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A Source of Error in Paper Extract pH Determinations: Contact Between Paper and Reference Electrodes

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Contents

1. SUMMARY

If the reference electrode of a pH meter is permitted to contact paper suspended in an aqueous medium, the pH observed is lower than that observed with no contact. The effect has been observed with papers of widely different pH, and varies in magnitude with the proximity of contact and with different papers. The problem can be avoided by taking measurements on decanted equilibrium solutions instead of suspensions of paper.

The cause of this effect may be analogous to the suspension effect in colloidal systems.

2. INTRODUCTION

The determination of paper acidity (pH) by standard methods (1,2) involves a fairly simple measurement of the pH of aqueous extracts, but results obtained by different operators vary widely (3). The work described in this report demonstrates that different pH values can be obtained on a single sample of paper by varying the proximity of the reference electrode to the paper in aqueous suspension and the effect of proximity can be a major source of error in pH tests. The error can be avoided simply by decanting the water after extraction and making pH measurements on the decantate. The phenomenon seems to be analogous to the well-known suspension effect of colloidal systems (4-7).

3. EXPERIMENTAL

All samples were prepared for testing according to TAPPI methods for cold or hot extraction pH (1,2).

The data in Table 1 were obtained on samples of paper made from a kraft pulp that had been deashed with 0.1N hydrochloric acid and washed until free of HCl. The specimens were aged in flowing air for six days at 90°C ± 0.1° and 0%, 5%, 20%, or 50% relative humidity. The data in Tables 2 and 3 were obtained on commercial book papers that had been used in interlaboratory testing programs (3). Table 4 represents data on the same samples as Table 1, in addition to an imaged specimen of the same paper.

The pH electrodes were positioned as follows:

(a) distance between electrodes and paper was visibly substantial, about 1 cm,

(b) close proximity, with light brushing contact, was permitted,

(c) the reference electrode was in close contact with the paper surface,

(d) measurements were made on decanted equilibrium solutions.

A research meter equipped with glass and calomel electrodes was employed for making the pH measurements.

4. RESULTS AND DISCUSSION

Table 1 shows wide variations in pH values obtained by varying the distance between the pH electrodes and the paper. Standard cold extraction pH tests are made with paper cut into small pieces and macerated with a glass rod. Opaque suspensions can result if the paper is extensively disintegrated by this maceration, while filler can make the resulting suspensions very opaque. It is difficult to prevent close proximity between electrodes and fibers when the suspensions are very opaque, so that conditions a, b, or c might occur during a pH measurement. Substantially lower pH values result when the reference electrode is brought into close proximity with the paper. It was possible to control the proximity of the electrodes to the paper in this study because the aqueous extracts were relatively clear. Nevertheless, a great deal of care had to be taken to avoid errors as a result of close proximity to the paper.

The data in Table 2 pertain to commercial book papers. These samples show smaller variations in pH than those found in Table 1, but again the pH readings are affected by the proximity of the electrodes to the paper, except for the alkaline paper. The magnitude of variation differs from paper to paper and indicates that the effect is real and not due to instrument error.

The pH data obtained in interlaboratory testing programs indicate that errors of the type due to close proximity or contact may occur quite frequently. For example, sample 1 in Table 2 has been subjected to analysis in a collaborative interlaboratory testing program involving eleven different laboratories (3), and the results are summarized in Table 3. The conclusion in reference 3 was that the most reliable pH values for sample 1 were 5.05 (cold extraction) and 4.50 (hot extraction). These pH estimates resulted from a careful evaluation of data obtained in the testing program over an extended period of time. The data contain several points of interest.

(a) There are large differences between laboratory means. The range of reported values for cold extraction pH is 4.51 to 5.66. That for hot extraction is 3.97 to 5.16.

(b) The most reliable pH values are very close to those listed for the respective decantates in Tables 2 and 3 indicating that decantates gave very good values.

(c) The two lowest values in Table 3 for both cold and hot extraction pH suggest the analyst permitted the pH electrodes to come into contact with the paper.

There are other unexplained sources of error reflected in interlaboratory tests as well as those apparently due to the closeness of the electrodes to the paper. Laboratories B and H, for example, report a high pH value of 5.66 for sample 1 after cold extraction, where the most reliable value is 5.05, suggesting incomplete extraction of the samples. The pH procedure described in this report would not prevent errors of this type, but high results would indicate procedural or instrument errors.

5. SUSPENSION EFFECT AS A SOURCE OF ERROR

In colloidal systems, the so-called suspension effect is the difference in e.m.f. obtained in the conventional determination of pH in a suspension and in its equilibrium solution (4). Theoretical (4) and more qualitative discussions (5,6,7) of the pH of colloidal systems show that the position of the reversible electrode (glass or hydrogen) is without influence on the measured potential, but the position of the reference electrode is important. Contact with the suspension results in greater potential readings because of a greater charge density at particle surfaces than in equilibrium solutions.

The similarity in the response of pH electrodes to paper suspensions suggests that charges on the paper surface similarly effect paper pH tests. These charges may be closely related to the zeta potential of pulp fibers. Current standard methods do not mention possible errors due to contact and analysts may not be aware of the need to avoid it, but it is likely that a substantial improvement in pH determinations could be made by testing decanted equilibrium solutions rather than suspensions of paper.

6. SHORT-CIRCUITING AS A SOURCE OF ERROR

An alternative explanation of the contact phenomenon was considered. A continuous matrix of fibers between the electrodes might cause shorting which would result in unpredictable electrical disturbances. This explanation was discounted when pH measurements were made with electrodes in separate beakers connected by a salt bridge. One beaker contained both paper and equilibrium solution; the other, only equilibrium solution. The data in Table 4 resulted from varying the contact of the reference electrode with the paper. These results indicate that shorting is not the cause for the great variations in pH values caused by contact of the electrodes with the paper.

7. CONCLUSIONS

1. The pH values obtained in the determination of the acidity (pH) of paper extracts are highly dependent on the proximity of the reference electrode to the test sample.

2. Contact between the reference electrode and charged surfaces of paper may result in an increase in the measured potential.

3. Error from this source can be minimized by making pH measurements on the decanted equilibrium solutions.

BIBLIOGRAPHY

1. ASTM Designation D778-50, "Standard Method of Test for Hydrogen Ion Concentration (pH) of Buffered Paper Extracts" 1975 Annual Book of ASTM Standards, Part 20.

2. T-435 SU-68, "Hydrogen Ion Concentration (pH) of Paper Extracts Hot Extraction Method", TAPPI Standards and Suggested Methods, Technical Association of the Pulp and Paper Industry.

3. Report No. 30A, "Collaborative Reference Program for Paper", E. G. Randall, Jr., J. Horlick, S. Prather, R. G. Powell, and R. L. Hebert. U.S. Department of Commerce, National Bureau of Standards, August 1974.

4. Overbeek, J. Th. G., J. Colloid Sci. 8, 593 (1953).

5. Kruyt, H. R., editor, Colloid Sci., Vol. 1, page 184, Elsevier, New York (1952).

6. Eriksson, E., Science 113, 418 (1951).

7. H. Jenny, T. R. Nielsen, N. T. Coleman and D. E. Williams, Science 112, 164 (1950).

TABLE 1

EFFECT OF PROXIMITY ON OBSERVED pH OF AQUEOUS EXTRACT OF HANDSHEETS AFTER 6 DAYS OF ACCELERATED AGING AT 90°C AND VARIOUS RELATIVE HUMIDITIES

Relative Humidities of Aging Atmosphere	No Contact	Decantate	Close Proximity	Contact
0%	4.90	4.90	4.48	3.76
5%	4.86	4.86	4.50	4.13
20%	4.43	4.44	3.98	3.76
50%	4.17	4.18	4.16	3.56

pH OF AQUEOUS EXTRACT OF SAMPLES OF BOOK PAPERS SHOWING EFFECTS OF PROXIMITY BETWEEN PAPER AND REFERENCE ELECTRODE

Sample No.	Extraction Process	No Contact	Decantate	Close Proximity	Contact
1	Cold	5.00	5.00	4.94	4.67
	Hot	4.49	4.51	4.41	4.19
2	Cold	5.58	5.57	5.54	5.38
	Hot	4.81	4.82	4.77	4.68
3	Cold	4.98	4.98	4.93	4.74
	Hot	4.50	4.52	4.42	4.24
4	Cold	5.93	5.89	5.80	5.44
	Hot	5.17	5.18	5.11	4.91
5	Cold	5.79	5.78	5.62	5.45
	Hot	5.15	5.16	5.01	4.82
6	Cold	6.00	5.98	5.78	5.57
	Hot	4.90	4.93	4.87	4.71
7	Cold	8.02	7.94	8.00	7.89
	Hot	8.78	8.72	8.82	8.74
8	Cold	5.26	5.27	5.17	5.01
	Hot	4.45	4.47	4.39	4.27
9	Cold	7.11	7.10	6.95	6.59
	Hot	6.87	6.89	6.79	6.48
10	Cold	5.69	5.67	5.51	5.46
	Hot	5.72	5.75	5.61	5.58

TABLE 3

pH OF AQUEOUS EXTRACT OF SAMPLE 1 IN TABLE 2, AS DETERMINED IN INTERLABORATORY TESTING PROGRAM[1]

COLD EXTRACTION				HOT EXTRACTION			
Laboratory	Lab Mean[2]	Deviation[3]	Normal Deviation[4]	Laboratory	Mean[2]	Deviation[3]	Normal Deviation[4]
A	5.34	0.24	0.66	A	4.14	-0.36	-1.08
B	5.66	.56	1.54	B	4.56	.06	.18
C	4.96	- .14	- .38	C	4.41	- .09	- .27
D	5.25	.15	.41	D	5.16	.66	1.97
E	5.00	- .10	- .26	E	4.52	.02	.07
F	4.66	- .44	-1.21	F	4.86	.36	1.08
G	4.91	- .19	- .53	G	4.37	- .13	- .38
H	5.66	.56	1.54	H	3.97	- .53	-1.59
I	4.51	- .59	-1.61	I	4.50	.00	.00
J	5.13	.03	.09	J	4.51	.01	.02
K	5.00	- .10	- .26				
Decantate	5.00	-0.06	-0.17	Decantate	4.51	0.03	0.09
Contact	4.67	-0.39	-1.11	Contact	4.19	- .29	-0.91

GRAND MEAN = 5.10
STANDARD DEVIATION OF THE GRAND MEAN = 0.36

GRAND MEAN = 4.50
STANDARD DEVIATION OF THE GRAND MEAN = 0.33

[1] Interlaboratory test data from laboratories A-K are taken from reference 3.

[2] Mean of five test values

[3] Deviation of lab mean from the grand mean for labs A-K

[4] Ratio of the deviation of lab mean to the standard deviation of the grand mean for labs A-K.

TABLE 4

COMPARISON OF pH VALUES USING
GLASS AND REFERENCE ELECTRODES IN (a) A SINGLE BEAKER
AND (b) SEPARATE BEAKERS CONNECTED BY A BRIDGE[1]

Relative Humidity of Aging Atmosphere	Proximity[2] Condition	Observed pH (a) Single Beaker	Observed pH (b) Two Beakers Joined by a Bridge
0%	No Contact	4.70	4.85
	Close Proximity	4.34	4.54
	Contact	3.98	4.11
	Decantate	4.65	4.80
5%	No Contact	4.80	4.50
	Close Proximity	4.34	4.28
	Contact	4.12	4.01
	Decantate	4.77	4.95
20%	No Contact	4.53	4.46
	Close Proximity	4.38	4.24
	Contact	4.00	4.02
	Decantate	4.54	4.34
50%	No Contact	4.35	4.52
	Close Proximity	4.06	4.32
	Contact	4.03	3.98
	Decantate	4.28	4.42
Unaged Paper	No Contact	5.30	5.42
	Close Proximity	5.10	5.12
	Contact	4.30	4.55
	Decantate	5.28	5.46

[1]The papers are identical to those in Table 1.

[2]Proximity conditions refer to the reference electrode.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

If the reference electrode of a pH meter is permitted to contact paper suspended in an aqueous medium, the pH observed is lower than that observed with no contact. The effect has been observed with papers of widely different pH, and varies in magnitude with the proximity of contact and with different papers. The problem can be avoided by taking measurements on decanted equilibrium solutions instead of suspensions of paper.

The cause of this effect may be analogous to the suspension effect in colloidal systems.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

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