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WORKING GROUP
CHAIRMAN _____

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.

**Surface pH measurement of paper
(Five-year review of Official Method T 529 om-14)
(No changes from previous draft, Standard reaffirmed)**

1. Scope

1.1 This non-destructive test may be used to measure the hydrogen ion concentration (pH) on the surface of the paper in books and documents that constitute the collections of libraries and government archives.

1.2 This method serves as an alternative to TAPPI T 509 "Hydrogen Ion Concentration (pH) of Paper Extracts - Cold Extraction Method," and TAPPI T 435 "Hydrogen Ion Concentration (pH) of Paper Extracts - Hot Extraction Method," because it avoids the destruction of printed material in the determination of the permanence expected for paper (see also 11.2).

1.3 pH values obtained through the application of this method to sized materials such as writing, printing, and industrial papers reflect only the pH of the surface of these materials and should not be construed as pH values which may be determined by the cold water extraction method of the same material (*I*).

2. Summary

A flat combination electrode is immersed in a drop of water on the surface of the paper sample. The pH of the surface of the paper is determined with high accuracy and repeatability without the requirement of sample destruction (2,3).

3. Significance

3.1 Because the useful life of most papers is primarily a function of the acidity of the paper (4,5), it is necessary that the concentration of the hydrogen ion in the paper be known (4) so that appropriate preservation and/or restoration techniques may be employed to extend the useful life of books and documents which are determined to be acidic.

3.2 Since books and documents (some of which are very valuable or irreplaceable) cannot be destroyed or otherwise defaced for the purpose of pH determination, a need exists for a convenient procedure which is accurate but does not require destruction or extensive water soaking of the paper samples to be tested. This non-destructive method accomplishes this need (6,7,8,9).

4. Apparatus

4.1 *Commercial pH meter*, with flat combination electrode¹, which can be immersed in a single drop of water. The pH meter must measure pH with a precision of 0.1 pH unit and should include temperature compensation.

4.2 *Backing material*, non-absorbent material, such as gum rubber, to allow firm contact of electrode against surface of paper.

4.3 *Absorbent cotton*, to remove water after completion of test.

4.4 *Timer*, stopwatch or electric timer.

4.5 *Thermometer*, 0-100°C range.

4.6 *Volumetric flasks*, 1000 mL, for buffer solutions.

5. Reagents

5.1 *Water*. Reagent grade water used in this test method shall conform to ASTM Specification D 1193, Type I or II, Standard Specifications for Water (10).

¹Names 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.

NOTE 1: Water meeting this specification is typically sold by many manufacturers for use in HPLC, residue analysis, and spectrometry, and is packaged under nitrogen.

5.2 Standard buffer solutions:

5.2.1 *Potassium hydrogen phthalate buffer*, pH 4.01 at 25°C; dissolve 10.21 g of $\text{KHC}_8\text{H}_4\text{O}_4$ (A.C.S. primary standard or certified grade) in water and dilute to 1000 mL.

NOTE 2: The buffer capacity of this buffer solution is rather low and the solution should be protected from contamination with acids or alkalis. Its pH, however, is not affected by atmospheric carbon dioxide. Replace the buffer solution every six weeks or if mold appears.

5.2.2 *Phosphate buffer*, pH 6.86 at 25°C: dissolve 3.40 g of monobasic potassium phosphate (KH_2PO_4 , A.C.S. primary standard) and 3.55 g of anhydrous dibasic sodium phosphate, Na_2HPO_4 , in carbon dioxide-free water and dilute to 1000 mL. When protected from undue atmospheric exposure, this buffer solution is quite stable.

NOTE 3: The Na_2HPO_4 will absorb moisture from the air at relative humidities exceeding 40% at 25°C and should be dried at 100 to 130°C for 2 h before use.

5.2.3 *Borax buffer*, pH 9.18 at 25°C: dissolve 3.81g of sodium tetraborate $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ in carbon dioxide-free water and dilute to 1000 mL.

NOTE 4: The dilution value of this buffer solution is so small that changes in the water content of the borax are usually of no concern. Precautions should be taken to protect solution from prolonged atmospheric exposure and subsequent CO_2 absorption. The shelf life of this solution is about one month.

5.2.4 *Propriety buffer solutions:* These are commercially available and may be purchased in a ready-to-use solution form. The pH of these buffer solutions, however, must be accurately known if they are used.

6. Calibration

6.1 Connect the combination surface electrode to the pH meter.

6.2 Soak the combination surface electrode for at least 2 h in distilled water.

6.3 Calibrate the pH meter at pH 4.01 using phthalate buffer and at 6.86 using phosphate buffer, following the instructions in the pertinent pH meter instruction manual. The borax buffer is used for calibration when an unusually high pH is indicated.

7. Sampling and test specimens

7.1 From each test unit of the sample obtained in accordance with TAPPI T 400 “Sampling and Accepting a Single Lot of Paper, Paperboard, Containerboard or Related Product,” select at random at least five different sheets, pages, or leaves. Since this procedure is normally applied to material that is not to be subjected to destructive testing, the test unit may be in the form of a book or bound pages.

7.2 The application of this procedure does not require cutting or any other destructive method of sampling.

8. Procedure

8.1 Follow instructions under 6.1.

8.2 Follow instructions under 6.2.

8.3 Back the specimen with a non-absorbing, resilient material such as gum rubber. Such a backing material allows the electrode to be contacted firmly and evenly with the surface of the paper.

8.4 Place one drop of room temperature ($25^{\circ} \pm 5^{\circ}\text{C}$) reagent water on a leveled surface of the specimen (do not spread the water droplet on the paper surface as this is accomplished when the electrode is lowered into the water).

8.5 Immerse the measuring surface of the electrode in the water droplet. Although equilibration is accomplished in about 2 min, it is desirable to allow about 10 min of immersion before each reading, but no immersion time greater than 30 min has yet been determined to be necessary even on highly sized or coated paper.

8.6 Determine pH according to the manufacturer’s instructions for the pH meter used. Read the pH to the nearest 0.1 pH unit.

8.7 After recording the pH value, immediately remove the electrode vertically from the water droplet.

8.8 Using absorbent cotton, blot the area of paper wetted by the droplet and allow to air dry before storage or further treatment.

NOTE 5: In the case of pH measurements of inner pages of whole books, allow the blotted area to dry before closing the book.

8.9 Wash the electrode with reagent water after each measurement. Recalibrate frequently and store the electrode in reagent water.

9. Report

Report the average of five determinations to the nearest 0.1 pH unit.

10. Precision

10.1 The following estimates of repeatability and reproducibility are based on data from an interlaboratory trial involving four laboratories and 8 different paper and board materials. The trial was conducted in November 1997 using the “om-88” revision of this method. Testing is based on 5 determinations per test result and 1 result per lab per material.

Repeatability (within the lab)	$r = 0.13$ pH units
Reproducibility (between labs)	$R = 0.41$ pH units

10.2 Repeatability and reproducibility are estimates of the maximum difference (at 95%) which should be expected when comparing test results for materials similar to those described above under similar test conditions. These estimates may not be valid for different materials or testing conditions.

11. Additional information

11.1 Effective date of issue: To be assigned.

11.2 Other TAPPI procedures for the determination of the pH of paper are TAPPI T 435 (hot extraction) and TAPPI T 509 (cold extraction).

11.2.1 The values obtained by these methods have been found to be somewhat different from surface pH measurements because of the rate of diffusion to the surface of hydrolyzed alum or other sulfates in the paper.

11.2.2 In the preparation of this method, surface pH measurements have been found to approximate more closely those values obtained by the cold extraction method than those obtained by the hot extraction method.

11.3 Other methods of pH determination have been discussed by Launer (11), Browning (4), Minor (12), and Barrow (13). These methods, however, either require destruction of the specimen or have been found to be unreliable as surface measurements (6).

11.4 It has also been determined that highly sized, calendered or coated papers require longer equilibration time to obtain a stable pH value since the nature of the surface slows the wetting action and subsequent hydrogen ion extraction from the paper fibers.

11.5 The 1994 revision of this method includes revision of the precision statement and inclusion of ASTM Type I or II water. Only editorial changes were made in the 2009 version.

12. Keywords

Paper, pH

Literature cited

1. Torbjorn, H., "Various Methods for Determining the pH Values on Paper Surfaces," *Norwegian Research Institute of Paper Industry*, 1960, p.5.
2. Schwabe, K., "Progress in pH Measuring Technique," *VEB publ Technik Berlin*, 1953, p. 23.
3. Stamm, A.J., "A Comparison of Three Methods for Determining the pH of Wood and Paper," *Forest Products Journal*, July 1961, pp. 310-312.
4. Browning, B.L. and Ulm, R.W.K., "The Nature and Measurement of Paper Acidity," *Paper Trade Journal* **102**(8): 69(1936).
5. Launer, H.F., "Determination of the pH Value of Papers," *J. Research* (National Bureau of Standards) **22**:663 (139).
6. Palenius, I., Olander, P., and Juselius, A., "Reliability of the Determination of the pH Value of Pulp, Paper and Board," *Paperi Ja Puu* **44**:85 (1962).
7. Flynn, J.H. and Smith, L.E., "Comparative pH Measurements on Papers by Water Extraction and Glass Electrode Spot Tests," *Tappi* **44**(3): 223 (1961).
8. Hudson, F.L. and Miller, W.D., "The Use of Flat Headed Glass Electrodes for Measuring the pH of Paper," *Svensk Paperstid* **62**: 83 (1959).
9. Huber, V.C., "The Use of Flat Headed Glass Electrode for Measuring the pH of Paper," *Papier* **18**: 45 (1964).
10. ASTM Standard D-1193, "Standard Specification for Reagent Water," American Society for Testing and Materials, Philadelphia, PA.
11. Launer, H.F., "Retention of Aluminum Ions and Hydrogen Ions in Paper," *J. Research* (National Bureau of Standards) **22**: 553 (1939).
12. Minor, J.E. and Farmer, M., "The pH Test for Paper," *The Paper Industry and Paper World* **22**: 565 (1940).
13. Barrow, W.J., "Spot Testing for Unstable Modern Book and Record Papers," *Permanence/Durability of the Book - VI*, 1969, p. 11.

References

Taylor, J.E., "An Apparatus for the Continuous Production of Triple Distilled Water," *Journal of Chemical Education* **37**: 204 (1960).

ASTM D 778-93, American Society for Testing and Materials, Philadelphia, PA.

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