

On the Colorimetric Determination of pH in Sea-Water.

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With 2 Figures in the Text.

It is not always possible accurately to carry out pH determinations on board ship, owing to bad light or other conditions, although it may be possible to collect water samples. Hitherto it has not been considered possible to determine pH more than a few hours after collection, owing to the action of bacteria and phytoplankton and the exchange of carbon dioxide with the atmosphere.

A method has now been found whereby the water may be kept in its original condition for some considerable time after collection, enabling the actual determination to be carried out under more favourable conditions in a shore laboratory.

Colorimetric estimation is made by matching the samples under examination with buffer solutions corresponding to known pH. Accurate comparison is dependent upon the quality of the light used, since the colour exhibited by an indicator is due to the selective absorption of certain frequencies of the incident light. An estimation made with sunlight is not rigorously the same as if it is made with diffused or artificial light which is richer in yellow and poorer in blue. When working with an accuracy greater than 0.1 pH it is better to use a source of constant light, operating under special conditions.

The bactericidal action of mercuric chloride prevents the troublesome activity of micro-organisms present in the sea-water whilst its very small dissociation coefficient ($\alpha=0.013$) is without effect on the pH. If when the samples are collected on board about four drops of a saturated solution of mercuric chloride is added to each 100 c.c., bacterial action is stopped, and furthermore if the sample bottle is completely filled, no air-space being left over the water, evasion or invasion of carbon dioxide is inhibited or at least very greatly restricted.

The determinations of pH in sea-water samples have been carried out by means of the well-known McClelland method (1) in order to obviate the salt error. The buffer solutions were "boric" (18.6 gm. boric acid and

22.5 gm. sodium chloride made up to 1 litre with boiled distilled water) and "borax" (28.67 gm. sodium borate and 19.0 gm. sodium chloride made up to 1 litre with boiled distilled water); the total volume of each standard made by mixing these two buffers in correct proportions was 10 c.c. against 30 c.c. used by McClendon. The indicator was 0.5 c.c. of 0.02% cresol red solution prepared from a 0.2% alcoholic solution. A stock solution of this strength was made in order to avoid the addition of a very little sodium hydroxide necessary for the complete dissolution of cresol red as an 0.6% solution. The test tubes, of Monax resistance glass (12 cm. in height and 1.3 cm. in diameter), were chosen so that, when 10 c.c. of water were added to each, the columns of liquid had approximately the same height. The tubes after washing with distilled water were steamed and finally dried in the stove at 110° C. Ten c.c. of the appropriate buffer mixture, 0.5 c.c. of the indicator and two drops of toluene were placed in each tube, which was closed by a cork coated with paraffin wax. Finally an efficient seal is ensured by a second coat of wax over the cork and top of the tube, and label. The standards remain unchanged and fit for use even after many months (2). When not in use the tubes are kept in the dark as a precaution. The standards were at $\text{pH} = 8.40 - 7.30$ with a difference of 0.05 or 0.03.

The addition of two drops of a 2.5% mercuric chloride solution to the sea-water samples in the test tubes does not interfere with the pH, and if these samples containing mercuric chloride are stored in darkness at a temperature of 12–14° C. in test tubes carefully sealed no changes in pH are noticed after some days. In water samples without mercuric chloride a much more rapid fading in the colour is observed. An unpreserved sea-water sample from one mile N.W. of the Eddystone, whose pH on the day of collection was 8.11, gave 8.06 on the following day, and 7.38 after 12 days. A sample of the same water containing mercuric chloride and also stored in darkness at 12–14° C. did not alter its pH for three weeks. Other samples also from the Eddystone, containing mercuric chloride, gave the same value of pH (8.11) for a month, after which the colour changed a little, giving the value 8.07.

The colour of certain samples, preserved and stored in the same way, changed after 5–6 days, but the tubes were found to have been imperfectly sealed. Thus the mercuric chloride stopped the activity of the micro-organisms, but the entry of atmospheric carbon dioxide modified the pH.

If the water samples are taken in ordinary bottles not completely full, to which mercuric chloride is added on collection and the addition of indicator made a few days afterwards, the pH observed is less than on the day on which they were taken. Determinations made on opening the tubes a week later, gave a result 8.05 on the water with mercuric chloride and

TABLE I.

EFFECT OF MERCURIC CHLORIDE AT 12° C.

St.	Water.	Day of																					
		collection.	One day	2 days	3 days	4 days	5 days	6 days	7 days	8 days	9 days	11 days	12 days	13 days	14 days	15 days	17 days	18 days	19 days	20 days	21 days	23 days	
			after.	after.	after.	after.	after.	after.	after.	after.	after.	after.	after.	after.	after.	after.	after.	after.	after.	after.	after.	after.	after.
L1	alone	8-05	8-04	7-92	7-83	7-58	7-38	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
L1	plus merc. chloride	8-05	8-05	8-05	8-05	8-05	8-05	8-05	8-05	8-05	8-05	8-05	8-05	8-05	8-05	8-05	7-97	7-95	7-96	7-95	7-91	7-91	7-91
L2	alone	8-07	8-05	8-03	7-88	7-73	7-68	7-53	7-38	—	—	—	—	—	—	—	—	—	—	—	—	—	—
L2	plus merc. chloride	8-07	8-07	8-07	8-07	8-07	8-07	8-07	8-07	8-07	8-07	8-07	8-07	8-07	8-07	8-07	7-95	7-94	7-91	7-91	7-90	7-90	7-90
L3	alone	8-09	8-09	8-00	7-88	7-78	7-68	7-58	7-58	7-58	7-56	7-56	7-56	7-56	7-56	7-56	7-56	7-50	—	—	—	—	—
L3	plus merc. chloride	8-09	8-09	8-09	8-09	8-09	8-09	8-09	8-09	8-09	8-09	8-09	8-09	8-09	8-09	8-05	8-05	8-04	8-02	8-01	8-01	8-01	8-01
L4	alone	8-10	8-10	8-05	7-93	7-75	7-63	7-58	7-53	7-48	7-38	—	—	—	—	—	—	—	—	—	—	—	—
L4	plus merc. chloride	8-10	8-10	8-10	8-10	8-10	8-10	8-10	8-10	8-10	8-10	8-10	8-10	8-10	8-10	8-02	8-02	7-99	7-96	7-96	7-96	7-96	7-96
L5	alone	8-11	8-09	8-00	7-93	7-73	7-63	7-55	7-43	—	—	—	—	—	—	—	—	—	—	—	—	—	—
L5	plus merc. chloride	8-11	8-11	8-11	8-11	8-11	8-11	8-11	8-11	8-11	8-11	8-11	8-11	8-11	8-10	8-11	8-11	8-11	8-11	8-11	8-09	8-06	8-06

7.93 on the water without antiseptic. These values are lower than the values found (8.10) on the day when the water was collected.

But if the samples containing mercuric chloride are drawn from bottles completely full the pH determined by adding the indicator some days afterwards is the same as the original value.

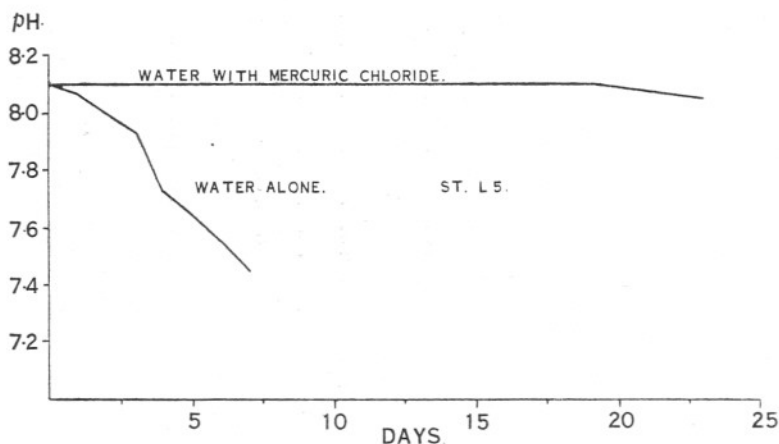


FIG. 1.

The following table contains the results obtained on sea-water samples from the International Hydrographical Stations L1, L2, L3, L4, and L5 (on Feb. 5th) with and without mercuric chloride. These were stored on the day of collection in carefully sealed test tubes and kept in darkness at 12–14° C. The data for Station L5 are shown graphically in Figure 1.

Other preservatives have been tried. Toluene was the best, but as the figures in Table II show, it is much less effective than mercuric chloride.

TABLE II.

EFFECT OF DIFFERENT PRESERVATIVES AT 12° C.

	1st day.	2nd day.	3rd day.	4th day.	6th day.	7th day.	8th day.	9th day.	10th day.
W. alone	8.11	8.11	8.06	7.91	7.78	7.73	7.63	7.53	7.48
W.+ toluene	8.11	8.11	8.10	7.98	7.93	7.93	7.83	7.83	7.83
W.+ mercuric chloride	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11	8.11

It is well known that temperature plays an important part in the determination of pH, because heat increases the dissociation of ions and correlatively the pH decreases. The determinations must be made with the water samples at the same temperature as the buffer mixtures.

If the test tubes containing the sea-water samples plus indicator are stored at a temperature higher than 12–14° C. the colour fades more quickly.

TABLE III.

EFFECT OF MERCURIC CHLORIDE AT 33° C.

Stn.	Water.	1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.	7th day.	8th day.	9th day.	10th day.	12th day.
L2	alone	8.07	8.00	7.80	7.43	7.20	—	—	—	—	—	—
L2	plus mercuric chloride	8.07	8.07	8.06	8.02	7.91	7.91	7.91	7.91	7.91	7.83	7.73
L5	alone	8.11	8.06	8.00	7.73	7.23	—	—	—	—	—	—
L5	plus mercuric chloride	8.11	8.11	8.10	8.05	7.88	7.88	7.88	7.88	7.88	7.88	7.88

Figure 2 shows these variations in sea-water from L2 and L5 with and without mercuric chloride kept in a thermostat at 33° C. We noticed that the pH of the sealed samples containing mercuric chloride show no

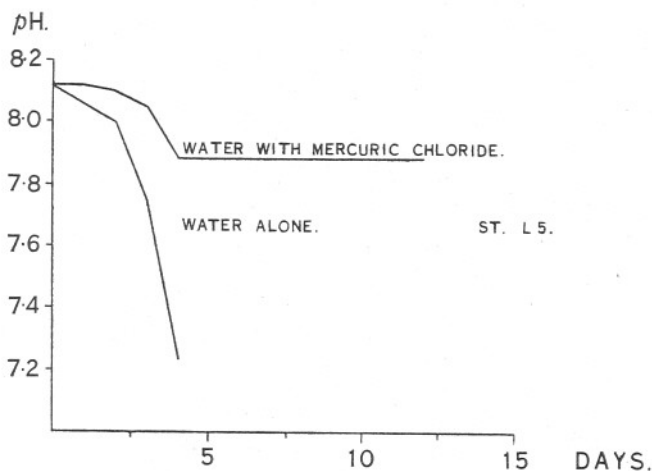


FIG. 2.

change after two days, but that in unpreserved water the decrease is very rapid indeed, somewhat naturally even more rapid than at the lower temperature.

The buffer mixtures did not change at 33° C. as judged by subsequent comparison with buffers kept at 12° C.

The erratic decreases are owing to different causes. According to Legendre proteins can influence the indicators, perhaps partially absorbing them, and although the sea-water contains these nitrogenous substances in very small amount, different proportions of them may produce a variable fading in the colour.

It was stated above that to every test tube containing McClendon mixtures two drops of toluene were added, to preserve them; but it is possible to work under the same conditions by adding two drops of a 2.5% mercuric chloride solution in place of toluene, making a correction in the value of pH. As is well known mercuric chloride gives a precipitate of basic salt with sodium borate, but in the presence of boric acid there is no precipitation since a complex is formed. The pH is therefore slightly changed. Buffer mixtures were prepared in this way and their values were 0.03 less than in the original mixtures with toluene.

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SUMMARY.

1. It is not always feasible to determine pH on board ship, owing to bad light and other conditions, although it may be possible to collect water samples.

2. By preserving the water samples on collection with mercuric chloride solution (four drops per 100 c.c. of water) and by taking care to leave only a small air-space in the bottles it is possible to keep the water practically unchanged for many days.

3. Test tubes containing such water (10 c.c.) plus 0.02% cresol red (0.5 c.c.) have been kept unchanged for three weeks at 12–14° C. and for two days at 33° C., whereas unpreserved water showed a drop in pH of 0.05 unit in one day at 12° C.

4. McClendon buffer solutions may also be preserved by mercuric chloride, but in this case a small correction must be applied since complex formation leads to a removal of effective buffer salts from the solution and a small decrease in pH.

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