Designation: D 6407 – 99

Standard Test Method for Analysis of Iron and Copper in Vegetable Tanning Materials[1]

This standard is issued under the fixed designation D 6407; 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 is intended for use in determining iron and copper content in vegetable tanning materials. This test method is applicable to liquid, solid, pasty and powdered extracts, to raw and spent materials, and to tannery liquors.

1.2 The values stated in SI units are to be regarded as the 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:*

D 4901 Practice for Preparation of Solution of Liquid Vegetable Tannin Extracts[2]

D 4902 Test Method for Evaporation and Drying of Analytical Solutions[2]

D 4905 Practice for Preparation of Solution of Solid, Pasty, and Powdered Vegetable Tannin Extracts[2]

D 6404 Practice for Sampling of Vegetable Materials Containing Tannin[2]

D 6405 Practice for Extraction of Tannins from Raw and Spent Materials[2]

2.2 *ALCA Methods:*

A31 Method for Copper and Iron in Tanning Materials[3]

3. Summary of Test Method

3.1 A specified quantity of the tanning material is analyzed for iron and copper and content.

4. Significance and Use

4.1 This test method is used to determine the quantity of iron and copper present in vegetable tanning materials or vegetable tannin extracts prepared using Practices D 4901, D 6404, or D 6405.

4.2 Because of the possibility of errors in this test method it is essential that the method be followed exactly in order to obtain reproducible results both among specimens within a laboratory and for analyses between laboratories.

5. Apparatus and Reagents

5.1 *Sulfuric Acid*, concentrated (96 %).

5.2 *Sulfuric Acid Solution*, diluted 1:20 with distilled water.

5.3 *Nitric Acid*, fuming.

5.4 *Hydrochloric Acid*, concentrated (36 %).

5.5 *Hydrochloric Acid Solution*, 0.1 *N*.

5.6 *Bromine Water*, saturated solution.

5.7 *Ammonium Hydroxide Solution*, concentrated diluted 1:1 with distilled water.

5.8 *Potassium Permanganate Solution*, 0.1 *N*.

5.9 *Potassium (or Ammonium) Thiocyanate Solution*, 10 g shall be dissolved in distilled water and diluted to 100 mL with distilled water.

5.10 *Stock Iron Solution*, This may be a purchased iron standard solution or may be prepared as follows:

5.10.1 0.70 g of crystallized ferrous ammonium sulfate [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$] shall be dissolved in 50 mL of distilled water and 20 mL of dilute sulfuric acid (diluted 1:4).

5.10.2 This solution shall be titrated with 0.1 *N* potassium permanganate solution until a faint pink persists for 1 minute and the iron is completely oxidized.

5.10.3 Dilute this solution to 1 L with distilled water. 1 mL of this solution is equivalent to 0.0001 g Fe. This solution shall be stored in brown bottles and be protected from light.

5.10.4 *Standard Iron Solution*, 10 mL of the prepared stock solution, or its equivalent of purchased iron standard solution, shall be diluted to 100 mL with distilled water. 1 mL of this standard solution is equivalent to 0.00001 g Fe. The standard solution shall be freshly prepared for each analysis.

[1] This test method is under the jurisdiction of ASTM Committee D-31 on Leather and is the direct responsibility of Subcommittee D31.01 on Vegetable Leather. This test method has been adapted from and is a replacement for Method A31 of the Official Methods of the American Leather Chemists Association.

Current edition approved May 10, 1999. Published August 1999.

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

[3] Official Methods of the American Leather Chemists Association. Available from the American Leather Chemists Association, University of Cincinnati, P.O. Box 210014, Cincinnati, OH 45221-0014.

5.11 *Stock Copper Solution*, 3.9283 g of copper sulfate crystals ($CuSO_4 \cdot 5H_2O$) shall be dissolved in distilled water and diluted to 1 L with distilled water. 1 mL of this solution is equivalent to 0.001 g Cu.

5.11.1 *Standard Copper Solution*, 10 mL of the stock copper solution shall be diluted to 1 L with distilled water and the pH adjusted to between 5.5 and 6.0. 1 mL of this standard solution is equivalent to 0.00001 g Cu. The standard solution shall be freshly prepared for each analysis.

5.12 *Xanthate Solution*, 1.0 g of potassium ethyl xanthate shall be dissolved in distilled water and diluted to 1 L with distilled water. The solution shall be freshly prepared for each analysis.

5.13 *Matched Nessler Tubes and Supporting Rack.*

5.14 *Balance*, analytical balance which will weigh up to 100 g with an accuracy of ± 0.1 mg (± 0.0001 g).

5.15 *Drying Oven*, a forced-air convection oven (or mechanical-convection draft oven) capable of maintaining a temperature of 100 ± 2.0°C.

5.16 *Thermometer*, accurate to ± 0.2°C used to check and monitor the oven set point.

5.17 *Dessicator*, any convenient form or size, using any normal desiccant.

5.18 *Glazed, Porcelain Dish or Crucible of Suitable Size*.

5.19 *Muffle Furnace*, capable of maintaining a temperature of 600° ± 25°C.

5.20 *Hotplate*, ordinary lab grade.

5.21 *Steam Bath*, ordinary lab grade.

5.22 *Volumetric Flasks*, 200 and 250 mL capacity.

5.23 *Beakers*, 250 mL.

5.24 *Filter Paper*, quantitative, Whatman grade 40 or 52 or similar.

5.25 *Buret*, 10 mL capacity is sufficient.

6. Test Specimen

6.1 The sample of material from which the test specimens are taken shall be prepared as described in Practice D 6404 for extracts and tannery liquor and as in the Preparation of Sample section of Practice D 6405 for raw and spent materials.

6.2 The specimen shall consist of 5 g of solid extract or its equivalent (that is 10 g of liquid extract; 25 to 50 g of tannery liquor; 5 g of raw or spent materials).

7. General Instructions

7.1 The distilled water shall be distilled from a glass, tin-lined, or block tin still and shall be stored in glass, tin-lined, or block tin containers.

7.2 All apparatus used in this analysis shall be cleaned with hot hydrochloric acid solution (diluted 1 to 1) and rinsed with distilled water before use.

7.3 Blank determinations shall be made to minimize errors due to iron or copper either present in the reagents used or picked up during the analysis.

7.4 Duplicate determinations are recommended whenever possible.

7.5 In the actual colorimetric determinations described below, the indicated volumes of reagents, and of the prepared solutions of the specimens and of standards, are based on the use 50 mL tall-form Nessler tubes. Other tube volumes and forms may be used, provided: they be used in matched sets and the volumes of reagents, specimen and standard solutions be adjusted so that similar color intensities are produced. Such adjustments are automatic with, and familiar to, the experienced analyst and are not precluded by the method. If, however, the analyst is in doubt as to the proper adjustment to be made, it is recommended that 50 mL tall-form tubes be used exactly as described.

7.6 Comparison of the colors developed in the Nessler tubes shall be made under a source of daylight from the north, the tubes being held vertically two inches above an inclined sheet of white paper, and viewed downward through the full depth of liquid.

8. Procedure

8.1 Transfer the specimen to a tared, glazed, porcelain dish or crucible of suitable size, taking care to avoid changes in moisture content, and weigh to the nearest 0.1 mg (0.0001 g). Where necessary, place the dish and specimen in the oven and evaporate to dryness (Test Method D 4902).

8.2 Ignite the dish containing the dried residue gently over a low flame, at as low a temperature as possible, until the residue is thoroughly charred and all smoke driven off. Then place the dish and charred residue in a muffle furnace and ash, at a temperature not exceeding 600°C, until all carbon has been removed.

NOTE 1—Occasionally, the specimen will be of such a nature that all the carbon cannot be removed as described above. In such a case, saturate the charred mass with hot distilled water and break it up as completely as possible with a glass rod. Then add more of the hot distilled water and digest the whole on the steam bath for a few minutes. Decant the supernatant through a quantitative filter paper, collect the filtrate in a suitable receiver. Digest the charred residue twice more with hot distilled water, decant the supernatant through the same filter each time, and combine the filtrates. Finally transfer the char to the filter and wash several times with hot distilled water, the washings being combined with the filtrates. Then replace the filter and residue in the original dish, dry, and ash the whole, as before, until all the carbon has been removed. Cool the dish, quantitatively transfer the combined filtrates and washings thereto and evaporate and dry. Then place the dish and contents in a cold muffle furnace, raise the temperature, slowly at first to avoid loss by spurting, and finally bring to a value not exceeding 600°C.

8.3 Cool the carbon-free ash, moisten with hot distilled water, 5 mL of concentrated hydrochloric acid added, and heat the mixture on the steam bath until the ash is dissolved. Add the five drops of fuming nitric acid and five drops of bromine water and heat the mixture on the steam bath, gently at first until evolution of gas ceases (use fume cupboard or hood), and finally evaporate to dryness. Then moisten the residue with distilled water, 5 mL of concentrated hydrochloric acid added, the mixture digested on the steam bath for a few minutes and finally transfer, quantitatively, into a 250 mL beaker. Adjust the volume to about 75 mL by boiling if necessary. Then make the solution faintly ammoniacal with ammonium hydroxide solution (diluted 1 to 1) and boil gently to remove excess ammonia and to coagulate the precipitated iron and aluminum hydroxides.

8.4 Then allow the mixture to stand on the hotplate, for a few minutes, until the precipitate has settled. As soon as possible thereafter, decant the hot supernatant through a