Designation: D6407 – 99 (Reapproved 2014)

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

This standard is issued under the fixed designation D6407; 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 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]

D4901 Practice for Preparation of Solution of Liquid Vegetable Tannin Extracts

D4902 Test Method for Evaporation and Drying of Analytical Solutions

D6404 Practice for Sampling Vegetable Materials Containing Tannin

D6405 Practice for Extraction of Tannins from Raw and Spent Materials

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 D4901, D6404, or D6405.

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.

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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 D31.01 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.

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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] 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 D6404 for extracts and tannery liquor and as in the Preparation of Sample section of Practice D6405 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 D4902).

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 suitable filter paper except when copper is to be determined, in which case use an asbestos-gooch filter (previously washed with hot, 1:1 hydrochloric acid, distilled water, 1:1 ammonium hydroxide, and distilled water) (ammoniacal copper solutions combine with cellulose). Wash the precipitate three times, by decantation, with hot, faintly ammoniacal, distilled water (five drops 1:1 ammonium hydroxide solution per liter of distilled water). Finally, quantitatively transfer the precipitate to the filter and wash four times with the hot, faintly ammoniacal distilled water. Reserve the residue on the filter for the determination of iron (8.5), and the combined filtrate and washings reserved for determination of copper (8.6).

8.5 *Determination of Iron:*

8.5.1 Dissolve the residue on the filter by running onto it two portions of 1:20 sulfuric acid solution, of 20 mL each, collecting the solution in a suitable receiver. Then thoroughly wash the filter, four times, with 1:20 sulfuric acid solution, the washings being added to the first 40 mL. Quantitatively transfer the combined acid solution and washings to a suitable volumetric flask (usually 200 mL is adequate), cool if necessary, and bring to the mark with 1:20 sulfuric acid solution. Make a quantitative test of this solution as a guide to the proper size of aliquot required in the quantitative determination below.

8.5.2 Add to the known aliquot of the above solution in a Nessler tube, sufficient 1:20 sulfuric acid solution to bring to a volume of 35 mL, two drops of 0.1 *N* potassium permanganate solution, and mix the contents of the tube and then allow to stand for 5 min, add more permanganate solution, if necessary, until a slight pink persists. (Where several specimens are being examined, prepare all the specimen tubes, as above, at the same time.)

8.5.3 Prepare a series of standard Nessler tubes similarly, containing 0.5 to 1.5 mL of standard iron solution in increments of 0.1 or 0.2 mL, add the iron solution from a buret. Mix the contents of the tubes and then allow to stand for 5 min, add more permanganate solution, if necessary, until a slight pink persists.

8.5.4 If the color of the specimen tube be outside the range of the standards, repeat the comparison with fresh standards and an aliquot of more suitable size from the solution prepared in 8.5.1.

8.6 *Determination of Copper:*

8.6.1 Adjust the pH of the combined ammoniacal filtrate and washings from 8.4 to between 5.5 and 6.0 by careful addition of 1.0 *N* hydrochloric acid. Then quantitatively transfer the pH adjusted solution to a suitable volumetric flask (250 mL is usually adequate), cool if necessary, and bring to volume with distilled water.

8.6.2 Prepare a series of standard Nessler tubes containing 0 to 4 mL of standard copper solution in 0.5 mL increments, add the copper solution from a buret. To each standard tube, add 10 mL xanthate solution and sufficient distilled water to bring to volume. Then thoroughly mix the contents of the tubes by inverting several times.

8.6.3 Add to another Nessler tube a known aliquot of the solution prepared as in 8.6.1, followed by 10 mL of xanthate solution and sufficient distilled water to bring to volume. Thoroughly mix the contents of the tube by inverting several times, and compare the color with that of the standards. Make the comparison within 15 min of the addition of xanthate to the specimen and standard tubes. Record the volume of standard copper solution in that standard whose color most closely matches that of the specimen tube. (With care, the color can be estimated to the equivalent of 0.25 mL of standard copper solution.)

8.6.4 If the color of the specimen tube be deeper than that of the 4.0 mL standard, repeat the comparison using a lesser aliquot.

9. Results

9.1 *Iron:*

9.1.1 Calculate iron content as follows:

$$\text{iron}\,(\%) = [(M - B) \times V]/[1000 \times Q \times W] \quad (1)$$

where:

M = mL of standard iron solution in the matching standard,
B = mL of standard iron solution matching the Q mL of the blank,
V = capacity of the volumetric flask used in 8.5.1 (usually 200 mL),
Q = aliquot (mL) taken in 8.5.2, and
W = g of specimen taken in 8.1.

9.1.2 Instead of the visual color comparison, the use of a standard photometer shall be permissible, provided the calibration curve be established on standards made up following the procedures in 8.5.2 and 8.5.3. (It is advisable to recheck the calibration curve at regular intervals.) In this case, the name of the photometer used shall be stated on the report.

9.2 *Copper:*

9.2.1 Calculate copper content as follows:

$$\text{Copper}\,(\%) = [(M - B) \times V]/[1000 \times Q \times W] \quad (2)$$

where:

M = mL of standard copper solution in the matching standard,
B = mL of standard copper solution matching the Q mL of the blank,
V = capacity of the volumetric flask used in 8.6.1 (usually 250 mL),
Q = aliquot (mL) taken in 8.6.3, and
W = g of specimen taken in 8.1.

9.2.2 Due to a cloudiness which develops, especially in the specimen solutions, this method is not suitable for use with photometers. This same cloudiness introduces difficulty in the visual method since it must be overlooked if reliable results are to be obtained.

10. Report

10.1 The iron and copper analysis results may be expressed either as percent (%) or as parts per million (ppm).

11. Precision and Bias

11.1 This test method is adopted from Method A31 of The Official Methods of the ALCA. This test method has long been in use and was approved for publication before the inclusion of precision and bias statements were mandated. The original inter-laboratory test data is no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias (or reproducibility) of this standard practice is adequate for the contemplated use.

11.2 The analytical results obtained by this method are operationally defined by the analytical procedures employed. There is no independent measure of the true iron or copper content of a sample. Therefore the bias cannot be related to the true component content of the sample.

12. Keywords

12.1 copper analysis; iron analysis; tannin analysis; vegetable tannin analysis