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T 553

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WORKING GROUP CHAIRMAN N/A

SUBJECT CATEGORY Chemical Properties

RELATED METHODS See "Additional Information"

CAUTION:
This Test Method may include safety precautions which are believed to be appropriate at the time of publication of the method. The intent of these is to alert the user of the method to safety issues related to such use. The user is responsible for determining that the safety precautions are complete and are appropriate to their use of the method, and for ensuring that suitable safety practices have not changed since publication of the method. This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this method, the user must determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Alkalinity of paper as calcium carbonate (alkaline reserve of paper)

(Five-year review of Official Method T 553 om-15)

(no changes from Draft 1; editorial corrections incorporated)

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

2. Referenced documents

2.1 TAPPI Test Methods:

TAPPI T 400 “Sampling and Accepting a Single Lot of Paper, Paperboard, Containerboard, or Related Product”

TAPPI T 266 “Determination of Sodium, Calcium, Copper, Iron and Manganese in Pulp and Paper by Atomic Absorption Spectroscopy”

TAPPI T 550 “Determination of Equilibrium Moisture in Pulp, Paper and Paperboard for Chemical Analysis”

TAPPI T 610 “Preparation of Indicators and Standard Solutions”

3. Terminology

3.1 Descriptions of terms specific to this method:

3.1.1 *Alkaline filled paper,* a paper containing an alkaline filler such as calcium carbonate, having a pH value in excess of 7 (extract pH usually in the range 7.5 to 10.0), and containing a reserve buffering capacity that can neutralize acidic materials formed in the paper or acidic gases sorbed from the atmosphere.

3.1.2 *Alkaline sized paper,* a paper that has been sized in an alkaline machine system during manufacture at a pH value in excess of 7 (generally 7.5 to 10.0), permitting the use of alkaline pigments such as calcium carbonate in the manufacturing process, and generally resulting in a paper having some level of resistance to water penetration.

3.1.3 *Alkaline reserve,* the level of alkaline materials such as calcium carbonate capable of neutralizing acidic materials formed in the paper or acidic gases sorbed from the atmosphere, expressed as moles per kilogram.

3.1.4 *Permanence,* a function of the chemical stability of paper and its ability to maintain initial properties over a long period of time.

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 has 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 7.5 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 alkaline 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 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 carbonate 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 T 266 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 mole per kilogram as alkaline reserve eliminates that possibility.

6.2 The use of sodium carbonate or bicarbonate or calcium carbonate in a size press treatment or coating of 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 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 by dissolving 0.2 g methyl red hydrochloride in 100 mL water, or 0.2 g methyl red (*o*-carboxybenzeneazo-dimethylaniline) in 100 mL ethyl alcohol.

7.4.1 The reagents and indicator shall be made in accordance with TAPPI T 610. The normality shall be known to the nearest 0.001 *N*.

7.5 ASTM Type I or Type II water should be used for this procedure, as described in ASTM Specification D 1193, Standard Specification for Reagent Water.

8. Sampling

8.1 Obtain the sample in accordance with T 400.

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 alkaline reserve (carbonate content) reported as calcium carbonate or alkaline reserve:

9.2.1 Determine the moisture content using T 550 “Determination of Equilibrium Moisture in Pulp, Paper and Paperboard for Chemical Analysis.”

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. Repeat steps 9.2.5, 9.2.6, and 9.2.7. 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 standardized 0.1 *N* HCl and repeat the titration. A 10% excess of acid is required to ensure repeatable results.

9.2.8 Titrate to the first lemon-yellow endpoint 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.

NOTE 1: A pH titration may be used as an alternate to the methyl red indicator procedure, especially if the paper causes the water to become colored. Use an endpoint of pH 5.0.

9.3 Make duplicate determinations.

10. Calculation

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

$$\text{alkalinity as } CaCO_3\% = \frac{[(\text{mL} \times N)\ \text{HCl} - (\text{mL} \times N)\ \text{NaOH}] \times 0.050 \times 100}{\text{DW}}$$

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:

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

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

12. Precision

12.1 Repeatability, (alkalinity) standard deviation 0.07%. Approximately 95% repeatability limits on differences of two individual test results are ± 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%. (Source: ASTM D 4988-96.)

12.2 Repeatability (alkaline reserve), standard deviation 0.014 and differences of two individual test results is 0.04 mol/kg. (Source: ASTM D4988-96.)

Table 1. Precision data.

Sample No.	Number of participating laboratories	Mean of the results (mol/kg)	Standard deviation of reproducibility
1	12	3.48	0.54
2	12	3.18	0.18
3	12	2.81	0.17
4	12	1.85	0.07
5	12	0.50	0.06
6	12	0.27	0.06
7	11	0.36	0.06
8	9	0.08	0.02
9	9	0.04	0.03

(Source: ISO 10716:1994 (E) Paper and board - determination of alkali reserve.)

12.3 *Reproducibility*. In an interlaboratory study conducted within ISO TC 46/SC 10/WG 1, the alkali reserve

of a range of printing and writing papers was tested by laboratories in different countries. The procedure used was similar to that described in this International Standard. Some of the results (in moles per kilogram) are quoted in Table 1. The data were obtained under reproducibility conditions.

13. Keywords

Alkalinity, Paper, Alkaline papers, Calcium carbonate

14. Additional information

14.1 Effective date of issue: To be assigned.

14.2 This method is the technical equivalent of ASTM 4988 and ISO 10716.

14.3 This procedure has been included in various ASTM permanent paper standards and in standards of the Federal Government for the Joint Committee on Printing and the Government Printing Office.

14.4 The only change in the 2015 edition was a minor spelling correction.

Appendix

A.1 Papers produced to be stable for long time periods normally contain some alkaline filler, commonly calcium carbonate, as an alkaline reserve to prevent attack from acid substances in ambient air or formed by deterioration of substances in the paper. Specifications for permanent papers may require a minimum alkaline reserve. This method is intended for checking the presence of such an alkaline reserve.

A.2 Normally the required alkaline reserve is obtained by adding some form of calcium carbonate to the paper furnish, but other substances can also be used for the purpose. By expressing the test result in moles per kilogram of alkaline reserve and not as a calcium carbonate content, no confusion arises when alkaline substances other than calcium carbonate are used. Furthermore, it has been reported that some forms of calcium carbonate do not readily react with acids, and thus do not contribute to the alkaline reserve.

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