (or ferrous sulfate) required to titrate the 25 mL aliquot of the specimen,

N = the normality of the thiosulfate (or ferrous sulfate) solution,

W = the weight of the specimen before dilution, g, and

V = the volume to which W was diluted, mL.

6.2 The chromic oxide in the sample for the test shall be the average of the test results obtained from the three aliquots tested.

6.3 Record the chromic oxide in the sample to the nearest 0.1 %.

7. Precision and Bias

7.1 *Precision*—The precision of test results obtained within a laboratory (repeatability conditions) was obtained under the defined conditions of the test method. Based on three daily repetitions on each of three days a maximum range of 0.12 % absolute and a standard deviation of 0.052 was obtained. The precision of test results obtained in different laboratories (reproducibility conditions) is a range of the average of determinations for fourteen laboratories of 0.27 % absolute and the standard deviation was 0.071.

7.2 *Bias*—Potassium dichromate, a primary standard, was used to determine bias. The chemical was treated with the oxidation procedure to determine any extraneous oxidation/reduction that may be occurring. Additionally, by applying the recovery factor to the results of the test results, errors in standardization might be nullified. The average recovery for ten laboratories was 99.89 % with a standard deviation of 0.54. The average standard deviation for an individual laboratory was 0.26.

8. Keywords

8.1 basic chromium tanning liquors; chrome oxide; ammonium persulfate

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