

Summary

1. The instability of phthalate buffer solutions toward the hydrogen electrode has been shown to be dependent upon the relative amount of platinum black on the electrode.

2. Complete reduction of potassium hydrogen phthalate to potassium hexahydrophthalate has been accomplished in aqueous solution, using heavily-platinized, gauze hydrogen electrodes.

3. Hexahydrophthalic acid has been recovered from the completely reduced solution.

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THE SALT ERROR OF CRESOL RED

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Determinations of the hydrogen-ion concentration of sea water or other saline media by colorimetric methods involve a greater or less degree of error, owing to a direct effect of the salt present on the color of the indicator. This effect is independent of the actual change in the Sørensen value (P_H) of an unbuffered solution which occurs on the addition of salt.

The effect of the salt is usually to change the color of the indicator slightly toward the alkaline side, so that the apparent Sørensen value of the solution is somewhat greater than the actual value. With a few indicators the effect is in the opposite direction. Kolthoff¹ has claimed that for certain indicators the direction of the error may be reversed at stated concentrations of salt. The causes of the salt effect are obscure, and the nature and degree of the error involved have never been thoroughly investigated.

Without actual determination of the salt error, certain methods of avoiding it have been devised. In the use of standard tubes for sea water, the error is avoided by addition of experimentally determined amounts of salt to the standards. The McClendon standards have been widely used for determinations of the Sørensen value in the range of normal sea water, and Wells² has given directions for the preparation of standard tubes for use in brackish waters.

In practice, however, it has often occurred that determinations of the Sørensen values of saline solutions have been made with standards uncompensated for the salt effect. Such results are most useful only when properly corrected for amounts of salt present in the samples. The cor-

¹ Kolthoff, *Rec. trav. chim.*, **41**, 54 (1922).

² Wells, *THIS JOURNAL*, **42**, 2160 (1920).

rection to be applied is problematical, and there has been no consistent practice in the handling of such data by different investigators.

The problem presented by the salt error has been emphasized anew in connection with the use of the double-wedge comparator method of Barnett and Barnett³ for determinations of the Sørensen value of sea water. The method consists essentially of the use of a narrow glass trough divided by a diagonal glass partition into two wedge-shaped compartments, into which are introduced solutions exhibiting, respectively, the two extremes of the range of color of the indicator which it is desired to use. By looking through the trough the observer gets the combined color effect of the two isolated solutions, so that the trough presents from one end to the other a gradual change in color through the complete range of the indicator used. A sample to be tested is placed in a square glass cup of the same fluid diameter as the trough, a measured quantity of indicator is added to bring the indicator concentration of the sample to that of the standard, and the cup is moved along the top of the trough to the point at which a color match is obtained. This point is noted on the scale of the comparator, and the Sørensen value is calculated from the indicator constant. An accuracy of 0.02 Sørensen unit is claimed for the method.

A modification of this method has been used with much success for determinations of the Sørensen value of sea water by Dr. E. G. Moberg of the Scripps Institution for Biological Research. This method the writers have used throughout in their analyses of San Francisco Bay waters in connection with the marine borer investigations of the San Francisco Bay Marine Piling Committee.

The most useful single indicator in the case of sea water is *o*-cresol-sulfonephthalein (Cresol Red), which has a range P_H 7.2 to 8.8. All Sørensen values of water in San Francisco Bay found by the authors have been within the useful range of this indicator.

With the accumulation of a large amount of uncorrected data regarding Sørensen values based on comparator readings with Cresol Red, it became increasingly necessary to determine the correction to be applied to such readings in order to give the absolute Sørensen values. This was accordingly undertaken in the following manner.

The Sørensen value of a sample of sea water of known salinity was accurately determined by means of the hydrogen electrode. Then immediately a colorimetric determination of the same sample was made by means of the comparator. The difference between the electrometric and colorimetric determinations was considered to represent the salt error at the salinity given.

The hydrogen electrode apparatus used was accurate to 0.005 P_H . In the electro-metric determinations the sample was brought to equilibrium by bubbling through of hydrogen for a half hour or more. This occasioned a certain amount of difficulty in the colorimetric determinations, as the sample, being thoroughly freed from carbon dioxide

³ Barnett and Barnett, *Proc. Soc. Exptl. Biol. Med.*, 18, 127 (1920).

on removal from the hydrogen electrode, absorbed this gas from the air with sufficient rapidity to cause a distinct fading of the indicator color within one minute. With practice, however, it was possible to make the colorimetric determination within a few seconds after removing the solution from the hydrogen electrode and this source of error is accordingly believed to be negligible.

By this method the salt error was determined at salinities of 5, 10, 15, 18 and 25 parts per 1000. The results are given in Table I, the hydrogen electrode readings being corrected to standard conditions.

TABLE I
THE SALT ERROR OF CRESOL RED AT STATED SALINITIES

Salinity of sample, parts per 1000	Hydrogen electrode determination	Comparator determination	Salt error
5.0	8.39	8.50	0.11
10.0	7.90	8.06	.16
15.0	7.96	8.18	.22
15.0	7.83	8.06	.23
18.0	8.08	8.31	.23
25.1	8.18	8.43	.25
25.1	7.90	8.05	.25

From these data a curve was plotted of the salt error of this indicator between salinities of 5 and 25 parts per 1000, as shown by the solid line in

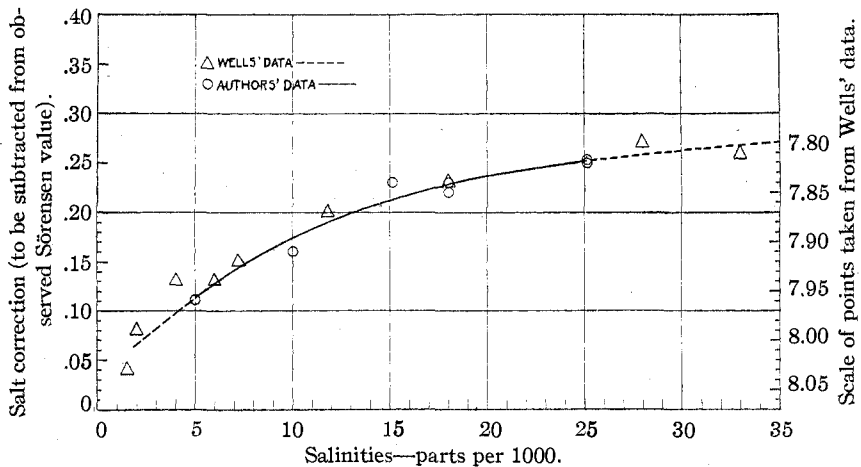


Fig. 1.

Fig. 1. This range being sufficient for the purposes of the authors at that time, the determinations were not carried into the higher and lower ranges of salinity.

It was observed, however, in a study of the work of Wells, mentioned above, that his data, when plotted on a direct scale instead of the logarithmic scale which he used, give a curve of very nearly the same form as ours. His results were obtained by hydrogen-electrode measurements of buffered

solutions which showed the same color in the presence of the same concentration of indicator, but which contained varying concentrations of salt. The only item lacking in Wells' data is a point of reference for plotting his results in a form which would indicate the absolute instead of a relative salt error. That is, he has determined the error at certain concentrations of salt with reference to the error at certain other concentrations, but not with reference to a zero salt concentration, as seen from the following partial tabulation of his results given in Table II.

TABLE II

DIFFERENCES IN SÖRENSEN VALUES AT VARIOUS CONCENTRATIONS OF SALT, THE INDICATOR COLOR REMAINING CONSTANT

Salinity, g. per liter.....	1.47	1.98	4.00	6.00	7.18	11.80	18.00	28.00	33.00
Hydrogen electrode detn. . .	8.03	7.99	7.94	7.94	7.92	7.87	7.84	7.80	7.81

It will be observed from Table II that the total range of the salt error between salinities of 4 (or 6) g. per liter and 28 g. per liter is 0.14 *PH*, which is the range found by the present authors between the salinities of 5 and 25 parts per 1000.⁴ Thus it appears that Wells' results are sufficiently in accord with ours to justify combining the two sets of data to afford certain conclusions for ranges of salinity not covered by our work.

A means of reducing the two sets of data to a comparable basis is found in the fact that each provides a value for a salinity of 18 parts per 1000. These two points were made to coincide in the graph, being indicated on our scale as 0.23, and on Wells' scale, at the right-hand margin of the graph, as 7.84. With this as a point of reference the other points taken from Wells' data were plotted on the graph. Thus 7.87 on Wells' scale becomes 0.20 on ours, etc.

On the basis of Wells' data, then, we have extended our curve into the lower ranges of salinity on the one hand and to a salinity of 35 parts per 1000 on the other. The portions of the curve which are not based on our own data are indicated by a broken line.

The nearly complete coincidence of these two sets of data, derived by entirely different methods, is a considerable factor in establishing the correctness of the basic assumptions. The smoothness of the resultant curve appears to afford ample justification of the combination of these data.

As regards salinities higher than 35 parts per 1000, Wells has some data to show that the curve proceeds slowly upward with increasing concentrations of salt, his determinations of Sørensen values at a constant color being 7.78 (0.29 on our scale) at a concentration of 41 g. per liter, 7.72 (0.35 on our scale) at 75 g. per liter and 7.67 (0.40 on our scale) at a salinity of 103 g. per liter. The nature of the salt error at salinities in excess of

⁴ The difference between grams per liter and parts per 1000 in the range of salinities considered is so small that for our purposes the terms may be used interchangeably.

35 parts per 1000 is, however, of hardly more than theoretical interest, at least as regards marine work.

In Table III are given the salt corrections to be applied at salinities from 5 to 35 parts per 1000, as taken from the above curve.

TABLE III

THE SALT ERROR OF CRESOL RED AT SALINITIES FROM 5 TO 35 PARTS PER 1000 OF SEA SALTS

Salinity	5	6	7	8	9	10	11	12
Correction	-0.11	-0.13	-0.14	-0.15	-0.16	-0.17	-0.18	-0.19
Salinity	13	14	15	16	17	18	19	20
Correction	-0.20	-0.21	-0.21	-0.22	-0.22	-0.23	-0.23	-0.24
Salinity	21	22	23	24	25	26	27	28
Correction	-0.24	-0.24	-0.25	-0.25	-0.25	-0.25	-0.26	-0.26
Salinity	29	30	31	32	33	34	35	
Correction	-0.26	-0.26	-0.26	-0.27	-0.27	-0.27	-0.27	

The absolute accuracy of these results depends on a factor not previously mentioned, namely, the *buffer error*. The introduction of such buffers as the borate, phosphate, or phthalate mixtures to maintain a stable hydrogen-ion concentration in the color standards of itself involves a certain salt effect. The concentration of buffer normally used is small, and the error thus introduced has usually, although perhaps not justifiably, been neglected in practice.

Wells' work was of course with buffered solutions and in our work the buffer error is included by virtue of the fact that the indicator constants of Barnett and Barnett were determined by the use of buffered solutions.

If the curve described above were extended to a zero salt concentration, the point at which the curve cuts the salt-error axis would represent the amount of the buffer error included in the salt corrections given. But in the absence of more data in the region between 0 and 5 parts per 1000 it is unsafe to attempt to approximate the zero point by extrapolation.

The fact that Wells' data become slightly erratic in the lower ranges of salinity appears to be primarily due to his failure to maintain a constant concentration of buffer.

Regardless of the consideration of the buffer error, however, it should be emphasized that the salt corrections given above apply to all determinations of the Sørensen value of sea water by the method of Barnett and Barnett. In establishing the indicator constants, the buffer error has doubtless resulted in the constants' being slightly too high. If we suppose, for example, that the buffer error involved in determining the indicator constant for cresol red is 0.05, our salt correction is 0.05 P_H too great. But, on the other hand, all sea water determinations made on the basis of this constant are also 0.05 P_H too high, and as the salt error is subtracted, the two errors cancel. Thus, the net result is the absolute Sørensen value of the sample.

The authors believe that determinations of the Sørensen value of sea water by the method of Barnett and Barnett, with the applications of the corrections given above, afford the most exact results attainable by any colorimetric method as yet developed. This is true also of straight sodium chloride solutions (Wells, Ref. 2), and probably of solutions of other uni-univalent salts of this general type.

As the indicator constant for cresol red (8.13) was determined on the basis of the standard borate and phosphate mixtures of Clark and Lubs, the corrections given should apply as well to tube determinations of the Sørensen value of saline solutions in which the buffered standards of those authors are used.

Summary

The salt error of cresol red (*o*-cresolsulfonephthalein) in solutions containing from 5 to 35 parts per 1000 of sea salts has been determined on the basis of comparative colorimetric and electrometric studies of the Sørensen values of samples of sea water of known salinity. The results are presented in tabular form.

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THE CATALYTIC COMBINATION OF ETHYLENE AND HYDROGEN IN THE PRESENCE OF METALLIC COPPER III. CARBON MONOXIDE AS A CATALYST POISON

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Facts of some importance to the adsorption theory of contact catalysis were established in a previous investigation¹ of the catalytic and adsorbent properties of metallic copper granules before and after "poisoning" with mercury. The adsorption isotherms at 0° of hydrogen, ethylene and carbon monoxide were displaced nearly parallel to themselves in the direction of less adsorption after the poisoning; that is, the mercury had the effect of preventing the "strong" (low-pressure) adsorption, though not affecting the weaker (high-pressure) adsorption appreciably. At the same time, the catalytic activity of the copper at 0° toward a hydrogen-ethylene mixture was almost completely destroyed. A correlation of catalytic activity and "strong," as opposed to general, adsorption was thus observed in the fact that poisoning brought about simultaneous disappearance of the two.

A detailed investigation of this relation promised to be somewhat laborious and unsatisfactory because of the difficulty of introducing very small but accurately known quantities of mercury and because this sub-

¹ Pease, *THIS JOURNAL*, **45**, 2296 (1923).