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An American National Standard

Standard Test Method for Determination of Alkalinity of Paper as Calcium Carbonate (Alkaline Reserve of Paper)[1]

This standard is issued under the fixed designation D 4988; 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 alkalinity or alkaline reserve of paper, or both.

1.2 A qualitative test is described that indicates the presence of carbonate. (The detection limit is approximately 5 % calcium carbonate.)

1.3 A qualitative test is described that determines the alkalinity expressed as percent calcium carbonate or alkaline reserve, or both, expressed as moles per kilogram of paper.

NOTE 1—A similar procedure for measuring the alkalinity or alkaline reserve or both of paper will be found in ISO 10716.

1.4 *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 585 Practice for Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Products[2]

D 644 Test Method for Moisture Content of Paper and Paperboard by Oven Drying[2]

D 1968 Terminology Relating to Paper and Paper Products[2]

2.2 *ISO Standard:*

ISO 10716 Paper and Board—Determination of Alkali Reserve[3]

2.3 *TAPPI Standards:*

T 266 Determination of Sodium, Calcium, Copper, Iron, and Manganese in Pulp and Paper by Atomic Absorption Spectroscopy[4]

T 610 Preparation of Indicators and Standard Solutions[4]

3. Terminology

3.1 For the meaning of terms used in this test method, consult Terminology D 1968, or *The Dictionary of Paper.*[4]

4. Summary of Test Method

4.1 *Qualitative Test*—The presence of carbonate is determined by immersing a sample of the paper in hydrochloric acid and observing effervescence. Any carbonate or bicarbonate salt present will produce this effect.

4.2 *Quantitative Determination of Carbonate*—The paper sample is subjected to digestion in a known quantity of standardized hydrochloric acid. Back titration with standardized sodium hydroxide is used to determine the amount of hydrochloric acid consumed in the digestion process. The subsequent calculation for alkalinity assumes that all of the alkaline material neutralized was calcium carbonate. The calculation of moles per kilogram is independent of the material providing the reserve.

5. Significance and Use

5.1 Growing concern regarding the deterioration of books and various documents in libraries and archives have led to the development of standards by standard-setting bodies for improved permanence in paper. By using alkaline sizing technology, it is possible to manufacture paper at a pH of 6.5 or above and, therefore, incorporate alkaline fillers such as calcium carbonate. Alkaline sizing in itself improves permanence by eliminating acid from the sheet normally associated with a rosin/alum sizing system. The presence of an alkaline filler gives an added measure of permanence because it has the capability of sorbing acidic gases from the environment that might otherwise cause deterioration of the paper.

5.2 Various paper product specifications specify an alkali reserve, frequently at a minimum of 2 % calcium carbonate. An alkaline reserve of 0.4 mol/kg is provided by 2 % calcium carbonate.

5.3 The qualitative test can be used to determine the presence of carbonate, although this may not necessarily confirm that the paper is alkaline-sized or that the filler is calcium carbonate. A paper sized with a rosin/alum system and coated with a coating containing any carbonate salt would give

[1] This test method is under the jurisdiction of ASTM Committee D06 on Paper and Paper Products and is the direct responsibility of Subcommittee D06.92 on Test Methods.

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[2] *Annual Book of ASTM Standards*, Vol 15.09.

[3] Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

[4] Available from the Technical Association of the Pulp and Paper Industry, P.O. Box 105113, Atlanta, GA 30348.

a positive qualitative reaction. Carbonate levels of less than 5 % may not show positive results.

5.4 The quantitative test assumes that the carbonate is calcium and reports as such.

5.5 If the sample is known to contain no other carbonate or alkaline material, then this test method can be used to determine the calcium carbonate content. If the composition is unknown, or if other materials are known to be present that will react with the acid, the results should not be reported as $CaCO_3$. TAPPI T266 may be used to determine calcium content.

6. Interferences

6.1 The calculation for alkalinity assumes that the neutralization of the hydrochloric acid is from calcium carbonate so that other alkaline or acidic materials in the paper could affect the results. Expression of results as moles per kilogram eliminates that possibility.

6.2 The use of sodium carbonate or bicarbonate or calcium carbonate in a size press treatment or coating on a rosin/alum sized paper made at a pH below 7 would affect the results. The residual acidity from the rosin/alum sizing system would lower the calculated value and the sodium carbonate or bicarbonate would raise the value. It is possible that sufficient carbonate could be added in a coating to completely neutralize the acidity of the base sheet during the digestion process, thus giving a false indication of an alkaline-filled paper.

7. Reagents

7.1 *Standardized 0.1 N Hydrochloric Acid (HCl)*.

7.2 *1 N Hydrochloric Acid (HCl)*.

7.3 *Standardized 0.1 N Sodium Hydroxide (NaOH)*.

7.4 *Methyl Red Indicator*—Prepare a 0.2 % solution of methyl red in ethyl alcohol by dissolving 0.2 g methyl red (*o*-carboxybenzeneneazo-dimethylaniline) in 100 mL ethyl alcohol.

7.4.1 The reagents and indicator shall be made in accordance with TAPPI T610. The normality shall be known to the nearest 0.001*N*.

8. Sampling

8.1 Obtain the sample in accordance with Practice D 585.

9. Procedure

9.1 *Qualitative Test for Carbonate Content*:

9.1.1 Place approximately 0.5 g of the paper sample in a test tube of any convenient size.

9.1.2 Cover it to a depth of about 10 mm with 1 *N* HCl.

9.1.3 A gentle continuous effervescence, (not to be confused with initial desorption of gases from the surface of the paper) indicates the presence of carbonate.

9.2 *Quantitative Test for Alkalinity (Carbonate Content)*:

9.2.1 Determine the moisture content using Test Method D 644.

9.2.2 Weigh out approximately 1 g dry basis of the paper sample to the nearest 1 mg.

9.2.3 Place it in approximately 25 mL of water in a 125 mL Erlenmeyer flask.

9.2.4 Pipette 20 mL of standardized 0.1 *N* HCl into the flask; heat to boiling.

9.2.5 Boil for approximately 1 min.

9.2.6 Cool to room temperature.

9.2.7 Add three drops of methyl red indicator.

9.2.7.1 For 1 g of paper, 20 mL of 0.1*N* HCl is sufficient to neutralize the carbonate in a paper containing approximately 10 % carbonate. However, if the solution has not turned pink or red at this point, pipet another quantity of HCl into the sample solution in order to completely neutralize the carbonate and turn the solution pink or red. The total amount of acid should be adjusted until *at least* 10 % of the total amount of acid added is in excess of the amount of alkaline materials present, as determined by the volume of 0.1 *N* NaOH required to neutralize the excess acid added. That is, if a total of 40.0 mL of 0.1 *N* HCl is added to the sample, the amount of 0.1 *N* NaOH required in 9.2.8 and 9.2.9 must be *at least* 10 % of 40.0 mL, or 4.0 mL. If a 10 % excess of acid is not present, pipet an additional aliquot of standardized 0.1 *N* HCl and repeat the titration. A10 % excess of acid is required to ensure repeatable results.

9.2.8 Titrate to the first lemon-yellow with standardized 0.1 *N* NaOH.

9.2.9 If a trace of pink indicator remains absorbed on the surface of the paper, boil the paper briefly to desorb the pink color. Usually a further drop of NaOH solution will restore the lemon-yellow to the solution.

9.3 Make duplicate determinations.

10. Calculation

10.1 Calculate the carbonate content of the paper as percent calcium carbonate ($CaCO_3$) as follows:

$$CaCO_3\% = \frac{[(ml \times N)\ HCl - (ml \times N)\ NaOH] \times 0.050 \times 100}{DW} \quad (1)$$

where:

0.050 = the milliequivalent weight of calcium carbonate, and

DW = dry weight of specimen, g.

10.2 Duplicate determinations should agree within 0.3 % $CaCO_3$. If not, repeat procedure.

10.3 Calculate alkaline reserve as moles per kilogram of paper as follows:

$$\text{Alkaline reserve (mol/kg)} = \frac{(mL \times N)\ HCl - (mL \times N)\ NaOH}{DW} \quad (2)$$

where:

DW = dry weight of specimen (g).

10.4 Duplicate determinations should agree within 0.07 mol/kg. If not, repeat procedure.

NOTE 2—One mole of acid is equivalent to 0.5 moles of calcium carbonate, or 50 g of $CaCO_3$. One percent of calcium carbonate thus gives an alkaline reserve of 0.2 mol/kg.

11. Report

11.1 Average determinations and report as percent $CaCO_3$ or moles per kilogram of the oven-dried paper to the nearest 0.1 % for alkalinity or 0.02 mol/kg for alkaline reserve.

12. Precision and Bias

12.1 *Precision*:

12.1.1 *Repeatability (Alkalinity)*—Standard deviation 0.07 %. Approximately 95 % repeatability limits on differences of two individual test results is ±0.20. This repeatability statement is based on determinations in duplicate of four samples ranging in calcium carbonate content from 3.25 % to 8.88 %.

12.1.2 *Repeatability (Alkaline Reserve)*—Standard deviation 0.014 and differences of two individual test results is 0.04 mol/kg.

12.1.3 *Reproducibility*—To be established.

13. Keywords

13.1 alkaline reserve; alkalinity; paper; permanence