Designation: D3898 – 93 (Reapproved 2015)

Standard Test Method for
Chromic Oxide in Basic Chromium Tanning Liquors[1]

This standard is issued under the fixed designation D3898; 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. Referenced Documents

2.1 *ASTM Standards:*[2]

D2807 Test Method for Chromic Oxide in Leather (Perchloric Acid Oxidation)

3. Summary of Test Method

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

4. Significance and Use

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

4.2 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.

5. Interferences

5.1 The test method is generally the most accurate and convenient for the purpose. However, if the liquor contains iron or copper, which interfere with the sodium thiosulfate titration, or complex organic or inorganic reducing agents (sodium thiosulfate, for example) which are not oxidized by alkaline peroxide but reduce hexavalent chromium on acidification, an alternate procedure must be used. The perchloric acid method described in Test Method D2807, using the ferrous sulfate titration, is suitable, although the results obtained may be one to two percent low.

6. Reagents and Materials

6.1 *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 Committee on Analytical Reagents of The American Chemical Society, 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.

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

6.3 *Sodium Peroxide,* (Na_2O_2). Store in original metal can.

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

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[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 This test method was developed in cooperation with the American Leather Chemists Assoc.

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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] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

6.5 *Sodium Thiosulfate Solution* , 0.1 N—Dissolve 24.85 g of $Na_2S_2O_3 \cdot 5\,H_2O$ in water, add 1 g Na_2CO_3, and dilute to 1 L.

6.5.1 *Standardization*—Dry potassium dichromate ($K_2Cr_2O_7$) 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 1 % starch solution and continue titrating until the deep blue color changes to a clear green. Record the titration.

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

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

6.6 *Potassium Dichromate,* $K_2Cr_2O_7$, Primary Standard Grade.

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

6.8 *Hydrochloric Acid,* 1:4. Dilute 250 mL concentrated hydrochloric acid (sp gr 1.19) to 1 L with water.

7. Procedure

7.1 Weigh the liquor to the nearest milligram before dilution. The specimen shall consist of a weighed quantity of the liquor diluted to a definite volume containing from 0.003 to 0.004 g of Cr_2O_3 per millilitre. Transfer a 25 mL aliquot to a 500 mL Erlenmeyer flask and dilute to approximately 250 mL. Add sodium peroxide, about 1 g at a time, with swirling, until all green color or green precipitate has disappeared, and the solution becomes a clear yellow. (The presence of a white percipitate is of no consequence.) Add a few boiling granules or glass beads and boil gently for at least 30 min to destroy peroxide. Cool, dilute to 250 mL, and add 1:4 hydrochloric acid until the yellow color changes to orange. Add an additional 25 mL of 1:4 hydrochloric acid, 20 mL of potassium iodide solution and stopper the flask. Allow to stand in the dark for 5 min. Titrate with 0.1 N sodium thiosulfate standardized as described in 6.4.1. When the color of the solution has faded to a brownish-green, add 2 mL of 1 % starch solution and continue the titration until the deep blue color changes to a clear green. Record the titration. Calculate results as described in Section 8.

8. Calculation

8.1 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.

8.2 Unless otherwise specified, test two 25 mL aliquots from the diluted specimen.

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

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

9. Precision and Bias

9.1 *Precision:*

9.1.1 Repeatability on triplicate runs by four laboratories on four samples shows an estimated deviation of 0.17 % of the chromium present.

9.1.2 Reproducibility between laboratories on the same factorial experiment shows an estimated standard deviation amounting to 0.9 % of the chromium present.

9.2 *Bias:*

9.2.1 The average result of the factorial experiment above shows a bias of +0.07 % of the chromium present and, hence on the average, the test method does not yield biased results.

9.2.2 On the four samples studied, the standard deviation due to variation in composition was 0.35 % of the chromium present.

10. Keywords

10.1 basic chromium tanning liquors; chrome oxide