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T 435

BALLOT NO. 02 SARG

DRAFT NO. 02

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WORKING GROUP CHAIR 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 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.

Hydrogen Ion Concentration (pH) of Paper Extracts (Hot Extraction Method)

(*Five-year review of Official Method T 435 om-22)*

(Changes from Draft 1 Incorporated)

1. Scope

1.1 This method measures the hydrogen ion concentration, expressed in terms of pH, of an aqueous extract of paper obtained by hot extraction (unfiltered and extracted by boiling water for one hour).

1.2 It may be applied to writing, printing and sized industrial paper, but it is not intended for unbuffered types such as electrical insulating and condenser papers. Values determined by this method will reflect changes resulting from heat-induced hydrolysis. Additives, such as those used in filled and coated papers can have an effect on the extract pH.

1.3 The cold extraction method is described in TAPPI T 509, "Hydrogen Ion Concentration (pH) of Paper Extracts (Cold Extraction Method)."

1.4 Surface pH measurement of paper is described in TAPPI T 529, "Surface pH Measurement of Paper."

2. Summary

This method consists of a boiling water extraction of the specimen for one hour followed by a pH measurement with a commercial pH meter.

3. Significance

The pH determination measures the extent to which the paper alters the hydrogen-hydroxyl equilibrium of pure water. The pH (acidity) is important because of its effect on the permanence of the paper. Although the acidity may be determined as the amount of water soluble acidity by titration with alkali, the hydrogen ion concentration (pH) is more indicative of the stability of paper than is the total acidity.

4. Definitions

4.1 *pH*, the negative logarithm (to base 10) of the hydrogen ion concentration of a solution.

4.2 *Paper acidity*, the extent to which water soluble material in the paper alters the hydrogen-hydroxyl equilibrium of pure water causing an excess of hydrogen ions, as measured by a commercial pH meter under specified conditions.

4.3 *Paper alkalinity*, the extent to which water soluble material in the paper alters the hydrogen - hydroxyl equilibrium of pure water causing an excess of hydroxyl ions, as measured by a commercial pH meter under specified conditions.

5. Apparatus

5.1 *pH meter*, a commercial pH meter including a glass electrode, a calomel reference electrode, and a potentiometer that will measure emf and indicate pH directly with a precision of 0.1 pH unit. The circuit should be compensated for temperature. Use of combination electrodes or FET electrodes (alternate acceptable electronic electrodes) is permissible.

5.2 *Erlenmeyer flasks*, 125-mL with standard taper joint.

5.3 *Reflux condensers*, preferably water cooled, West or Allihn Type, with 300-mm jackets, standard taper (ST) 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.

5.4 *Gas dispersion tube*, with 20 mm coarse fritted disc at 90° angle.

5.5 *Other apparatus*: 100-mL beakers; 100-mL graduated cylinder; 1000-mL volumetric flasks; stirring rods, all carefully cleaned and rinsed with distilled water before use.

6. Reagents

6.1 Reagent grade water used in this test method shall conform to ASTM Specification D 1193, Type I or II, Standard Specifications for Water (*1*).

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.

6.2 *Standard buffer solutions*:

6.2.1 *Potassium hydrogen phthalate buffer*, pH 4.01 at 25°C. Dissolve 10.21 grams of $KHC_8H_4O_4$ (A.C.S. Primary Standard or certified grade) in water and dilute to 1000 mL.

NOTE 2: As the buffer capacity of this solution is rather low, protect the solution from contamination with acids and alkalies. However, the pH is not affected by atmospheric carbon dioxide. The solution should be replaced after six weeks, or earlier if mold appears.

6.2.2 *Phosphate buffer*, pH 6.86 at 25°C. Dissolve 3.40 grams of monobasic potassium phosphate KH_2PO_4 (A.C.S. Primary Standard) and 3.55 grams anhydrous dibasic sodium phosphate, Na_2HPO_4, in carbon dioxide-free water and dilute to 1000 mL.

NOTE 3: The Na2HPO4 will absorb moisture at relative humilities exceeding about 40% at 25°C and should be dried for two hours at 110-130°C before use. This buffer solution is quite stable when protected from undue exposure to the atmosphere.

6.2.3 *Potassium hydrogen tartrate buffer*, pH 3.56 at 25°C. Add one gram of $KHC_4H_4O_6$ to 100 mL water about 30°C, shake for several minutes, cool at 25°C, decant, and filter to secure an approximately saturated solution.

NOTE 4: The pH is insensitive to changes of concentration, so elaborate precautions to ensure saturation are unnecessary. The temperature of saturation may vary from 22 to 28°C. Excess solid should be removed as it may cause erratic potentials at the liquid junctions. The tartrate solution is subject to molding accompanied by an increase of pH. Consequently, it cannot be used for more than a few days unless a preservative, such as a crystal of thymol, is added.

6.2.4 *Borax buffer*, pH 9.18 at 25°C. Dissolve 3.81 grams (air-dry weight) of $Na_2B_4O_7 \bullet 10H_2O$ in carbon dioxide-free water and dilute to 1000 mL.

NOTE 5: The dilution value of this solution is so small that changes in the water content of the borax will not affect the pH of the solution. However, exposure to atmospheric carbon dioxide may change its value. It is advisable to replace the solution about a month after preparation.

6.2.5 *Proprietary buffers*, these are permitted provided they are of the proper pH value. Standard buffers of the proper pHs may be purchased and used.

7. Calibration

Before measuring the pH of the specimen solution, calibrate the pH meter at pH 4.01 using the phthalate buffer, and check the phosphate buffer which should have a pH of 6.80 to 6.90. On long runs, check the calibration with a buffer solution having a pH nearest to the measured value of the specimen after measuring approximately every five specimens. After checking, wash the electrode several times with distilled water. The borax buffer and the tartrate buffer may be needed for a specimen with an unusually high or low pH.

8. Sampling

8.1 Obtain a sample of the paper in accordance with TAPPI T 400 “Sampling and Accepting a Single Lot of Paper, Paperboard, Containerboard, or Related Product.” Avoid touching paper with fingers.

9. Test specimen

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

9.2 Take an equal number of sheets (one or more) from each test unit obtained in accordance with TAPPI T 400, but not less than a total of five sheets, combining the sheets from all test units. Holding the sheets at one end, cut and crosscut the other end into 5-10 mm squares. Do not include any paper touched with the fingers. From each quantity of cut paper, weigh a test specimen of 1 ± 0.01 g.

9.3 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 same procedure as specified for the composite.

10. Procedure

10.1 Transfer the test specimen to a 125-mL Erlenmeyer flask. Add 70 mL of reagent grade water, stir well and attach the condenser.

NOTE 6: Water-cooled condensers are desirable. The air condensers may be used if the temperature of the hot plate can be reduced as indicated below.

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

10.3 At the end of the extraction period cool the flask in running water (to about 35-40°C), with the condenser tube in place and its upper end protected by a loosely fitted small beaker.

10.4 Transfer the extract to a 100-mL beaker. Pass nitrogen or CO_2-free air through the solution while cooling to room temperature.

NOTE 7: Air may be cleaned by passing it through a gas washing bottle containing at least 200 mL of 3N H2SO4 and then through a tower or U-tube containing ascarite or soda lime, 120-150 mm long.

10.5 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 according to instructions for the pH meter used. Keep the electrodes, buffer, test solution and wash water at the same temperature and set the compensator for this temperature.

10.6 Before recording the pH, leave the electrodes in the solution until there is no measurable drift in 30 s. Wash the electrodes with reagent grade water after each measurement and recalibrate frequently.

10.7 For best results, do not use soap or detergent to clean glassware. Use an acid cleaning solution and rinse adequately.

11. Report

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

12. Precision

12.1 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 results from the same composite sample, as specified in this method should be equal to or smaller than this figure.

12.2 Reproducibility (between laboratories) = ± 0.5 pH units.

12.3 Comparability = not known.

12.4 The precision values stated above are based upon 14 reports of 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.

12.5 The user of these precision data is advised that it is based on actual mill testing, 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 this method is routinely used by two or more parties.

13. Keywords

pH, Paper, Extraction, Acidity, Alkalinity.

14. Additional information

14.1 Effective date of issue: To be assigned.

14.2 This revision consists of a review and development of precision statement based on data collected from reports on the Collaborative Reference program for paper. It has also been put into the current format for TAPPI test methods.

14.3 Previously, in TAPPI T 435 m-52, two procedures for pH were given, a cold and a hot extraction. This method is applicable only to hot extractions and should also be differentiated from TAPPI T 428, "Hot Water Extractable Acidity or Alkalinity of Paper" which measures the titratable hot water extracted acidity or alkalinity of paper. The changes in this procedure from the previous method are: Specifying additional buffers for calibration and permitting the use of a hot plate.

14.4 It has been found (*2*) that melamine-formaldehyde resin hydrolyzes during hot extraction and releases alkaline products which tend to increase the pH value of the extract. Consequently, when a paper contains both alum and melamine resin, the pH of the hot extract may be higher, or lower than, or equal to a cold extraction value, depending on the relative amounts of alum and melamine resin present.

14.5 The pH of a hot extract of paper sized with rosin and alum is lower than that of a cold extract typically by 0.5 or 0.6 units (*2*).

14.6 Proponents of hot extraction believe that the hydrolysis simulates changes which might occur during natural aging and that values obtained by this method correlate with paper-ink reactions in printing (*3,4*). On the other hand Barrow (*5*) found that cold extraction correlated better with his accelerated aging tests.

14.7 An additional list of reference material for this method is found in *Tappi* **50** (12): 195-A (1967).

14.8 Related methods: French AFNOR NFQ 03-005; Canadian PAPTAC G.25; AS/NZS 1301.422; ISO 6588-2.

14.9 This method was revised in 1942, corrected in 1952, and revised in 1968.

14.10 The 1994 revision of this method includes revision of the precision statement and inclusion of ASTM Type I or II water.

Literature cited

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4. *Patra BP & BMA*, **34:**204 (1954).
5. Barrow, W. J., *Tappi* **46:**468 (1962).

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1. Palenius, I., Alander, P., and Juselius, A., *Paperi Puu* **44:**85 (1962).
2. Taylor, J. E., *J. Chem. Educ.* **37:**204 (1960).
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4. Cranston, J. A. and Brown, H. F., *Trans. Faraday Soc.* **33:**1455 (1937).(7): 1091 (1972).
5. ASTM Method 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.

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