



Standard Test Method for Acidity in Basic Chromium Tanning Liquors¹

This standard is issued under the fixed designation D 3913; 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 the titratable acidity of chromium tanning liquors. By *titratable acidity* is meant not only free acidity, which is rarely present, but also anions combined with weakly basic cations such as Chromium (III), which can be titrated with base at the phenolphthalein end point.

1.2 *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:

D 3898 Test Method for Chromic Oxide in Basic Chromium Tanning Liquors²

E 180 Practice for Determining the Precision of ASTM Methods for the Analysis and Testing of Industrial Chemicals³

3. Summary of Test Method

3.1 A sample of suitable size is taken by diluting and aliquoting, if necessary. The sample is then heated to boiling and titrated hot to the first appearance of a pink color, stable to boiling in the supernatant solution, as determined by viewing the settled solution against the rim of a porcelain dish, or against the light in a tall beaker or Erlenmeyer flask.

4. Significance and Use

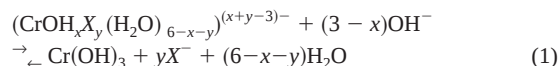
4.1 The acidity of a chrome tanning liquor, as determined by this test method, is rarely employed as such. This result is normally combined with the results of a chromium analysis (see Test Method D 3898) to determine a property of the liquor called basicity. This property, equal to the percentage by which anions in a normal chromic salt have been replaced by

hydroxyl in the solution being analyzed, is closely related to the tanning behavior of the solution.

5. Interferences

5.1 Although for most purposes, the results of this analysis are intended to give a measure of the acid anions associated with chromium, it should be mentioned that any weak basic cation will behave similarly. Hence, aluminum, zirconium, ferric iron, and weak organic bases will all yield salts with acidity titratable by this test method. A discussion of the effect of these interferences has been published.⁴

5.2 If there are anions which form very stable complexes with chromium present in the solution, the titration:



where:

X = stable complexes,

will not go to completion at the phenolphthalein endpoint and the acidity reported will be low. Large excess of oxalate or complexing anions of lesser affinity used for masking effect will introduce this error.⁵ To obviate this, an entirely different method has been developed in which the hydroxyl groups are titrated and the chromium is completely complexed by oxalate. This is generally referred to as the *Lehigh* method and may be used if complex ions are present in interfering amount.^{6,7}

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise specified, 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.⁸ Other grades may be

¹ This test method is under the jurisdiction of ASTM Committee D-31 on Leather and is the direct responsibility of Subcommittee D31.06 on Chemical Analysis-General Methods. This test method was developed in cooperation with the American Leather Chemists Assoc.

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² *Annual Book of ASTM Standards*, Vol 15.04.

³ *Annual Book of ASTM Standards*, Vol 15.05.

⁴ Hartford, W. H., *JALCA*, Vol 56, 1961, p. 568.

⁵ Thorstensen, T. C., and Theis, E. R., *JALCA*, Vol 47, 1952, p. 583.

⁶ Theis, E. R., and Thorstensen, T. C., *Journal International Society Leather Trade Chemists*, Vol 31, 1947, p. 124.

⁷ Serfass, E. J., Theis, E. R., and Clark, A., Jr., *The Journal of the Leather Chemists Association*, Vol 42, 1947, p. 360.

⁸ *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.

used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

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

6.3 *Sodium Hydroxide*, 0.1 N—Dissolve 42 g NaOH in about 60 mL water. Cool and transfer to a 100-mL volumetric flask; dilute to the mark, stopper, mix, and allow any turbidity to settle. Pipet 10 mL of the clear solution to a 1-L volumetric flask; dilute to mark and mix well. Keep stoppered and protected from atmospheric carbon dioxide.

6.3.1 *Standardization*—Dry potassium hydrogen phthalate, $\text{KHC}_8\text{H}_4\text{O}_4$, in an oven for 2 h at 120°C and cool in desiccator. Weigh about 0.8 g to an accuracy of 0.1 mg into a 400-mL tall beaker or Erlenmeyer flask. Dissolve in 200 to 250-mL water and titrate with the sodium hydroxide to be standardized, using phenolphthalein indicator.

$$\text{normality of sodium hydroxide} = \frac{\text{weight K phthalate}}{0.20423 \times \text{mL titration}} \quad (2)$$

6.4 *Phenolphthalein Indicator*, 5 %—Dissolve 5 g phenolphthalein in 100 mL 95 % ethanol.

7. Procedure

7.1 The results are more meaningful if the same sample used for the chromium determination is used for the acidity determination; for example, a specimen that consists of a weighed quantity of the liquor diluted to a definite volume containing from 0.003 to 0.004 g of chromic oxide per millilitre. Transfer 25-mL aliquots for testing.

7.2 Two procedures have been found about equally effective for determining the endpoint. The results differ slightly, as shown in the section on precision and bias. Hence, the results by the two procedures cannot be compared exactly.

7.3 *Procedure 1*—Transfer the 25-mL aliquot to a 7-in. porcelain casserole. Add 400 mL water and 1 mL 5 % phenolphthalein. Boil and titrate while boiling with standardized 0.1 N sodium hydroxide until a faint pink color, as seen at the side of the casserole after settling, persists for one minute.

7.4 *Procedure 2*—Transfer the 25-mL aliquot into a 400-mL tall beaker. Dilute to 250 mL. Heat to boiling, remove from the heat, add 10 drops 5 % phenolphthalein and titrate until a pink color is barely noted. Boil again for ten minutes and retitrate until a faint pink color is barely noted on settling. Boil a third time and complete the titration. (The process may be expedited

by using two, preferably three, aliquots of the sample, in which one is titrated according to the above procedure, and the others have 0.5 mL increments of additional 0.1 N NaOH added. Interpolate the end point after the second boiling.

8. Calculation

8.1 Calculate acidity in milliequivalents per millilitre of original sample as follows:

$$\text{Acidity, me/mL} = \frac{A \times N}{W} \times \frac{V}{25} \quad (3)$$

where:

- A = the number of mL of standard sodium hydroxide required to titrate the 25 mL aliquot of the specimen,
- N = the normality of the sodium hydroxide solution,
- W = the weight of the specimen before dilution, g, and
- V = the volume to which W was diluted, mL.

NOTE 1—The acidity in me/mL is numerically equal to equivalents/litre or normality.

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

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

8.4 Record the acidity to the nearest 0.1 %.

9. Precision and Bias

9.1 The precision of this test method, as determined by analysis of variance on a round robin test using triplicate determinations on four samples in three laboratories gave the following deviations, expressed as a percentage of the acidity present:

	Procedure I	Procedure II
Repeatability (within laboratories)	0.48	0.72
Reproducibility (between laboratories)	1.84	2.78

9.2 Although an attempt was made to refer the results of this test to knowns and so determine accuracy, the analysis of variance shows a significant variability attributable to sample makeup (variations in acidity, formate, and sugar content). This amounts to an estimated standard deviation, 2.6 and 2.86 % by Procedure I and Procedure II, respectively. The overall average bias for all samples is −0.46 % for Procedure I and −0.94 % for Procedure II.

10. Keywords

10.1 acidity; basic chromium tanning liquor; basicity

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