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*THE LIMITATIONS OF
MEASURING pH BY COLOUR INDICATORS*

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B. C. SYRETT AND J. G. GARRISON

PHYSICAL METALLURGY DIVISION

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THE LIMITATIONS OF MEASURING pH BY COLOUR INDICATORS

by

B. C. Syrett* and J. G. Garrison**

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ABSTRACT

Aqueous solutions containing various amounts of NaCl and FeCl₂ were prepared and their pH's estimated using pH-indicators in three forms: indicator-impregnated filter paper, indicator-coated silica gel particles, and aqueous solutions of the indicators.

It was found that silica gel was an unsuitable medium for carrying the indicator because of its own acidic nature, and that the proportion of indicator to test solution can influence the accuracy of the pH estimation. It was also found that the success of the indicator-paper method depends on the concentration of the indicating solution used in the preparation of the paper, and on the concentration of dissolved salts in the test solution.

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Direction des mines

LES LIMITES DE LA MESURE DU pH À L'AIDE
D'INDICATEURS COLORÉS

par

B. C. Syrett* et J. G. Garrison**

RÉSUMÉ

Les auteurs ont préparé des solutions aqueuses contenant des quantités différentes de NaCl et de FeCl₂ et ont déterminé leur pH à l'aide d'indicateurs se présentant sous trois formes: papier-filtre imprégné d'indicateur, particules de gel de silice recouvertes d'indicateur, et solutions aqueuses des indicateurs.

Ils ont observé que le gel de silice n'est pas un véhicule convenable pour l'indicateur en raison de sa propre acidité, et que la quantité d'indicateur utilisée pour faire réagir la solution peut affecter l'exactitude de la détermination du pH. Ils ont également remarqué que le succès de la méthode employant un papier-indicateur dépend de la concentration de la solution indicatrice utilisée pour imprégner le papier et de la concentration des sels dissous dans la solution soumise à l'essai.

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INTRODUCTION

There has been considerable interest in the recently proposed method (1) of estimating the pH of the corrodent at the tip of an advancing stress-corrosion crack. This test method involves the use of pH-indicator-impregnated filter paper or indicator-coated silica gel, prepared by saturating the paper or gel with dilute aqueous solutions of indicator drying completely. A propagating stress-corrosion crack is stopped short of failure, and the corrodent within the crack is frozen in liquid nitrogen; the stress corrosion crack is then extended mechanically to failure to expose the frozen solution on the stress-corrosion-crack surfaces. As soon as the solution has thawed, the gel or paper is applied and the pH estimated from the subsequent colour indication.

The present investigation is not concerned with the general concept of the above test method, but only with the limitations of measuring pH by colour indicators under experimental conditions analogous to those experienced within an advancing stress-corrosion crack in high-strength steels.

EXPERIMENTAL PROCEDURE

Because Brown et al. (1,2) report a pH of about 3.8 at the tip of an advancing crack in steel immersed in distilled water or 3.5% NaCl solution, indicators were chosen for testing which would cover the pH range 3.0 to 6.2. Table 1 shows the important characteristics of the indicators and the concentrations used for these tests.

Indicator-impregnated filter paper, indicator-coated silica gel, and aqueous solutions of the indicators were evaluated.

The first evidence that silica gel was unsuitable as a carrier became apparent during its standardized preparation. The 80-mesh gel particles had to be given several washings before they were observed to take up the same colour as the fresh indicating solutions; upon drying, the gel changed colour once again (see Table 2).

Furthermore, when 100 ml of distilled water, initially of pH 5.70, was added to 10 g of silica gel particles, the pH of the resultant slurry was found to be 3.80. Thus the silica gel is itself acidic in nature and can be expected to influence the colour of the indicator coating when moistened.

Test solutions of various pH values were prepared and standardized, using a Beckman Zeromatic SS-3 pH meter. These solutions were prepared from distilled water and contained 0-35 g/l NaCl, 0-461 g/l FeCl₂ (added as FeCl₂·4H₂O), the pH being adjusted, when desired, by small additions of hydrochloric acid.

RESULTS

(a) Indicator-coated silica gel

Whichever indicator was used to coat the gel, its performance was found to be satisfactory in commercially obtained buffer solutions, but when it was used in distilled water or 3.5% NaCl solutions the results were invariably misleading. There was ample evidence that additions of silica gel to the test solution, whether coated with indicator or not, were actually altering the pH of the test solution substantially. For instance, when 25 mg of uncoated silica gel was added to 5 ml 3.5% NaCl solution, the pH of the solution dropped from 5.82 to 4.30; a further 25-mg addition reduced the pH to 4.07.

When the volume of test solution added to the indicator-coated silica gel was increased, the colour indications were nearer those anticipated for that indicator (see Table 1), but under no circumstances were they entirely accurate. However, the effect of increasing the volume of test solution beyond a certain point was to wash the indicator off the silica gel particles and make pH estimates more inaccurate. In general, the closest estimates of pH were made when 0.5 ml of test solution was added to each 10 mg of indicator-coated gel particles. Even under these conditions, estimates were poor and it was as important to note the colour of the test solution as to note the colour of the gel; methyl red did not perform satisfactorily under any circumstances in distilled water-hydrochloric acid solutions (see Table 3). Addition of 35 g/l NaCl to the test solutions did not improve matters, and in the case of congo red the reddish-brown colour noted at all levels of acidity was some indication of a worsening of the conditions.

Clearly, indicator-coated silica gel would be an unsatisfactory means of estimating pH in the type of stress-corrosion-cracking test envisaged, on two counts: (a) when measuring the pH of small volumes of test solution (e.g. within an advancing stress-corrosion crack), the acidic nature of the silica gel strongly affects the original pH of the test solution; (b) even when this effect is minimized by using larger volumes of solution, the colour indications are ambiguous.

(b) Liquid indicating solution

The most obvious method of avoiding some of the problems associated with silica gel would be to spray a fine mist of the indicating solution directly on to the corrodent lying on the stress-corrosion crack surface. For the purposes of evaluation, however, larger volumes of liquid were used. As before, the behaviour of the indicators in buffered solutions was quite satisfactory, but when volume ratios of indicating to test solutions became too high in 3.5% NaCl solutions, the indicator addition itself began to affect test solution pH. At pH 3.5, this "indicator error" began to become apparent at ratios higher than 1:50. At a pH of 5.89, the indicator error appeared to be much more serious; for bromocresol green (pH 5.10) it was evident at ratios as low as 1:125, and at 1:25 the test solution actually adopted the pH of the indicator (see Table 4).

However, in distilled water-hydrochloric acid solutions of various acidities, the pH, as estimated by the colour of either bromocresol green or bromophenol blue, was of reasonable accuracy at a 1:25 volume ratio (see Table 5). Methyl orange and, particularly, methyl red gave colour indications of no practical significance under these conditions.

In summary, it has been shown that the indicator cannot satisfactorily be used in its original liquid form when the volume ratio of indicator to test solution exceeds a certain critical value; this value will depend in a complex way upon such factors as the difference in pH between indicating and test solution and the presence of foreign ions, e.g., Na^+ and Cl^- ions.

(c) Indicator-impregnated filter paper

It would become increasingly more difficult to control the volume ratio as the volume of test solution became smaller. In the case of corrodent on a stress-corrosion-crack surface, for instance, only minute quantities of indicator could be permitted if colour indications are to be valid. Unfortunately, even if it were possible to control additions to this extent, observations of colour in such small volumes of liquid would prove difficult.

One method of circumventing this problem is to impregnate filter paper strips with a suitably weak solution of indicating solution, dry thoroughly, and use the indicating paper, so formed, to absorb the test solution.

Since it was suspected that both indicator concentration and the presence of dissolved salts in the test solution might influence the estimated pH of the solution, tests were designed to separate these effects. Tables 6-11 summarize the results. A question mark entered in the tables indicates that an unexpected colour was observed and that a pH value could not be assigned.

The bromocresol green paper prepared from the 0.02% solution gives satisfactory results in distilled water-hydrochloric acid solutions, but becomes increasingly more unsatisfactory as NaCl is added to the solution. There was some evidence that the 0.004% bromocresol green paper was giving fairly valid pH indications, even in the presence of NaCl, but the colours shown were, at best, faint. Tables 9, 10 and 11 show the very limited success of this indicator when FeCl₂ is present in the test solution.

Far more successful were papers prepared with 0.02% bromophenol blue or 0.01% methyl orange. Both of these indicating papers estimated pH to within an accuracy of 0.5 pH over their useful indicating range, whether or not NaCl or FeCl₂ was present. However, even these indicators were not always satisfactory when used in a more concentrated or diluted form (see Tables 6-8).

The methyl red and congo red appeared to be of very little practical use, whatever the concentration and whatever the test solution. It is not recommended, therefore, that these indicators be used in determining pH by this method.

The alkacid paper was fairly accurate in 3.5% NaCl solutions of pH 5.0 or below, but in solutions of higher pH it still indicated pH 5.0. When FeCl₂ solutions were tested in the alkacid paper, results were not as accurate and pH 5.0 was indicated in all solutions less acid than pH 4.21. The combined effect of 3.5% NaCl and 0.1 g/l FeCl₂ was to produce even less accurate indications; all solutions of pH 3.52 or higher appeared to have a pH value of 4.5. This last result agrees well with the observation that alkacid paper indicates a pH of 4.5 in a 3.5% NaCl solution in which steel had been freely corroding for several days. When checked with a pH meter, the solution was actually found to have a pH of 6.8, in line with the expected value (3).

SUMMARY

When using indicators to estimate the pH of the corrodent within an advancing stress-corrosion crack, the limitations of the method should be appreciated. The present investigation has shown that, for this type of usage:

1. Silica gel is an unsuitable medium for carrying the indicator, because of its own acidic nature.
2. In tests using liquid indicators, the proportion of indicator to test solution is an important consideration, since there may be a pH shift produced when excessive amounts of indicator are present. The optimum volume ratio will depend upon the relative pH values

of indicating and test solutions, and upon the effect of interfering ions.

3. Congo red and methyl red indicating papers do not give satisfactory results under any of the test conditions.
4. The success of alkacid and bromocresol green papers depends largely on which salts are present in the test solution.
5. Methyl orange (0.01%) and bromophenol blue (0.02%) papers give satisfactory colour indications under all of the test conditions.

FUTURE WORK

Since 0.01% methyl orange paper and 0.02% bromophenol blue paper give reasonably accurate pH indications, even in the presence of Fe^{++} ions and 3.5% NaCl, it is intended that these papers be used to estimate the pH of the corrodent in an advancing stress-corrosion crack in steel (see Introduction). In the first instance the steel will be stressed in 3.5% NaCl solution under freely corroding conditions, but later the test will be repeated using samples polarized either anodically or cathodically. If the polarizing potential influences the pH of the corrodent at the crack tip appreciably, it may eventually prove necessary to appraise indicators which cover other pH ranges.

REFERENCES

1. B. F. Brown, C. T. Fujii and E. P. Dahlberg - J. Electrochem. Soc., 116(2), 1969, 218.
2. B. F. Brown - "On the Electrochemistry of Stress Corrosion Cracking of High Strength Steels", presented to the Fourth International Congress on Metallic Corrosion, Amsterdam, Netherlands, 7-14 September, 1969.
3. H. H. Uhlig - "Corrosion and Corrosion Control", John Wiley and Sons, Inc., N.Y., London (1963), 80.

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TABLE I

Anticipated pH Ranges and Colour Ranges of the Indicators, and
Concentrations of Their Aqueous Solutions Used in the Tests

Indicator	Indicating pH-range and colour-range						Concentrations, %
Bromocresol Green	pH	≤3.8	4.2	4.6	5.0	≥5.4	0.04, 0.02, 0.004
	colour	yellow	yellow- green	green	green- blue	blue	
Bromophenol Blue	pH	≤3.0	3.4	3.8	4.2	≥4.6	0.04, 0.02, 0.004
	colour	yellow	yellow- green	green	green- blue	blue	
Methyl Orange	pH	≤3.0	3.4	3.7	4.1	≥4.4	0.1, 0.01, 0.001
	colour	red	red- orange	orange	orange- yellow	yellow	
Methyl Red	pH	≤4.2	4.7	5.2	5.7	≥6.2	0.02, 0.002, 0.0002
	colour	red	red- orange	orange	orange- yellow	yellow	
Congo Red	pH	≤3.0	3.5	4.0	4.5	≥5.0	1.0, 0.01, 0.001
	colour	blue	blue- purple	purple	purple- red	red	
Alkacid Paper †	pH	3.5	4.0	4.5	5.0	5.5	
	colour	orange	yellow	yellow- green	pale green	green	

† Obtained commercially as a paper only.

TABLE 2

Colour Changes Observed When 10 g of Silica Gel Particles Was Given Successive Washings in 15-ml Batches of Fresh Indicator; and Colour After Drying

No. of Washings	Bromocresol Green (0.04%)	Bromophenol Blue (0.04%)	Methyl Orange (0.1%)	Methyl Red (0.02%)	Congo Red (1.0%)
1	yellow-brown	yellow-orange	red	orange*	black*
2	green-brown	rust red	orange-red	orange	deep red
3	green-brown	red	orange-red	orange	deep red
4	dark green	red	orange-red	orange	deep red
Dry powder	yellow-orange	yellow	orange	pink	beige

* Most of the indicating solution was absorbed by the gel particles.

TABLE 3

Colour of Silica Gel Particles and Test Solution in Distilled Water - Hydrochloric Acid Mixtures of Different pH, and Estimated pH.
(The optimum volume of test solution has been added (see text).)

Indicator (Concn.)	COLOUR (and estimated pH)							
	pH 3.00		pH 4.08		pH 5.00		pH 5.70	
	silica gel	soln.	silica gel	soln.	silica gel	soln.	silica gel	soln.
Bromocresol Green (0.04%)	yellow (≤ 3.8)	clear	yellow (≤ 3.8)	clear	yellow-green (4.2)	blue (≥ 5.4)	yellow-green (4.2)	blue (≥ 5.4)
Bromophenol Blue (0.04%)	yellow (≤ 3.0)	yellow (≤ 3.0)	yellow-green (3.4)	clear	yellow-green (3.4)	mauve (?)	blue (≥ 4.6)	mauve (?)
Methyl Orange (0.1%)	red (≤ 3.0)	pink (≤ 3.0)	red-orange (3.4)	yellow-orange (4.1)	red-orange (3.4)	orange-yellow (4.1)	red-orange (3.4)	yellow (≥ 4.4)
Methyl Red (0.02%)	red (≤ 4.2)	pink (≤ 4.2)	red (≤ 4.2)	pink (≤ 4.2)	red (≤ 4.2)	pink (≤ 4.2)	red (≤ 4.2)	pink (≤ 4.2)
Congo Red (1.0%)	blue (≤ 3.0)	purple (4.0)	purple-red (4.5)	pink (≥ 5.0)	beige (?)	pink (≥ 5.0)	beige (?)	pink (≥ 5.0)

TABLE 6

The Effect of the Indicator Concentration Used in the Preparation of Indicator-Impregnated Filter Paper on the Estimated pH of Distilled Water, the pH being Adjusted by Small Additions of Hydrochloric Acid

Indicator (conc.)	Estimated pH of Standard Solutions						
	pH 2.60	pH 3.00	pH 3.49	pH 4.08	pH 4.45	pH 5.00	pH 5.75
Bromocresol Green (0.04%)	≤3.8	≤3.8	≤3.8	4.2	4.2	5.1	5.1
Bromocresol Green (0.02%)	≤3.8	≤3.8	≤3.8	≤3.8	4.6	5.1	≥5.4
Bromocresol Green (0.004%)	N.I.	N.I.	N.I.	4.6	4.6	≥5.4	≥5.4
Bromophenol Blue (0.04%)	≤3.0	≤3.0	3.8	≥4.6	≥4.6	≥4.6	≥4.6
Bromophenol Blue (0.02%)	≤3.0	≤3.0	3.8	3.8	≥4.6	≥4.6	≥4.6
Bromophenol Blue (0.004%)	N.I.	N.I.	N.I.	N.I.	≥4.6	≥4.6	≥4.6
Methyl Orange (0.1%)	≤3.0	≤3.0	3.7	3.7	3.7	3.7	≥4.4
Methyl Orange (0.01%)	≤3.0	≤3.0	3.7	≥4.4	≥4.4	≥4.4	≥4.4
Methyl Orange (0.001%)	≤3.0	≤3.0	N.I.	N.I.	N.I.	N.I.	N.I.
Methyl Red (0.02%)	?	?	?	?	?	?	?
Methyl Red (0.002%)	≤4.2	≤4.2	?	?	?	?	?
Methyl Red (0.0002%)	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.
Congo Red (1.0%)	≤3.0	≤3.0	≥5.4	≥5.4	≥5.4	≥5.4	≥5.4
Congo Red (0.01%)	≤3.0	≤3.0	≥5.4	≥5.4	≥5.4	≥5.4	≥5.4
Congo Red (0.001%)	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.

N.I. No indication, paper white.

TABLE 7

The Effect of the Indicator Concentration Used in the Preparation of Indicator-Impregnated Filter-Paper on the Estimated pH of 0.5% NaCl Solutions, the pH being Adjusted by Small Additions of Hydrochloric Acid

Indicator (concn.)	Estimated pH of Standard Solutions						
	pH 2.61	pH 3.07	pH 3.52	pH 4.00	pH 4.45	pH 5.05	pH 5.50
Bromocresol Green (0.04%)	≤3.8	≤3.8	4.2	4.6	4.6	4.6	4.6
Bromocresol Green (0.02%)	≤3.8	≤3.8	≤3.8	≤3.8	4.6	4.6	4.6
Bromocresol Green (0.004%)	≤3.8	≤3.8	4.2	4.6	4.6	5.0	≥5.4
Bromophenol Blue (0.04%)	≤3.0	≤3.0	3.4	4.2	≥4.6	≥4.6	≥4.6
Bromophenol Blue (0.02%)	≤3.0	≤3.0	3.8	3.8	≥4.6	≥4.6	≥4.6
Bromophenol Blue (0.004%)	≤3.0	3.4	3.4	4.2	≥4.6	≥4.6	≥4.6
Methyl Orange (0.1%)	≤3.0	≤3.0	3.7	3.7	3.7	4.1	≥4.4
Methyl Orange (0.01%)	≤3.0	≤3.0	3.7	4.1	≥4.4	≥4.4	≥4.4
Methyl Orange (0.001%)	≤3.0	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.
Methyl Red (0.02%)	?	?	?	?	?	?	?
Methyl Red (0.002%)	?	?	?	?	?	?	?
Methyl Red (0.0002%)	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.
Congo Red (1.0%)	≤3.0	≤3.0	≥5.0	≥5.0	≥5.0	≥5.0	≥5.0
Congo Red (0.01%)	4.0	≥5.0	≥5.0	≥5.0	≥5.0	≥5.0	≥5.0
Congo Red (0.001%)	≤3.0	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.

N.I. No indication, paper white.

TABLE 8

The Effect of the Indicator Concentration Used in the Preparation of Indicator-Impregnated Filter-Paper on the Estimated pH of 3.5% NaCl Solutions, the pH being Adjusted by Small Additions of Hydrochloric Acid

Indicator (concn.)	Estimated pH of Standard Solutions							
	pH 2.70	pH 3.00	pH 3.50	pH 4.00	pH 4.50	pH 5.00	pH 5.50	pH 6.30
Bromocresol Green (0.04%)	≤3.8	≤3.8	4.2	4.6	4.6	4.6	4.6	4.6
Bromocresol Green (0.02%)	≤3.8	≤3.8	≤3.8	≤3.8	≤3.8	4.2	4.6	
Bromocresol Green (0.004%)	≤3.8	≤3.8	4.6	N.I.	4.6	≥5.4	≥5.4	
Bromophenol Blue (0.04%)	≤3.0	≤3.0	3.8	?	?	?	?	?
Bromophenol Blue (0.02%)	≤3.0	≤3.0	3.8	≥4.6	≥4.6	≥4.6	≥4.6	
Bromophenol Blue (0.004%)	≤3.0	≤3.0	3.8	≥4.6	≥4.6	≥4.6	≥4.6	
Methyl Orange (0.1%)	≤3.0	≤3.0	3.4	3.7	3.7	3.7	3.7	3.7
Methyl Orange (0.01%)	≤3.0	≤3.0	3.7	4.1	4.1	≥4.4	≥4.4	
Methyl Orange (0.001%)	≤3.0	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.	
Methyl Red (0.02%)	≤4.2	≤4.2	≤4.2	≤4.2	≤4.2	≤4.2	≤4.2	≤4.2
Methyl Red (0.002%)	?	?	?	?	?	?	?	
Methyl Red (0.0002%)	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.	
Congo Red (1.0%)	≥5.0	≥5.0	≥5.0	≥5.0	≥5.0	≥5.0	≥5.0	≥5.0
Congo Red (0.01%)	?	?	?	≥5.0	≥5.0	≥5.0	≥5.0	
Congo Red (0.001%)	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.	
Alkacid † paper	≤3.5	≤3.5	3.7	4.2	4.7	4.8	5.0	5.0

N.I. No indication, paper white.

† Obtained commercially,

TABLE 9

The pH of Aqueous Solutions of FeCl₂, as Estimated
by Indicator-Impregnated Filter Papers

Indicator (concn.)	FeCl ₂ Concentration**, g/l (pH in brackets)								
	461 (1.50)	200 (2.30)	100 (2.52)	50 (2.68)	25 (2.88)	10 (3.22)	1.0 (4.21)	0.1 (4.38)	0.01 (4.75)
Bromocresol Green (0.04%)	≤3.8	≤3.8	≤3.8	≤3.8	≤3.8	≤3.8	4.6	4.6	4.6
Bromophenol Blue (0.02%)	≤3.0	≤3.0	≤3.0	≤3.0	≤3.0	≤3.0	≥4.6	≥4.6	≥4.6
Methyl Orange (0.01%)	≤3.0	≤3.0	≤3.0	≤3.0	3.4	3.7	4.1	≥4.4	≥4.4
Methyl Red (0.002%)	5.2	?	?	?	?	?	?	?	?
Congo Red (0.01%)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Alkacid Paper †	<3.5	<3.5	<3.5	<3.5	≤3.5	4.0	5.0	5.0	5.0

** There was some very light precipitation of rust before tests were performed.

† Obtained commercially.

TABLE 10

The pH of Aqueous Solutions Containing FeCl₂ and 3.5% NaCl
as Estimated by Indicator-Impregnated Filter Papers

Indicator (concn.)	FeCl ₂ Concentration, g/l (pH in brackets)								
	461 (1.40)	200 (2.23)	100 (2.75)	50 (3.10)	25 (3.32)	10 (3.61)	1.0 (4.36)	0.1 (4.99)	0.01 (5.22)
Bromocresol Green (0.04%)	≤3.8	≤3.8	≤3.8	≤3.8	4.2	4.2	4.6	4.6	4.6
Bromophenol Blue (0.02%)	≤3.0	≤3.0	≤3.0	≤3.0	≤3.0	3.8	≥4.6	≥4.6	≥4.6
Methyl Orange (0.01%)	≤3.0	≤3.0	≤3.0	3.4	3.7	3.7	4.1	≥4.4	≥4.4
Methyl Red (0.002%)	?	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.
Congo Red (0.01%)	≤3.0	4.0	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.	N.I.
Alkacid Paper †	<3.5	<3.5	<3.5	3.5	4.0	4.5	4.8	4.8	4.8

N.I. No indication, paper white.

† Obtained commercially.

TABLE 11

The pH, as Estimated by Indicator-Impregnated Filter Papers, of Aqueous Solutions Containing 0.1 g/l FeCl₂ and 3.5% NaCl Solution, the pH being Adjusted by Small Additions of Hydrochloric Acid

Indicator (concn.)	pH of Solution					
	2.41	3.02	3.52	4.09	4.51	4.99
Bromocresol Green (0.04%)	≤3.8	≤3.8	≤3.8	4.2	4.6	4.6
Bromophenol Blue (0.02%)	≤3.0	≤3.0	4.2	4.2	≥4.6	≥4.6
Methyl Orange (0.01%)	≤3.0	3.4	3.7	4.1	≥4.4	≥4.4
Methyl Red (0.002%)	?	N.I.	N.I.	N.I.	N.I.	N.I.
Congo Red (0.01%)	4.0	N.I.	N.I.	N.I.	N.I.	N.I.
Alkacid Paper †	≤3.5	4.0	4.5	4.5	4.5	4.5

N.I. No indication, paper white.

† Obtained commercially.

