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T_____429_____

BALLOT NO.____03 SARG_____

DRAFT NO._____01_____

DATE_____October 26, 2023_____

WORKING GROUP
CHAIR_____Walter Rantanen_____

SUBJECT
CATEGORY_____Chemical Properties_____

RELATED
METHODS_____See "Additional Information"

Alpha-cellulose in paper
(Reconfirmation of Classical Method T 429 cm-10)
(No changes from the previous draft)

CAUTION: The procedure in this test method utilizes quantities of unusually concentrated acid (24N H_2SO_4) and base (17.5% NaOH). This method should be performed only by trained laboratory personnel under adequate supervision and utilizing safety equipment including but not limited to safety shield, goggles, gloves, and protective clothing. Safety shower, eyewash equipment, and similar protective supporting safety devices but not limited only to those mentioned shall be readily available when this method is performed.

1. Scope

This method describes a procedure for determining the alpha-cellulose in paper. Alpha-cellulose is empirically defined as the fraction that can be filtered out of a mixture consisting of the fibrous material and sodium hydroxide solution (7.3%) of maximum dissolving power, after the fibers have previously been swollen with sodium hydroxide

solution (17.5%). This method is applicable to and is intended primarily for papers made from rags or chemical wood fibers. It is not suitable for papers containing large amounts of lignin such as newsprint.

2.   Summary

This method consists of treating the specimen with a 17.5% sodium hydroxide solution for 10 min. Distilled water is then added to reduce the sodium hydroxide to 7.3% and the resultant mixture is allowed to stand for 1 h. The alpha-cellulose fraction is collected by filtering and is determined volumetrically after oxidation with potassium dichromate.

3.   Definitions

Alpha-cellulose is that fraction resistant to 17.5% and 7.3% sodium hydroxide under conditions of the test.

4.   Significance

The division of the cellulose in paper into alpha, beta, and gamma-cellulose fractions is an empirical procedure, originally devised by Cross and Bevan (*1*) around 1900 and has been widely used to evaluate papers for such properties as aging characteristics. In general the alpha-cellulose indicates undegraded, higher molecular weight cellulose content of the paper.

5.   Apparatus

5.1   *Grinder*,[1] a Koerner (*2*) or equivalent type grinder which will completely disintegrate the paper without heating or contaminating it.

5.2   *High-speed mixer*.[1]

5.3   *Bath*, a water bath which can be maintained at 20 ± 0.1°C.

5.4   *Electrometric titration apparatus*. For rapid, accurate analysis, an electrometric apparatus is required. Any ordinary potentiometric circuit with a platinum wire electrode and crude calomel half cell may be used. More simply, a nichrome wire may be substituted for the calomel half cell. The nichrome wire is prepared for use by heating momentarily to bright redness, and then scraping the surface clean with a knife. The potentiometric arrangement may consist of a galvanometer with a sensitivity of 0.5 to 1 μA/mm scale division, a dry cell, and a sliding-contact rheostat having a total resistance of approximately 400 Ω. Smaller rheostats will suffice, but they drain the dry cell more

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[1]Names of suppliers of testing equipment and materials for this method may be found on the Test Equipment Suppliers list, available as part of the CD or printed set of Standards, or on the TAPPI website general Standards page.

quickly. The simplest form of the apparatus is shown in Fig. 1. The large deflection at the end point is unmistakable from any possible slow creeping during the titration. The galvanometer is adjusted to zero by varying the resistance at the beginning of the titration.

　　5.5　　*Miscellaneous*: beakers, 100 and 400 mL; volumetric flask, 100 mL; pipets, 25 and 50 mL; graduated cylinders, 5, 25, 100 and 1000 mL; Gooch crucible, fitted with 80-mesh copper or brass wire screen, or sintered glass crucible; rubber stopper, fitted with funnel for neck of 100-mL volumetric flask and with glass tube for suction; thermometer; and stirring rods.
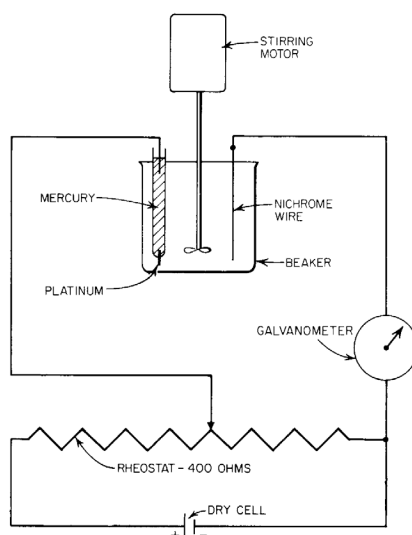

Fig. 1. Electrometric titration apparatus.

6.　　Reagents (SEE CAUTION STATEMENT ON PAGE 1)

　　6.1　　*Sodium hydroxide solution* (17.5%, 5.24N). Allow a 50% solution of NaOH to stand about one week in a stoppered vessel to permit settling of Na_2CO_3. Draw off 2 mL of the supernatant liquid with a pipet, add about 50 mL of distilled water and 1 mL of 1.5N $BaCl_2$ to lessen the effect of CO_2 on the end point, and titrate with standard 1N HCl, using phenolphthalein as indicator. Knowing the approximate normality of the concentrated NaOH, dilute with distilled water to $5.24 \pm 0.05N$, checking the diluted NaOH by titrating 5 mL of it as before, and diluting further if necessary to obtain the normality specified, which will correspond to $17.5 \pm 0.2\%$ NaOH.

　　6.2　　*Potassium dichromate solution*. Dissolve 90.0 g of oven-dry (100-105°C) $K_2Cr_2O_7$ in hot water (70-90°C), and dilute to 1000 mL after allowing the solution to cool.

　　6.3　　*Ferrous ammonium sulfate solution*. Dissolve 195 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in water containing 10 mL of H_2SO_4 (sp gr 1.84) and dilute to 1000 mL. If the solution is kept out of contact with oxygen, by means of a

slow, continuous stream of nitrogen for example, its strength will remain quite constant. The amount of nitrogen thus used is about one-fifth of a 32 m^3 (200 ft^3) cylinder per year. This precaution is not necessary but reduces the frequency with which the potassium dichromate-ferrous ammonium sulfate ratio must be determined from once each day to two or three times a month.

6.4   *Barium chloride* (1.5N). Dissolve 37 g of BaCl$_2$ • 2H$_2$O in water and dilute to 100 mL.

6.5   *Sulfuric acid* (24N). Perform the following procedure with extreme caution! Add three volumes of concentrated H$_2$SO$_4$ (sp gr 1.84) to two volumes of water in a heat-resistant flask and cool by tap water, being sure that acid is added in small portions, mixing by gently swirling after each addition. The acid will then be approximately 72% by weight. Also prepare 6N sulfuric acid by diluting one volume of the 24N H$_2$SO$_4$ to 3.5 volumes in a volumetric flask. After mixing, standardize against the 5.24N NaOH and then dilute to 6.0 ± 0.1N.

7.   Test specimen

Obtain a sample of the paper in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product." Combine equal portions from each test unit, reduce them to cotton-like form in the grinder and then thoroughly mix to form a composite for this test. If the moisture content is not known, determine this in accordance with TAPPI T 412 "Moisture in Paper and Paperboard."

8.   Procedure

USE EXTREME CAUTION IN PERFORMING ALL OF THE STEPS IN THE FOLLOWING PROCEDURE:

8.1   Perform all operations, except weighing, at 20° ± 0.1°C.

8.2   Weigh a 0.30 ± 0.01-g specimen in a 100-mL beaker. Cautiously add 20 mL of the 17.5% NaOH, macerate until the fibers are uniformly wet and dispersed, and let stand 10 min from the time of the addition of the NaOH. Then add 33 mL of water, stir the mixture thoroughly, and let stand 1 h longer, stirring once during the interval. After stirring once more, pour about 5 mL of the unsettled mixture on a sintered glass crucible or an 80-mesh copper or brass wire screen fitted into a Gooch crucible. The crucible and ring are supported by a funnel fitted into the neck of a 100-mL volumetric flask with a rubber stopper, through which passes a glass tube for suction. Form a mat with gentle suction (pressure differential, 10-20 mm Hg). Avoid excessive packing of the fibers, as this retards filtering. It may be necessary to refilter the first filtrate, but loss of 0.001 to 0.002 g α-cellulose to the filtrate does not affect the results within the stated precision of this method. Pour the remainder of the mixture on the mat, and before the last of the liquid has run through, wash the beaker and the mat with 35 mL of water. Dilute the filtrate in the volumetric flask to 100 mL and reserve to be tested as in 8.5.

8.3   Moisten the residue of α-cellulose with water and remove it from the crucible. Place the crucible upright in a 400-mL beaker, fill it with 25 mL of 24N H$_2$SO$_4$ at room temperature and rinse it after a few minutes with 50 mL more of the acid and remove the crucible. Disintegrate the α-cellulose pad in the acid, using a stirring rod. Add

with a pipet 25 mL of the $K_2Cr_2O_7$ and heat at 140−150°C for 10 min. Bubble air in a fine stream through the solution to prevent bumping, and keep the beaker covered with a watch glass notched to permit entrance of a thermometer and the bubbling tube.

8.4   After the solution has cooled to 130°C, using extreme caution, slowly add 50 mL of water, rinse the thermometer, and cool the solution to 60°C or lower. Titrate the remaining $K_2Cr_2O_7$ with the ferrous ammonium sulfate solution (using the electrometric titration apparatus).

8.5   Pipet 50 mL of the filtrate from the α-cellulose, after all fibers present have settled, into a 400-mL beaker containing 5.0 mL of $K_2Cr_2O_7$. If the paper contains oxidizable fillers such as ZnS pigment or $CaSO_3$, filter the filtrate once in a Gooch or sintered glass crucible before taking the portion for analysis. (Such fillers remaining with the α-cellulose may introduce some error; see 12.4.) Cautiously, while stirring constantly, pour 50 mL of concentrated H_2SO_4 down the side of the beaker containing the portion of the filtrate for analysis. Then heat and titrate as described previously for the α-cellulose solution.

9.   Calculations

Calculate the percentage of α-cellulose from the following equations:

$$A = 25 - (V_1 r) \tag{1}$$

$$B = 2 (5 - V_2 r) \tag{2}$$

$$\text{α-cellulose, \%} = [A / (A + B)] \times 100 \tag{3}$$

A =   volume of $K_2Cr_2O_7$ required to oxidize the α-cellulose, mL
B =   volume of $K_2Cr_2O_7$ required to oxidize the filtrate, mL
V_1, V_2 =   volume of ferrous ammonium sulfate required for titration of the $K_2Cr_2O_7$ remaining after oxidation
            of the α-cellulose and filtrate, respectively, mL
r =   volume of $K_2Cr_2O_7$ equivalent to 1 mL of ferrous ammonium sulfate solution, mL, determined
            frequently by titrating 5 mL of $K_2Cr_2O_7$ in 100 mL of diluted H_2SO_4 (1:1)

NOTE 1:   If resin, starch, or glue are present, the amounts of these sizes in the paper must be determined separately [see T 419 "Starch in Paper," T 493 "Identification and Determination of Melamine Resin in Paper," and T 504 "Glue in Paper (Qualitative and Quantitative Determination)"]. The $K_2Cr_2O_7$ volumes required by the α-cellulose and by the β-plus-γ-cellulose are then corrected as follows before calculating the percentage of α-cellulose: The amounts of sizing materials remaining with the α-cellulose are taken as 0.25% glue, 0.2% starch, and 0.2% resin, based on the dry weight of the sample. Convert these values into weights and then into mL of the $K_2Cr_2O_7$ solution by dividing each weight by the corresponding factors, which are 0.0154 g/mL for glue, 0.0129 g/mL for starch, and 0.0066 g/mL for resin. Subtract the resulting volumes in milliliters of the $K_2Cr_2O_7$ solution from the volumes of $K_2Cr_2O_7$ consumed by the alpha fraction and by the beta-plus-gamma fraction, and substitute the corrected values in Eqs. 2 and 3.

NOTE 2:   These are average values, but actual amounts have been found to vary not more than 0.1% from them, regardless of the content of glue, starch, or resin in the papers. For example, if a paper were found to contain 3.4% glue, 0.7% starch, and 1.1% resin, then the sizing material remaining in the beta-plus-gamma portion would be 3.15, 0.5, and 0.9%, respectively.

10.   Report

10.1   Report the percentage of α-cellulose based upon the total weight of the alpha-plus-beta-plus-gamma-cellulose and including pentosans, but excluding moisture, ash, resin, or any sizing or other added nonfibrous materials.

10.2   Make all determinations of α-cellulose in duplicate.

10.3   Express the average to the nearest 1%.

11.   Precision

Results (repeatability) should agree at least within 0.4% of the dry weight of the sample. The precision of the volumetric method is much greater than these requirements would indicate. It is felt, however, that the average value of two determinations which differ by no more than 0.4 when expressed as a percentage, adequately represents the specimen as prepared for testing. When, however, a given sample is ground and tested in different laboratories, greater disagreement may arise, due to the differences in freeness and extent of fibrillation of the fibers on the one hand, and individual differences in analysts on the other, added to the lack of perfect uniformity of the test specimen and ordinary errors in analysis. Therefore, the reporting of α-cellulose values to the nearest 1% is more compatible with experience and is sufficient for its practical usefulness.

12.   Keywords

Paper, Alpha-cellulose, Cellulose

13.   Additional information

13.1   Effective date of issue: To be assigned.

13.2   This 2010 version emphasizes the need for extreme caution and awareness of safety procedures in the laboratory when using highly concentrated chemical reagents. This version retains the elimination of procedures for beta and gamma cellulose as was done in the 1969 revision. Also, the volumetric procedure utilizing the electrometric titration apparatus is required, and the external indicator alternate procedure is eliminated because of the difficulty in accurately determining the end point.

13.3   Careful notation should be made of the limitations of the α-cellulose test, both as to application and significance of results, concerning which considerable controversy has arisen. It is especially important that discretion

be exercised in relating this test to the permanence of paper. Investigations are under way which indicate that there are more efficient methods for measuring permanence. Results to date have shown, however, that if any given paper is tested for α-cellulose content after selected periods of natural or artificial aging, the rate of change is a measure of permanence. For paper containing lignified pulp, coatings, fillers, etc., applicable corrections should be made as indicated in the literature (*2, 4*).

13.4   This method was revised in 1939, 1969, and 1978, and corrected in 1936, 1942, and 1948.

13.5   This method, formerly T 429 os-78, has been reclassified as a Classical Method. Such procedures are no longer in common use or have been superseded by advanced technology; they are technically sound, have a history of use, and contain a body of literature references that make their preservation valuable.

References

1.   Cross, C. F., and Bevan, E. J., "Researches on Cellulose," Vol. III, Longmans, Green and Company, London, 1912.

2.   Burton, J. O., and Rasch, R. H., *J. Research National Bureau of Standards* **6**:603 (April 1931), RP295.

3.   Launer, H. F., "Simplified Volumetric Determinations of Alpha, Beta, and Gamma Cellulose in Pulps and Papers," *J. Research National Bureau of Standards* **18**:333 (March 1937), RP979.

4.   Launer, H. F., "Volumetric Determination of Alpha, Beta, and Gamma Cellulose in Pulps and Papers Containing Sizing, Filler, and Other Materials," *J. Research National Bureau of Standards* **20**:87 (January 1938), RP1068.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Standards Department.   ■