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## DETERMINATION OF THE pH VALUE OF PAPERS

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## ABSTRACT

A simple and rapid procedure for the determination of the pH value of papers is described. The paper is mixed with water, and after letting it stand for 1 hour in the cold, the pH is determined in the unfiltered mixture, using a glass electrode. The values so obtained are in good correlation with the amounts of alum used in the manufacture of the papers and are useful in predicting the chemical stability of the papers. The relationship between the percentages of alum and the pH obtained with the method described and with the method in general use employing hot extraction, was studied in detail for a large number of experimental papers produced in the paper mill at the National Bureau of Standards. The experiments showed that the increase in acidity upon heating, observed by previous workers, is usually three to four times the hydrogen-ion concentration of the cold paper-water mixtures. No advantage of using hot water for the extraction was observed.

Experiments showed that the usual fibrous papermaking materials have the property of raising the pH of an acidic solution containing  $\text{CO}_2$  or aluminum sulfate, and that neutral papers gave essentially the same pH, whether extracted with water of pH=6.7 or with some of the same water containing  $\text{CO}_2$  and having a pH=5.9. Therefore, the requirements of present standard methods, with respect to the pH of the distilled water used for extraction, appear to be unnecessarily severe.

Other factors studied were time and temperature of extraction, neither one of which appears to be critical in the cold extraction. Previous workers have found that these two factors are important in the method of hot extraction.

Grinding was found to be unnecessary for the papers studied, but the aqueous mixtures of unground, thick, "kraft" papers should be allowed to stand 20 hours before determination of the pH.

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## I. INTRODUCTION

The pH of a paper extract is now usually considered one of the most reliable indices of the permanence of a paper, although the first

applications of pH values for papers were reported scarcely a dozen years ago.<sup>1</sup> Prior to the use of pH values, paper acidity was identified with the "total acidity" or titratable acid in extracts of the paper, an unstable paper usually having a higher acidity than a stable one. In order to find a method more suited to modern control work for measuring acidity than the measurement of total acidity, Hoffman<sup>2</sup> sought to replace it with the measurement of pH, and found that both types of data could be correlated equally well with the stability of a wide variety of papers. His results are in agreement with the later work of Köhler,<sup>3</sup> who previously had developed the method for titratable acid. Hoffman measured the pH of extracts prepared in the same manner as those for total acidity, namely, by extraction near 100° C for 1 hour.

This method, with changes for eliminating the possible effect of CO<sub>2</sub>, both in the filtration and cooling procedure and with the specification that the water used for extraction should have a pH value between 6.6 and 7.0, was adopted by the Technical Association of the Pulp and Paper Industry.<sup>4</sup> Grinding of the paper was further specified and the extraction temperature was fixed between 95° and 100° C. The method of measuring the pH was left to the choice of the analyst, and the values obtained were to be expressed to the nearest 0.05 pH unit for the electrometric and 0.1 pH unit for the colorimetric determination. The Federal specifications<sup>5</sup> are essentially the same, except that water of pH 6.9 to 7.1 is prescribed.

The accuracy implied in the TAPPI method is, however, much higher than is compatible with actual experience. Under the supervision of Wehmhoff,<sup>6</sup> three different Government laboratories conducted cooperative tests on given papers, using procedures essentially within the specifications of the TAPPI method. Variations between laboratories in pH values obtained were 0.34 pH unit, on the average, with a maximum variation of 1.0 pH unit, indicating that some modification of either the method or the precision requirements, or both, was necessary.

Investigators have studied the factors involved in the hot extraction. Browning and Ulm<sup>7</sup> found that hot extraction gave lower pH values than cold extraction for three commercial papers, and that the temperature at which the hot extraction is made should be controlled to 99° to 100° C instead of 95° to 100° C as permitted in the standard methods. They found, in agreement with Wehmhoff,<sup>6</sup> that the pH values, obtained using hot extraction, are not equilibrium values, since they tend to rise if the mixtures are allowed to stand in the cold. They also found that atmospheric CO<sub>2</sub> has no appreciable effect in the pH range up to 6.0, during either the hot extraction or the cooling process and, therefore, that the precautions prescribed by the TAPPI method in this respect are not necessary. Furthermore, they question the wisdom and feasibility of grinding the paper.

<sup>1</sup> W. Holweck, *Papier-Fabr.* 25, 659 (1927).

<sup>2</sup> W. F. Hoffman, *Paper Trade J.* 86, TS143 (March 1, 1928).

<sup>3</sup> Sigurd Köhler, Investigations into the determination of acidity and copper number in paper, Report No. 56 of the Statens Provninganstalt, Stockholm (1932). See especially pages 7 and 11. (In Swedish.)

<sup>4</sup> TAPPI-T435m, Hydrogen ion concentration (pH) of paper extracts, Sept. 6, 1934. Copies may be obtained from the Association, 122 E. 42d Street, New York, N. Y.

<sup>5</sup> Federal Specification for Paper: General Specification UU-P-31a, page 10 (June 1937). Obtainable from the Superintendent of Documents, Government Printing Office, Washington, D. C., price 5 cents.

<sup>6</sup> B. L. Wehmhoff, Progress Report on the Determination of pH Values and Total Acidity in Paper. United States Government Printing Office (1930).

<sup>7</sup> B. L. Browning and R. W. K. Ulm, *Paper Trade J.* 102, 89 (Feb. 20, 1936). This contains an extensive bibliography and a historical survey.

The procedure of hot extraction has been adhered to in the past, doubtless because the data have been lacking which are necessary to show that extraction in the cold gives a pH value which is representative of the paper. Furthermore, the TAPPI method of preparing the paper extract involves filtration to allow application of a wide variety of methods of measuring the pH. Colorimetric methods, which are known to depend largely upon the psychological and physiological qualities of the analyst, usually require colorless, clear extracts, and necessitate filtering and excessive handling, which normally involve the danger of contamination. Again, the use of the hydrogen electrode demands filtration and a knowledge of the chemical composition of the solution to be tested to insure against poisoning of the electrode. Thus, in limiting the method of measuring the pH to glass electrodes, which do not require preliminary handling of the extracts, a simplicity of procedure can be achieved, which is especially important in pH work.

In previous investigations in which commercial papers were studied, the proportions of alum used in their manufacture were either not known or not given. In the present investigation a large number of experimental papers were available whose papermaking details were known and had been varied in such a manner as to permit a study of the relationships between the proportions of alum used in the manufacture of the papers, the pH values, and the chemical stability of the papers. Such data should show whether pH values obtained by cold extraction are as valid as those obtained by hot extraction. The experimental papers were produced under carefully controlled conditions in the semicommercial paper mill of the National Bureau of Standards. One commercial coated paper and eight samples of file-folder stock were also included in the study.

## II. METHOD OF MEASURING THE pH

A commercial glass electrode, in conjunction with a saturated potassium chloride-calomel half cell, calibrated in the usual manner with 0.05 *M* potassium acid phthalate of pH=4.0, was used for all determinations of pH throughout the present work. The advantages of this electrode are well-known, but some care must be used in applications to paper-water mixtures. When determinations in neutral or nearly neutral systems were made, after the glass electrode had been used in solutions either distinctly acidic or alkaline, the values obtained were at first too low or too high, in the direction of the previously measured pH. This is shown in table 1 for paper 21. The glass electrode was carefully rinsed with distilled water after each treatment described in column 2 and then inserted in the unfiltered extract of the ground paper. For papers farther removed from neutrality, as for example paper 24, the effect was no longer noticeable. Another glass electrode gave similar results with a paper extract of pH=7.1, while a paper extract of pH=6.0 showed a smaller but nevertheless appreciable effect. Ordinarily 1 to 2 minutes appear to suffice for the attainment of equilibrium, but for measurements in the neutral range, especially if the preceding measurement was of an alkaline solution, approximately 15 minutes time should be allowed, or the electrode should be immersed for 1 minute in a solution having a lower pH than the one about to be measured. The phthalate

buffer, pH=4.0, was found convenient for this purpose. Thus, the large errors involved in approaching from the alkaline side are replaced by the smaller errors involved in approaching from the acidic region.

TABLE 1.—*Effect of previous treatment of glass electrode when used to measure pH of paper extracts*

PAPER SAMPLE 21

Previous treatment of glass electrode	Time interval after insertion of electrode (minutes)	pH measured after Time Interval	Relative error (pH Units)
One hour in distilled water.....	10	6.6	-----
Ten minutes in paper extract of pH=9.4.....	1	7.8	1.2
	9	6.9	.3
	14	6.7	.1
Twenty minutes in solution of pH=4.0.....	1	6.4	-.2
	3	6.4	-.2
	11	6.5	-.1
One hour in distilled water.....	10	6.6	0

PAPER SAMPLE 24

Fifteen minutes in distilled water.....	10	5.6	-----
Ten minutes in solution of pH=4.0.....	1	5.6	0
	10	5.6	0
Ten minutes in paper extract of pH=9.4.....	1	5.6	0
	10	5.6	0

### III. COMPARISON OF THE pH VALUES OBTAINED WITH HOT AND WITH COLD EXTRACTION

#### 1. RELATIONSHIP BETWEEN THE pH VALUES AND THE AMOUNTS OF ALUM USED

The acidity of newly made paper is practically all derived from the salt, aluminum sulfate, termed in the trade "papermakers alum", which is used to aid the formation of the fibers into a sheet, to precipitate rosin from rosin size onto the fibers to make the paper water-repellent, and as a mordant for coloring materials. Therefore, the relationship between the amounts of alum used in the papermaking process and the pH values is an important criterion of the validity of the latter.

The pH values for cold extraction were obtained after mixing 1.00 g of ground paper with 70 ml of distilled water, pH=6.6 to 6.9, at 20° to 30° C, allowing the mixture to stand for 1 hour and then measuring with a glass electrode by direct insertion into the paper-water mixture. After this measurement, the same mixtures were used to obtain the pH values for hot extraction. They were heated in a Pyrex flask covered loosely with a watch glass and immersed to the neck in a steam bath (99° to 100° C) for 1 hour, after the temperature of the mixture had become constant. After cooling the mixture, the pH values were obtained, and were the same as those obtained from mixtures made up directly with hot distilled water and kept in the steam bath for 1 hour, and subsequently cooled.

The pH values are listed in table 2, along with the alum percentages. A comparison between these variables must be limited, however, to papers made with like amounts of rosin size,<sup>8</sup> inasmuch as the pH values are affected also by the rosin size. This is owing to the fact that rosin size, which is a suspension of free rosin in sodium resinate solution, reacts with strong acids to precipitate rosin, which is a weak insoluble acid or group of acids, and reacts with aluminum ion to form a more or less well-defined insoluble compound of aluminum and rosin, thus reducing the concentration of aluminum ion. The effect on the values for pH-cold and on the changes in (H<sup>+</sup>) during heating, of varying the amount of rosin size, is easily seen in the pairs 12 and 13, 25 and 26, and, to a smaller extent 1 and 2, 3 and 4.

TABLE 2.—Relation between the acidity values and chemical characteristics of the papers

1	2	3	4	5	6	7	8	9
Sam- ple num- ber	Resin	Alum <sup>a</sup>	pH, using cold extrac- tion	pH, using hot extrac- tion	Δ pH	Δ (H <sup>+</sup> )	(H <sup>+</sup> ) Cor- respond- ing to pH cold	Decrease in alpha- cellulose
NEW RAGS								
						<i>Equiv/liter</i> (x10 <sup>-7</sup> )	<i>Equiv/liter</i> (x10 <sup>-7</sup> )	<i>Percent</i>
1	0.9	4.0	4.9	4.3	0.6	380	130	8.0
2	1.7	4.0	5.1	4.4	.7	320	79	7.0
3	.9	2.0	5.2	4.5	.7	250	63	4.9
4	1.7	2.0	5.4	4.7	.7	160	40	5.3
5	.2	1.5	5.5	4.9	.6	94	32	3.2
6	1.8	1.2	5.6	5.0	.6	75	25	4.6
7	.9	1.1	5.6	5.0	.6	75	25	2.9
8	1.6	.9	6.4	5.9	.5	9	4	2.0
9	.3	.8	6.4	6.0	.4	6	4	.9
10	.8	.7	6.3	6.0	.3	5	5	1.4
11	.3	.5	7.2	7.3	-----	-----	.6	.3
SODA-SULFITE (1:1)								
12	1.2	2.4	5.2	4.6	0.6	190	63	6.3
13	.2	2.1	4.9	4.3	.6	380	130	7.6
14	.2	1.5	5.3	4.8	.5	110	50	3.3
15	1.6	1.4	5.5	4.9	.6	94	32	5.0
16	0.9	1.3	5.8	5.1	.7	63	16	2.0
17	1.0	1.3	5.9	5.1	.8	66	13	3.2
18	1.2	1.1	6.0	5.3	.7	40	10	4.0
19	.3	1.0	6.4	5.7	.7	16	4	1.2
20	.9	.8	6.2	5.5	.7	26	6	2.6
21	.3	.5	6.6	6.2	.4	4	2.5	1.0
22	.3	0	6.9	6.4	.5	3	1.3	0
SPECIAL SULFITE <sup>b</sup>								
23	1.9	2.3	5.2	4.9	0.3	63	63	4.6
24	1.7	1.1	5.6	5.3	.3	25	25	3.6
25	1.1	.8	5.6	5.0	.6	75	25	2.9
26	1.6	.8	6.1	5.7	.4	12	8	.8
27	1.1	.6	6.0	5.7	.3	10	10	1.8
28	.2	0	6.9	7.2	-----	-----	1	.4

See footnotes at end of table.

<sup>8</sup> Papers with resin contents, shown in table 2, from 0.8 to 1.2 percent, were made with a definite volume of rosin size calculated to contain a total amount of rosin, the weight of which was 1 percent of that of the dry fibers. Papers with resin contents from 1.6 to 1.9 percent were made with double this volume of rosin size. All other papers had no added rosin but contained natural resins or waxes in small amounts. Added rosin and natural resins are termed "resin" when determined analytically.

TABLE 2.—Relation between the acidity values and chemical characteristics of the papers—Continued

1	2	3	4	5	6	7	8	9
Sam- ple num- ber	Resin	Alum	pH, using cold extrac- tion	pH, using hot extrac- tion	$\Delta$ pH	$\Delta$ (H <sup>+</sup> )	(H <sup>+</sup> ) Cor- respond- ing to pH cold	Decrease in alpha- cellulose
BLEACHED SULFATE <sup>b</sup>								
29	1.0	2.3	5.2	4.9	0.3	63	63	1.4
30	.9	1.0	5.8	5.0	.8	84	16	.8
31	.9	.7	6.4	6.0	.4	6	4	.7
32	.1	0	6.8	7.0	-----	-----	2	.2
OLD RAGS								
							Surface sizing	
33	1.1	1.6	5.0	4.7	0.3	100	Glue: pH=4.7 Starch: pH=7.2 None ° Glue: pH=4.7	
34	1.1	1.6	5.8	4.9	.9	110		
35	1.1	1.5	5.7	4.9	.8	110		
36	1.1	1.5	5.2	4.8	.4	97		
NEW RAGS								
37	1.1	1.5	5.7	5.1	0.6	59	Glue: pH=4.5	
COMMERCIAL COATED								
38	-----	-----	6.3	5.4	0.9	35	None.	

<sup>a</sup> Percentage of alum was based on dry weight of solid materials in the chest.

<sup>b</sup> Pulp subjected to special purifying process by the manufacturers.

° No surface sizing; starch added to beater.

In figure 1 the alum percentages are plotted against the pH values, for series of papers made with like amounts of rosin size and made from the same fibrous materials. The heavy lines connecting the points represent hot extractions, and the light lines of similar structure represent corresponding cold extractions. Figure 1 shows that the much simpler method of cold extraction gives pH values which are related to the amounts of alum used in making the papers, and that there is no advantage in this respect, in using the method of hot extraction.

Such an analysis for papers 33 to 38 was not possible, since the surface-sizing solutions also may be expected to affect the pH-alum relationship somewhat. It should be noted, however, that the pH changes upon heating the extracts, for these papers, are not greatly different from those of the other papers.

The decrease in pH during heating, for papers 1 to 32, table 2, is shown in column 6 as " $\Delta$ pH," and it appears to be similar, 0.6, expressed as pH units, for all papers made with more than 0.5 percent of alum. Such a comparison is misleading, however, since the pH is a logarithmic function. When these changes in pH are expressed as increases in the hydrogen-ion concentration,  $\Delta$ (H<sup>+</sup>), column 7, the changes are seen to vary greatly and depend generally upon the proportions of

alum originally added. It is of interest to note that the changes in acidity upon heating,  $\Delta(H^+)$ , are usually three to four times as

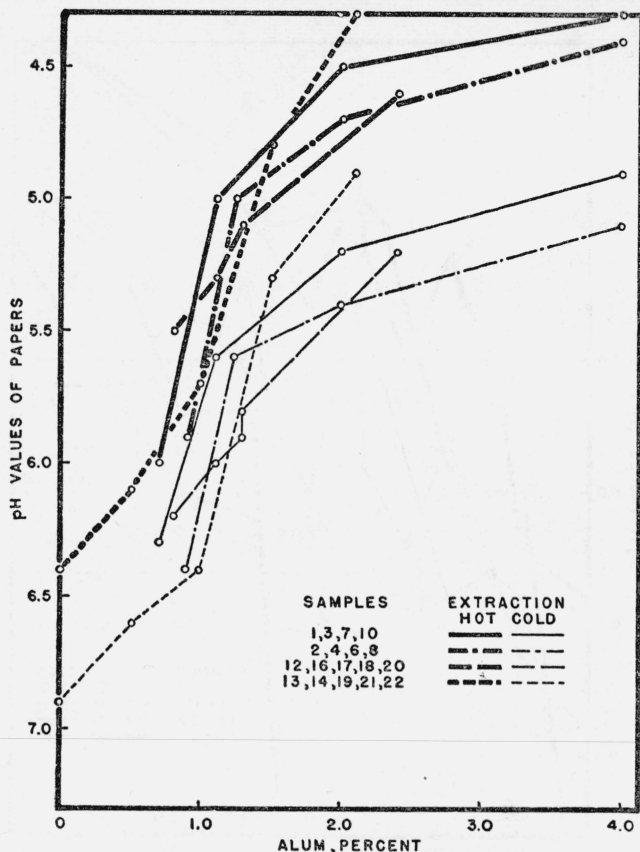


FIGURE 1.—Relationship between the amounts of alum used in making the papers and the pH values for hot and cold extractions.

large as the original acidity,  $(H^+)$ , column 8, calculated from the values for pH-cold.

## 2. RELATIONSHIP BETWEEN THE pH VALUES AND THE STABILITIES OF THE PAPERS

Another important requirement of a method of extraction is that the acidity values thus obtained may be used as a basis for predicting relative stability of the papers. The change in alpha-cellulose content of a paper upon accelerated aging by heating is regarded as an index of relative stability. This criterion is especially applicable when comparisons are restricted to papers made from the same fiber.

The relative stability in terms of change in alpha-cellulose content upon accelerated aging, which consisted in heating the papers in air for 72 hours at  $100^{\circ}C$ , is given in table 2, column 9. When these are plotted against pH and the points connected as before with heavy and light lines, corresponding to hot and cold extractions, respectively,

it is seen from figure 2 that the method of cold extraction results in pH values which are as useful for predicting relative stability as are those of the method of hot extraction.

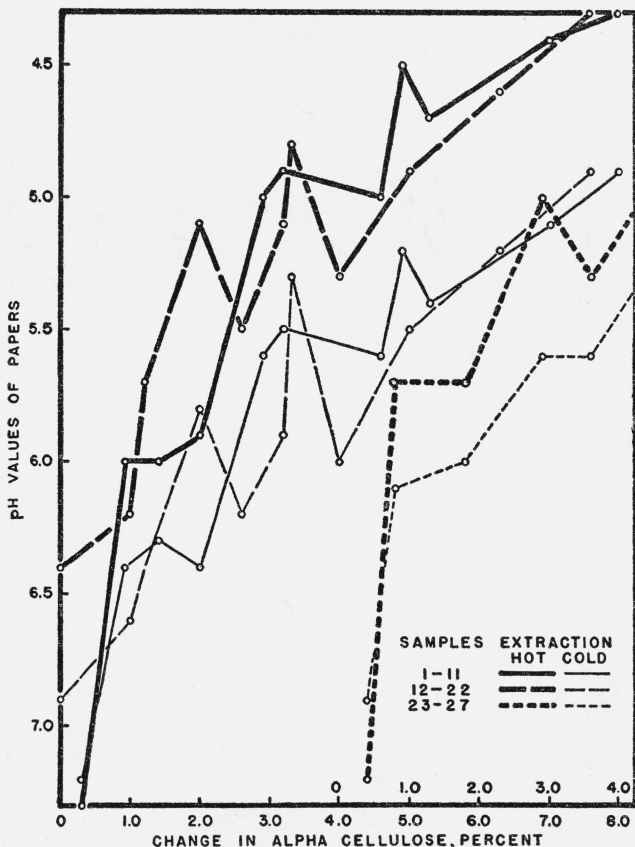


FIGURE 2.—Relationship between the pH values for hot and cold extractions and the stabilities of the papers

#### IV. STUDY OF THE FACTORS INVOLVED IN THE METHOD OF COLD EXTRACTION

##### 1. PURITY OF THE WATER REQUIRED FOR THE EXTRACTION AND THE EFFECT OF FIBERS UPON THE pH

The use of water with a pH between 6.6 and 7.0 or 6.9 and 7.1, as prescribed by the TAPPI method and the Federal specification, requires redistillation of ordinary distilled water in a well-ventilated laboratory.

It is doubtful, however, if water of such purity is ever necessary in extractions of paper. Distilled water, which contains enough  $\text{CO}_2$  to give a pH=6.1, but which is pure in other respects, contributes, according to calculation, only 0.1 pH unit in a paper-water mixture of which the measured pH=5.8. Actually, the effect of  $\text{CO}_2$  is far less



than this, for the pH values of the practically neutral papers were not affected significantly by ordinary amounts of  $\text{CO}_2$ , as shown in table 3. Such papers gave practically the same pH, whether mixed with water of pH=6.7 or with a portion of the same water to which  $\text{CO}_2$  had been added to give a pH=5.9. Water containing enough  $\text{CO}_2$  to give a pH=5.0 underwent a rise in pH of approximately 1 unit when these papers were added. Acidity from other sources was similarly reduced by the fibers. For example, when these papers were mixed with water of pH=4.8, containing 0.013 g of alum per liter, the pH rose markedly in every case, as shown in column 5.

TABLE 3.—Effect of fibers <sup>a</sup> upon pH values

Sample number	pH values			
	pH of water =6.7	pH of water =5.9, $\text{CO}_2$ added	pH of water =5.0, $\text{CO}_2$ added	pH of water =4.8, alum added, 0.013 g per liter
11.....	7.1	7.0	6.0	5.9
20.....	6.2	6.2	-----	-----
22.....	6.9	6.8	6.0	6.1
28.....	6.7	6.6	5.8	5.8
32.....	6.6	6.6	5.9	6.0
39 <sup>b</sup> .....	6.9	6.8	-----	5.7
40 <sup>b</sup> .....	6.7	6.6	-----	5.4

<sup>a</sup> Extractions were made on ground papers for 1 hour at room temperature.

<sup>b</sup> Papers 39 and 40, not listed in table 2, were made from old rags.

Since the samples listed in table 3 were representative of all of the usual papermaking materials, it appears that otherwise pure distilled water, containing small amounts of  $\text{CO}_2$ , of pH=5.9 or higher, is satisfactory for use in paper extractions, even at room temperature, and that the requirements of present standard methods employing hot water are unnecessarily severe in this respect.

## 2. EFFECT OF TEMPERATURE

No appreciable systematic difference in pH was found between extractions made at 20° and at 30° C over a wide range of pH. This is in agreement with the results obtained by Browning and Ulm, who found only small differences for the two temperatures, 20° and 50° C. They found, however, that the temperature of hot extraction should be rather closely controlled, between 99° and 100° C. It thus appears that the method of cold extraction has an important advantage in that extraction may be safely made over the rather wide range loosely designated as room temperature.

## 3. EFFECT OF TIME

Experiments in which the pH values of papers were determined at various intervals after mixing showed that time is not a critical factor for papers of ordinary weight and that the values obtained after 1 hour do not change significantly upon much longer standing. This applies to well-sized as well as poorly sized papers, and is especially significant for the surface-sized papers. The results are shown in table 4.

TABLE 4.—Effect of time of extraction <sup>a</sup> upon the pH values of papers

Sample number	Sizing value	pH values after various intervals			
		10 minutes	30 minutes	1 hour	20 hours
	<i>Seconds</i>				
1	5	5.0	-----	5.0	5.0
3	5	5.3	-----	5.2	5.2
9	0	-----	-----	6.4	6.2
10	2	6.3	-----	6.3	6.3
11	0	-----	-----	7.1	7.1
12	47	5.3	-----	5.2	5.0
13	0	4.9	4.9	4.9	4.9
14	0	5.4	5.3	5.3	-----
16	49	-----	-----	5.8	5.6
17	42	-----	-----	5.9	5.8
18	41	-----	-----	6.0	5.9
19	0	6.3	6.3	6.4	6.3
20	45	-----	-----	6.2	6.1
21	0	6.7	6.6	6.6	6.6
22	0	6.8	6.8	6.8	6.9
23	35	5.3	5.2	5.2	5.2
24	31	5.7	5.7	5.7	-----
27	13	-----	-----	6.0	5.9
28	1	7.0	6.9	6.9	6.8
31	14	-----	-----	6.6	6.6
32	4	7.0	6.9	6.8	6.7
33	31	4.9	-----	4.9	5.0
34	24	5.7	-----	5.7	5.7
35	9	-----	-----	5.9	5.8
36	19	-----	-----	5.2	5.3
37	21	-----	-----	5.7	5.7
38	-----	6.3	-----	6.3	6.3

<sup>a</sup> Extractions were made of ground papers at room temperature.

#### 4. MANNER OF PREPARING THE PAPER FOR EXTRACTION

Although required by the TAPPI method and given as an alternative to shredding in the Federal specification, advisability of grinding has been questioned by Browning and Ulm. Aside from the practical difficulty that many laboratories in which pH measurements of papers are made are not equipped with a grinder, it is of major importance, for this determination, that the paper be subjected to a minimum of treatment before testing. Contamination of the paper in the grinder by residues of previous papers is an ever-present possibility, despite careful cleaning.

During a period of 5 months, the papers described in this investigation were tested at intervals, both in the ground condition and in the form of cuttings, approximately 0.1 to 2 cm<sup>2</sup> in area. The results listed in table 5 show no important systematic difference between the values obtained from the unfiltered aqueous mixtures of the ground and cut materials. Each individual value is the average value of duplicate determinations. The maximum disagreement between the several values for each paper has an average value of 0.13 pH unit for the ground and 0.10 pH unit for the cut samples, showing reproducibility to be practically the same for both. Out of 28 comparisons, the average values for the ground material were higher in 11 cases and lower in 9 than those from the cuttings, and equal in 8 cases.

The specification of grinding, to the exclusion of cutting the sample, does not, therefore, appear justified in the testing of papers such as

those listed in table 5. When a paper is especially thick, however, proper extraction is not obtained with cut samples in 1 hour. Results with eight samples of commercial file-folder stock, with a thickness of approximately 0.01 inch, showed that very incomplete extraction is obtained unless such papers are ground, or unless the time is extended to 20 hours. The results are shown in table 6.

TABLE 5.—Comparison of pH values <sup>a</sup> obtained from ground samples and from cuttings of papers

Sample No.	Ground paper pH values at various intervals during 5 months	Maximum disagreement	Cut paper pH values at various intervals during 5 months	Maximum disagreement
1	4.9, 5.0	0.1	4.9, 4.9	0
2	5.1, 5.3	.2	4.9	-----
4	5.4, 5.4	0	5.4	-----
6	5.6, 5.7	.1	5.9, 5.9	0
7	5.6, 5.6	0	5.8, 5.8	0
8	6.4, 6.4	0	-----	-----
9	6.3, 6.4	.1	6.0, 6.1	.1
10	6.0, 6.1, 6.0, 6.3	.3	6.2, 6.6	.4
11	7.2, 7.4, 7.1	.3	6.9, 6.7, 6.7	.2
12	5.2, 5.2, 5.2	0	5.0, 5.0, 5.0	0
13	5.0, 4.9, 4.9	.1	4.8, 4.9, 4.9	.1
14	5.4, 5.3, 5.5	.2	5.4, 5.6	.2
15	5.6, 5.5	.1	5.6, 5.8	.2
16	5.7, 5.8	.1	5.8, 5.9	.1
17	5.9, 5.9	0	5.8, 6.0	.2
18	6.0, 6.0	0	6.2, 6.1, 6.3	.2
19	6.4, 6.4, 6.3	.1	-----	-----
20	6.2, 6.2	0	6.2, 6.3	.1
21	6.6, 6.6, 6.5	.1	-----	-----
22	6.8, 6.9	.1	6.7, 6.6, 6.6	.1
23	5.1, 5.3, 5.2	.2	5.0	-----
24	5.6, 5.6, 5.7	.1	5.6, 5.6	0
25	5.6, 5.6	0	5.4, 5.4	0
27	6.0, 6.0, 6.1	.1	-----	-----
28	6.7, 6.8, 6.7, 6.9, 6.7	.2	6.5, 6.5, 6.4, 6.5	.1
29	5.2, 5.1, 5.2, 5.3, 5.3, 5.4	.3	4.8, 4.8, 4.9, 4.9	.1
30	5.6, 5.8	.2	5.9, 5.8	.1
31	6.4, 6.7, 6.6	.3	-----	-----
32	6.6, 6.8, 6.8	.2	6.6, 6.8	.2
33	5.0, 4.9, 5.0	.1	5.0, 4.9	.1
34	5.9, 5.8, 5.9, 5.7, 5.9	.2	5.9, 5.9	0
35	5.9, 5.7, 5.9, 5.9	.2	5.7, 5.8, 5.7	.1
36	5.1, 5.2, 5.2	.1	5.2, 5.1	.1
37	5.4, 5.7, 5.7	.3	5.5, 5.5, 5.5	0
38	6.3, 6.3	0	6.4, 6.4	0
	Average	0.13	Average	0.10

<sup>a</sup> Extractions were made for 1 hour at room temperature.

TABLE 6.—Comparison of pH values <sup>a</sup> obtained from ground and cut samples of file-folder stock

Samples	pH after 1 hour		pH after 20 hours	
	Ground	Cut	Ground	Cut
A	5.1	5.4	4.9	4.9
B	5.1	5.4	5.0	5.0
C	4.7	4.9	4.7	4.7
D	5.1	5.7	5.1	5.1
E	5.5	6.1	5.4	5.4
F	5.8	6.5	5.9	5.9
G	5.3	6.1	5.2	5.3
H	5.3	6.1	5.3	5.3

<sup>a</sup> Extractions were made at room temperature.

## V. RECOMMENDED PROCEDURE

On the basis of the experimental results of this investigation, the following procedure is recommended for obtaining the pH value of paper. Weigh 1.0 g of ground, air-dry paper, and transfer to a 100-ml beaker. Instead of grinding the paper it may be cut into pieces of roughly 1 cm<sup>2</sup> if the paper is not especially thick. Add 20 ml of distilled water and macerate with a flattened stirring rod until the specimen is uniformly wet. Then add 50 ml more of the distilled water, stir well, cover with a watch glass, and allow to stand approximately 1 hour. If the paper is thick or dense, and if no grinder is available, the extraction time must be prolonged to 20 hours. The entire procedure is carried out at room temperature. After stirring the mixture once more, measure the pH of the unfiltered mixture with a glass electrode and report to the nearest 0.1 pH. Duplicate determinations should agree within 0.1 pH. The distilled water used in the extraction should not contain more CO<sub>2</sub> than corresponds to a pH=5.9, but it must be tested for alkaline impurities by boiling a small portion to expel the CO<sub>2</sub>. If the pH of the water, after boiling, is definitely above 7.0, it should be redistilled, preferably from alkaline permanganate, to oxidize organic substances.

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