Designation: D 778 – 97 (Reapproved 2002)

An American National Standard

Standard Test Methods for Hydrogen Ion Concentration (pH) of Paper Extracts (Hot-Extraction and Cold-Extraction Procedures)[1]

This standard is issued under the fixed designation D 778; 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 These test methods cover two procedures for determination of the hydrogen ion concentration, expressed in terms of pH, of an aqueous extract of paper.

1.2 These test methods may be applied to writing, printing, and sized industrial papers.

1.3 These test methods are not intended to be used for determination of pH of insulating papers, for that see Test Methods D 202.

1.4 The test methods appear as follows:

	Section
Test Method A—pH of Paper (Unfiltered Extract) After Extraction for 1 h in Cold (25 ± 5°C) Water	11.1
Test Method B—pH of Paper (Unfiltered Extract) After Extraction for 1 h in Boiling Water	11.2

1.5 Specifications may be based on Test Method A or Test Method B, or both.

1.6 Where a specification or specific instructions or agreement to use only one of these test methods is absent, determine pH using both procedures, and interpret results based on Section 12.

1.7 *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 202 Test Methods for Sampling and Testing Untreated Paper Used for Electrical Insulation[2]
D 585 Practice for Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard and Related Product[3]
D 1193 Specification for Reagent Water[4]
D 1293 Test Methods for pH of Water[4]
D 1968 Terminology Relating to Paper and Paper Products[3]
E 70 Test Method for pH of Aqueous Solutions With the Glass Electrode[5]
E 122 Practice for Choice of Sample Size to Estimate a Measure of Quality for a Lot or Process[6]

3. Terminology

3.1 *Definition:* Definitions shall be in accordance with Terminology D 1968 and the *Dictionary of Paper.*[7]

4. Summary of Test Methods

4.1 Test Method A consists of the extraction of a 1-g test specimen in 70 mL of cold distilled water (25 ± 5°C) for 1 h, and determination of pH without filtration using a commercial pH meter.

4.2 Test Method B consists of the extraction of a 1-g test specimen in 70 mL of boiling distilled water for 1 h, followed by cooling of the extract and determination of the pH without filtration using a commercial pH meter.

5. Significance and Use

5.1 The acidity or alkalinity of a paper sample extract is important because of the effect of paper acidity or paper alkalinity on the permanence of the paper. Although acidity or alkalinity may be determined by titration the pH is often more indicative of the stability of paper than is the total acidity or alkalinity.

6. Apparatus

6.1 *pH Meter*—Use a pH meter of Type II or Type III as specified in Test Methods D 1293. In general terms this is a pH meter accurate to 0.01 pH units with temperature compensation suitable for making pH measurements over the 0 to 14-pH range.

6.2 Reflux condensers, preferably water cooled, West or Allihn Type, with 300-mm jackets, standard taper inner joints and drip tips; or air condensers, 10-mm diameter and 1000 mm long with ST inner joints and drip tips, ST joints to fit the flasks (required on hot-extraction procedure, only).

---

[1] These test methods are under the jurisdiction of ASTM Committee D06 on Paper and Paper Products and are the direct responsibility of Subcommittee D06.92 on Test Methods.

Current edition approved Dec. 10, 1997. Published November 1998. Originally approved in 1944. Last previous edition approved in 1993 as D 778 – 93.

[2] *Annual Book of ASTM Standards*, Vol 10.01.

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

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 15.05.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

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

7. Reagents

7.1 *Distilled Water*—The distilled water used in these test methods must comply with Type II or Type III reagent water as specified in Specification D 1193.

7.2 *Standard Buffer Solutions*:

7.2.1 If buffer solutions are prepared in the laboratory, their preparation and corporation must comply with applicable sections of Test Method E 70 or Test Methods D 1293. Some knowledge of the expected pH may be required to indicate which buffers (pH values) will be required for use.

7.2.2 Commercially available pH buffers may be used if desired. Common pH values are 4.0, 7.0, and 10.0. Purchase the ones appropriate for samples being tested.

8. Sampling

8.1 *Acceptance Sampling*—Acceptance sampling shall be in accordance with Practice D 585.

8.2 *Sampling for Other Purposes*—The sampling and the number of the test specimens depends on the purpose of the testing. Practice E 122 is recommended.

9. Test Specimen

9.1 A composite evaluation is considered appropriate for these test methods unless otherwise specified.

9.2 Take an equal number of sheets (one or more) from each test unit, but not less than a total of five sheets, and combine the sheets from all test units. Holding the sheets at one end, cut and cross-cut the other end into 5 to 10-mm square.

9.3 If the paper is more than 0.012 in. (0.30 mm) in thickness, or greater in apparent density than 0.90 g/cm^3, the specimen must be split by delamination into thickness of not over 0.008 in. (0.20 mm) before it is cut into the small squares.

9.4 From each quantity of cut paper, weigh a test specimen of 1 ± 0.01 g, using an equal amount of material from each layer in cases where the sample has been delaminated as required in 9.3. Do not include any material in the specimen that has been touched by the fingers.

9.5 Perform determinations at least in duplicate. In special cases where it is necessary to evaluate different portions of the lot separately, take a portion from each test unit of the sample and perform duplicate determinations on each portion independently, using the procedure specified for the composite.

10. Calibration

10.1 Calibration of the pH meter must be done following applicable sections of Test Methods D 1293 or Test Method E 70. The instruction manual of the specific pH meter must be consulted for any operations specific to that pH meter.

11. Procedure

11.1 *Test Method A—pH of Paper (Unfiltered Extract) After Extraction for 1 h in Cold (25 ± 5°C) Water:*

11.1.1 Transfer the test specimen to a 100-mL beaker. Add about 5 mL of cold (25± 5°C) distilled water and macerate with a flattened glass stirring rod until the specimen is wet.

11.1.2 Add more water to bring the volume to 70 mL, stir well, cover with a watch glass, and allow to stand for 1 h at 25 ± 5°C. The specimen may stand for 3 or 4 h **(1)**[7] if no contamination occurs.

11.1.3 When making referee or research tests, pass pure nitrogen or CO$_2$-free air through the solution until the pH is measured.

NOTE 1—Air may be cleaned by passing it through a gas washing bottle containing at least 200 mL of 3*N* H$_2$SO$_4$ and then through a tower or U-tube containing ascarite or soda lime, 120 to 150 mm long.

11.1.4 Measure the pH on the prepared extract (see 11.1.1 through 11.1.3) as specified in 11.3.

11.2 *Test Method B pH of Paper (Unfiltered Extract) After Extraction for 1 h in Boiling Water*:

11.2.1 Transfer the test specimen to a 125-mL Erlenmeyer flask. Add about 70 mL of distilled water, stir well, and attach the condenser.

NOTE 2—Water-cooled condensers are desirable. The air condensers may be used if the temperature of the hot plate can be controlled as indicated in 11.2.2.

11.2.2 Place the flask on the hot plate. Reduce the hot plate temperature as necessary using the hot plate controls and boil gently for 1 h, taking care not to exceed the capacity of the condenser. The temperature should be maintained between 98 and 100°C (208 and 212°F).

11.2.3 At the end of the extraction period cool the flask in running water (to about 35 to 40°C), with the condenser tube in place and its upper end protected by a loosely fitted small beaker. Replace the condenser with a glass stopper and cool at room temperature. Transfer the mixture to a 100-mL beaker.

11.2.4 Transfer the extracts for referee or research tests to the 100-mL beakers while hot. Pass nitrogen or CO$_2$-free air through these extracts while cooling and until the pH is measured.

11.2.5 Measure the pH on the prepared extract (see 11.2.1 through 11.2.4) as specified in 11.3.

11.3 *pH Measurement*:

11.3.1 Keep a nitrogen or CO$_2$-free air cap over the solution during pH measurement. Stir and measure to 0.1 pH unit the pH of the unfiltered mixture in accordance with the instructions for the pH meter used.

11.3.2 Through observation, make certain that no plies of paper adhere to the electrodes during pH measurement.

11.3.3 Before recording the pH, leave the electrodes in the solution until there is no measurable drift in 30 s.

11.3.4 Wash the electrodes with distilled water after each measurement and recalibrate frequently.

11.3.5 Keep the electrodes, buffer, test solution, and wash water at the same temperature and set the compensator for this temperature.

12. Interpretation of Results

12.1 The pH of an extract of a paper sample indicates the extent to which components of the paper alter the hydrogen-hydroxyl equilibrium of pure water. In the case where the paper sample consists of highly purified cellulose having a low level of inorganic or noncellulosic organic impurities or additives, the alteration of this equilibrium will be slight, and a pH near 7, the neutrality point on the pH scale is likely. Additionally, the difference in pH measured by the two test methods described will be small.

12.2 In cases where inorganic or noncellulosic organic materials were present in the raw materials from which a paper was made, or were deliberately added during processing, the pH of the resulting paper extract will generally show greater deviation from pH 7 than in the case of the highly purified cellulosic paper described in 12.1. Further, the direction of the deviation from pH 7 and its magnitude cannot be predicted without information regarding the identity and quantity of noncellulosic materials present. In addition, the relationship of the results from the two test methods cannot be predicted for such samples.

12.3 When these test methods are referenced in specifications, an understanding of the noncellulosic materials present and the specific information needs of the buyer and seller must be considered in deciding whether Test Method A or Test Method B, or both, must be required.

12.4 When these test methods are used for analysis of materials of unknown origin or prior history, use of both Test Methods A and B is highly recommended, as suggested in 1.6.

12.5 It must be clear to the user of these test methods that an understanding of the composition of the paper being tested and the specific information required are the only unequivocal factors that can be used to determine whether Test Method A or Test Method B, or both, are best suited for a given analysis.

12.6 Examples of the relationship between results from Test Method A and Test Method B for specific papers are in 12.6.1-12.6.7. Additional information may be found in the technical literature for those wishing to pursue this topic.

12.6.1 The pH of the extract of a paper sized with rosin and alum is typically lower by 0.5 to 0.6 pH units when tested by Test Method B in comparison with data when Test Method A is used. This is believed to be caused by hydrolysis of the sizing components in boiling water to release hydrogen ions or acidic materials **(1)**[8].

12.6.2 On the other hand, it has been reported that melamine-formaldehyde resin hydrolyzes during extraction by Test Method B to release alkaline products that tend to increase the pH value of the extract when compared to the result measured by Test Method A **(1)**.

12.6.3 The consequence of 12.6.1 and 12.6.2 is that when a paper is made containing rosin and alum sizing as well as melamine-formaldehyde resin, the pH measured by Test Method A may be higher than, lower than, or nearly equal to that measured by Test Method B, depending upon the relative amounts of the various noncellulosic materials present.

12.6.4 Other materials are believed to exhibit similar effects.

12.6.5 Some believe that the hydrolysis occurring when Test Method B is used simulates changes that might occur during natural aging, and that values obtained by Test Method B correlate with paper-ink reactions in printing **(2, 3)**.

12.6.6 Barrow **(4)**, however, found that Test Method A correlated better with his accelerated aging tests.

12.6.7 In published data relating to the use of pH measurement by Test Method A or B in studying paper stability, Palenius **(5)**, Kelly **(6)**, and Wilson **(7, 8)** and co-workers report values on a variety of papers where results by Test Method B range from 2.5 units higher to 1.5 units lower than those determined by Test Method A.

12.7 It must be emphasized that no generalizations regarding the relationship of results by Test Method A and B is possible, nor can any simple rules of interpretation be provided.

13. Report

13.1 Report the following information:

13.1.1 The average of the two determinations to the nearest 0.1 pH unit, and

13.1.2 The test method used (Test Method A or Test Method B) for each result reported.

14. Precision and Bias

14.1 *Precision*:

14.1.1 *Test Method A (Cold Extraction)*:

14.1.1.1 *Repeatability (Within a Laboratory)*—±0.1 pH units for comparison of test results from the same test unit, where each test result is the average of two determinations, one each on separate sheets from the same test unit. Repeatability on test units from the same composite sample, as specified in this test method, should be equal to or smaller than this figure.

14.1.1.2 *Reproducibility (Between Laboratories)*—±0.5 pH units.

14.1.2 *Test Method B (Hot Extraction)*:

14.1.2.1 Repeatability is identical with that for Test Method A, in accordance with 14.1.1.1.

14.1.2.2 Reproducibility is identical with that for Test Method A in accordance with 14.1.1.2.

14.1.3 These limits of repeatability and reproducibility are the critical limits between which results obtained under the conditions specified in these test methods may be expected to lie 95 % of the time.

14.1.4 For additional information regarding expected precision of pH measurements of aqueous solutions, consult Test Method E 70.

14.1.5 The precision values stated above are based upon 14 reports on the TAPPI Collaborative Reference Program for paper for samples in the pH range from 5.0 to 6.0. Similar precision may be expected at other pH levels in the range from 4.0 to 10.0.

14.1.6 The user of these precision data is advised that it is based on actual mill testing or laboratory testing, or both. There is no knowledge of the exact degree to which personnel skills or equipment were optimized during its generation. The precision quoted provides an estimate of typical variation in test results which may be encountered when the test method is routinely used by two or more parties.

14.2 *Bias*—The procedures in these test methods for measuring the hydrogen ion concentration (pH) of paper after cold or hot extraction have no bias because the value for the pH is dependent upon the extraction conditions used as defined in terms of these test methods.

---

[8] The boldface numbers in parentheses refer to a list of references at the end of the text.

15. Keywords

15.1 cold extraction; hot extraction; industrial paper; paper; paper acidity; paper aging; paper alkalinity; pH; printing papers; writing papers

REFERENCES

(**1**) Wilson, W. K., Harvey, J. L., and Padgett, A. A., *Tappi*, Vol 34, 1951, p. 410.

(**2**) Grant, J., "The Determination of the pH Value of Paper," *British Paper and Board Makers' Association Proceedings Technical Section 36*, 1955, p. 473.

(**3**) Discussion of Printing, Packaging, and Allied Trades Research Association (PATRA) work on pH in paper, held at the 67th General Conference of the British Paper and Board Makers Association, London, 1954, and recorded in the article "The Quality of Paper and Board in Relation To Its Usage-Printing," *Proceedings of the Technical Section, British Paper and Board Makers' Association,* Vol 35: pp. 191–211, with specific reference on p. 204, 1954.

(**4**) Barrow, W. J., *Tappi* Vol 46, 1962, p. 468.

(**5**) Palenius, I., Åländer, P., and Juselius, A., *Papper Och tra*, No. 3, 1962.

(**6**) Kelly, G. B., *Bulletin of the American Institute for Conservation*, Vol 13, No. 1, 1972.

(**7**) Wilson, W. K., and Hebert, R. L., *TAPPI,* Vol 55, 1972, p. 1103.

(**8**) Wilson, W. K., and Hebert, R. L., *TAPPI,* Vol 52, 1969, p. 1523.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).