ized milk, with an actual iron content of 0.73 mg. per liter, by the method used by Soxhlet. The results were 0.6 mg. and 0.8 mg. per liter. Kugelmass used amyl alcohol as solvent for ferric sulfocyanate; but his results were subject to error on account of the small amount of milk taken for analysis. Ashing in a glass tube seems also to result in contamination with iron since the same milk, containing 0.73 mg. of iron per liter, gave a result of 1.3 mg. by the method of Kugelmass.

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The Buffer Capacity of Sea Water[1]

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The buffer capacity of sea water is defined and the principle of the determination demonstrated. The buffer capacity is differentiated from such terms as "alkaline reserve," "methyl orange alkalinity," etc., because the effects upon the indicator by variations in the concentration of the dissolved salts and of the excess acid are considered.

The buffer capacity is shown to be a rather constant function of normal sea waters, and the value of the constant for the Puget Sound region and the San Juan Archipelago shown to be 0.1250 with chlorinity per liter as unity. However, variations in conditions affecting the sea water, such as land drainage, pollution, and photosynthesis, cause noticeable deviations.

The total carbon dioxide cannot be determined by direct acidimetric titration methods. Sea water diluted by streams tends to give a high value for the buffer capacity. Photosynthetic processes and industrial pollution of sulfite liquor give low buffer-capacity values.

The determination is one that may be easily and quickly performed under rigorous field conditions.

THE buffer capacity of sea water may be defined as the number of millimoles of hydrogen ions which a unit volume of sea water will neutralize when an excess of standard acid is added. The principle of the method is to add a measured quantity of standard acid to a known amount of freshly sampled sea water, determine the hydrogen-ion concentration of the resultant solution, using special standards for comparison, and calculate the amount of acid neutralized.

The buffer capacity is in the category of the "alkalinity" of Ruppin as cited by Helland-Hansen (*1*). It is analogous to the "alkaline reserve" of McClendon (*3*) because no difference was noted in the buffer capacity when the sea water was boiled, either before or after the addition of the acid. It is also similar to the "titrable alkalinity as bicarbonate" of Lucas and Hutchinson (*2*), if certain corrections are made for the end points. However, the use of the term distinguishes it from others that are analogous because recognition is made of the effects produced by varying the concentration of dissolved salts and the excess of acid. The present paper is an extension and improvement of previous work reported from the authors' laboratories (*5*).

Variations in the concentration of the dissolved salts occurring in sea water have variable "salt effects" upon the indicators. Thus in the determination of the buffer capacity, certain corrections must necessarily be applied. This is best accomplished by the use of what is termed "base-free" sea water. Colorimetric standards may be prepared by adding varying known quantities of acid to the base-free sea water, the latter being first diluted to a salt content equivalent to the waters being studied.

Preparation of Base-Free Sea Water

Four liters of sea water are boiled with a small excess of sulfuric acid. Three or four drops of the concentrated acid are sufficient. After thorough boiling, 0.01 *N* sodium hydroxide is added until a pH of 6.6 is obtained, using bromothymol blue and La Motte standards. The sea water is again boiled, cooled, and the chlorinity (*6*) determined.

Knowing the latter and the chlorinities of the samples of sea water to be studied, the base-free sea water is diluted with distilled water until analogous conditions of concentration are obtained. The base-free sea water is used for the preparation of standards within the range of bromophenol blue by the addition of carefully measured amounts of standard 0.0100 *N* hydrochloric acid. It is necessary to prepare different sets of standards of the varying quantities of acid for different ranges of chlorinity. In practice it is found more convenient to restandardize by comparison with the La Motte color standards. Bromophenol blue is used because it is not sensitive to the hydrogen ions of the carbonic acid formed, and thus the boiling of the solution is not necessary.

The method for the determination of the buffer capacity has been subjected to four modifications. The first, applicable to waters having chlorinities between 14.50 ‰ and 18.00 ‰, was to add 25.00 ml. of 0.0100 *N* hydrochloric acid to 100 ml. of sea water and then take the pH of the resultant solution,

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using bromophenol blue as the indicator and standards of base-free sea water of a given chlorinity for comparison. This method, because of its rapidity, has proved particularly useful aboard ship and under the most rigid conditions, as a large number of bottles containing the necessary amount of acid may be prepared in advance.

The second modification consisted in varying the concentration of the acid for waters of lesser or greater chlorinities so that the excess acid would come within the proper range of the bromophenol blue.

The third modification was to titrate with 0.01 N hydrochloric acid to a color approximately in the middle of the range of bromophenol blue and to determine the pH of the resultant solution in the usual manner.

The fourth modification might be termed a micro-method as a 10-ml. sample was measured into a calibrated pH tube, titrated with the standard acid with a microburet, and the pH noted.

It is essential that the 0.0100 N hydrochloric acid be prepared by dilution with distilled water from 0.1000 N hydrochloric acid in order to minimize titration errors.

The computations to be considered in the determination of the buffer capacity of sea water are the calculations of the amount of acid added and the calculations of the concentration of the resultant acid, using the standards prepared from base-free sea water. For convenience, results are reported as millimoles per liter of sea water, and may be calculated from the following formula:

$$Bc = \left[\left(\frac{1000}{Vs}\right)(V)(N)\right] - \left[\frac{1000\,(Vs + V)Hs}{Vs}\right] \qquad (1)$$

where Bc is the buffer capacity; Vs is the volume of sea water used; V, the volume of acid in milliliters; and N, the normality of the acid. The first part of the expression is the millimoles of hydrogen ions added per liter of sea water, while the second part of the expression is the millimoles of hydrogen ions in excess. The latter is found by determining the pH, which is designated as pHs because of correction for salt effects, where

$$\text{pH}s = \log\frac{1}{[Hs]} \qquad (2)$$

Hs may be determined for any given series of determinations for the chlorinity range under consideration and for the nature and the concentration of the indicator utilized, as follows:

$$Hs = \frac{(V_1).(N)}{(Vb + V_1)} \qquad (3)$$

where Vb is the volume of base-free sea water, and V_1, the volume of the acid added to the base-free sea water in the preparation of the color standards.

It is obvious that the buffer capacity is practically independent of the original pH of the sea water under consideration.

ILLUSTRATION—A sample of sea water had a chlorinity of 17.95 grams per liter. A 100-ml. portion of this water was added to 25 ml. of 0.0100 N hydrochloric acid and a quantity of the resulting solution measured in a pH tube. Bromophenol blue indicator was added and the color produced compared with standards made from base-free sea water of approximately the same chlorinity. A match with the color standards showed a pHs of 3.8. This particular standard had been made by adding 1.50 ml. of 0.0100 N hydrochloric acid to 100 ml. of base-free sea water. Thus

$$3.8 = \log\frac{1}{Hs}$$

$$Hs = 0.00015$$

or, substituting in Equation 3,

$$Hs = \frac{1.5 \times 0.01}{100 + 1.5} = 0.00015$$

Then applying Equation 1

$$Bc = \left[\frac{1000}{100} \times 25 \times 0.01\right] - \left[\frac{1000\,(100 + 25)\,0.00015}{100}\right] = 2.31$$

Experimental Procedure

The data presented in Table I emphasize the errors that may be produced by dissolved salts and variations of excess acid. In order to get concordant and comparable results, it is necessary to use sufficient hydrochloric acid in excess to give a color reading equivalent to a pH between 3.7 and 4.4, and to standardize color-comparison tubes in terms of a base-free sea water.

Table I—Variations in Acidity with Bromophenol Blue
(100 ml. of base-free sea water; chlorinity, 15°/₀₀)

0.01 N HCl ADDED	CONCENTRATION OF RESULTING SOLUTION Calcd. H^+	Obsd. H^+	Diff.
Ml.			
1.00	0.099	0.028	0.071
2.00	0.196	0.063	0.133
3.00	0.291	0.100	0.191
4.00	0.384	0.140	0.270
5.00	0.476	0.200	0.276

From August, 1928, to March, 1930, 452 samples, taken at different depths from various parts of the San Juan Archipelago and the Puget Sound region, were studied. Of these samples, 130 gave abnormal values of buffer capacity because of land drainage or industrial pollution. The remaining 322 will serve for the development of the behavior of standard sea water.

The effect of silicates cannot be ignored, as the waters of the Puget Sound region contain at least 0.05 milliequivalent. The concentration of borates is unknown. On the other hand, the total effect of phosphates and hydroxyl ions is less than 0.01 milliequivalent. Likewise, ammonia, in the quantities usually present, is negligible. The carbonates and the bicarbonates are the predominating ions affecting the buffer capacity of sea water, but from a study of the data given, the authors are of the opinion that the buffer capacity is also a function of some inherent basic property of the sea.

The usual standard of comparison for sea-water behavior is the chlorinity (grams of halide as chloride) per liter or per kilo (*4*, *7*). Thus the first step is to find the ratio of the buffer capacity to chlorinity. The 322 samples gave an average ratio of 0.1252—that is

$$\frac{Bc}{Cl} = 0.1252$$

The average of the deviations of the individual samples was determined from this average ratio. A statistical method was then applied, and it was found that 283 samples, or 88 per cent of the total number, whose deviations were not more than twice the average deviation, gave an average ratio of 0.1251. Applying this method again to the 283 samples, it was found that 254, or 79 per cent of the 322, gave an average ratio of 0.1250. This figure may thus be taken as the buffer capacity–chlorinity ratio for the waters of the Puget Sound region and the San Juan Archipelago, and those ocean waters of the Northeast Pacific which serve as sources of waters for these regions. In other words, the buffer capacity expressed as millimoles is one-eighth of the chlorinity and is practically constant for waters in which the equilibria have not been subjected to any marked stress.

The next step is to multiply the difference between the standard ratio and the ratio for a given sample of water having an abnormal buffer capacity, by the chlorinity of the sample. This gives the actual deviation of the buffer capacity, in millimoles, from normal behavior. It was found that 162 samples, or 50 per cent of the 322 samples, agree with the ratio to within the error of the determination, ±0.04 *Bc*, while 48, or 15 per cent, have a deviation just equal to the difference between the normal and the next adjacent value. Unmistakable deviations were shown by the other 112 samples, or 35 per cent of the total.

Table II—Distribution of Deviations of Buffer Capacity with Depth

	1–5 Meters	6–10 Meters	11–25 Meters	26–50 Meters	Over 50 Meters	Total
Number of samples	111	51	66	45	49	322
Number deviations	45	18	24	11	14	112
Per cent deviations	41	35	36	24	29	35
Increments:						
Number	30	12	13	4	6	65
Per cent deviations	67	67	54	36	44	59
Average deviations	0.07	0.07	0.07	0.06	0.05	0.06
Maximum deviations	0.17	0.13	0.14	0.08	0.06	
Decrements:						
Number	15	6	11	7	8	47
Per cent deviation	33	33	46	64	56	41
Average deviation	0.08	0.06	0.07	0.05	0.05	0.06
Maximum deviation	0.14	0.09	0.12	0.07	0.07	

The distribution of deviations from the normal buffer capacity is summarized and shown in Table II.

The data show that the greatest deviations are in the waters between the surface and depths of 25 meters. Abnormally high values occur more often than low values in these surface layers. The samples that deviated from the normal in the deeper samples showed greater tendency to give lower values.

Factors producing deviations in the buffer capacity are land drainage, effects of biological phenomena, and industrial pollution. In all cases of land drainage, high values for the ratio have been obtained. Photosynthetic action may be such as to give low ratios, whereas industrial pollution, such as discharge from sulfite paper mill, will give very low values for the ratio.

Table III—Data Illustrating Definite Buffer-Capacity Behavior Found in Estuaries of Puget Sound

Source of Samples	Chlorinity	Buffer Capacity	*Bc/Cl*	Devn., *Bc*	Carbon Dioxide	Oxygen	pH
	Grams/ liter	*Millimoles*		*Mm./ liter*	*Millimoles*	*Mg./ liter*	
			LAND DRAINAGE				
Oyster beds near mouth of stream:							
High tide	13.08	1.84	0.141	0.20	1.86	5.90	7.70
Low tide	10.30	1.47	0.143	0.14	1.36	13.40	7.95
			PHOTOSYNTHESIS				
Oyster beds in lagoon:							
Low tide 1	14.72	1.55	0.105	−0.29	1.07	21.53	Over 8.8
Low tide 2	14.75	1.62	0.110	−0.22	1.38	24.67	Over 8.8
			SULFITE LIQUOR				
Near mill	5.91	0.46	0.078	−0.28	..	0.00	Less than 6.0
			COMBINED EFFECTS				
Photosynthesis, land drainage, and sulfite liquor	12.31	1.03	0.084	−0.51	1.75	6.69	7.45

Many investigators have shown that photosynthesis is always accompanied by an increase in the pH of the waters, a decrease in the total carbon dioxide content, and an increase in dissolved oxygen. Sulfite liquor has a tendency to lower the pH and the dissolved oxygen, and increase the total carbon dioxide. In the latter case, the buffer capacity generally will be considerably lower than the effect produced by marked conditions of photosynthesis. In complex situations where there is much photosynthesis occurring in the sea water polluted by sulfite liquor, the pH and the dissolved oxygen may vary considerably, the total carbon dioxide will be greater than with waters subjected only to photosynthetic action, and the buffer capacity will be low. The data in Table III illustrate the effects produced.

From these data three conclusions may be drawn: (1) The buffer capacity may be only partially dependent upon the concentration of carbonates and bicarbonates; (2) the formulation of McClendon, correlating pH, carbon dioxide, and alkali reserve, lacks universal application; and (3) the determination of total carbon dioxide by titration and colorimetric methods is not feasible.

All values for total carbon dioxide reported herein were obtained by boiling off the gas after acidifying the sea water and collecting the gas in standard barium hydroxide solutions.

In order to show the contrasts between various methods for the determination of alkalinity, carbon dioxide, and buffer capacity, six different samples of sea water were collected in the San Juan Archipelago and analyzed. The data obtained are given in Table IV.

Table IV—Comparison of Methods for Determination of Alkalinity, Carbon Dioxide, and Buffer Capacity, with Related Data on Surface Waters of Washington Sound

	1	2	3	4	5	6
Chlorinity, grams per liter	16.83	16.71	16.93	17.01	16.23	15.10
Temperature, ° C.	8.1	8.2	8.2	8.3	8.7	8.8
pH	7.95	8.10	7.90	7.85	7.80	7.85
Dissolved oxygen, mg. per liter	10.08	10.68	9.24	8.92	9.36	9.16
Total carbon dioxide, millimoles per liter	1.82	1.86	1.82	1.94	1.80	1.69
Buffer capacity,[a] millimoles H^+ per liter	1.85	1.95	1.99	1.95	1.91	1.73
Buffer value per chlorinity, *Bc/Cl*	0.110	0.117	0.118	0.115	0.118	0.115
Deviation of buffer capacity	−0.25	−0.14	−0.13	−0.18	−0.12	−0.16
Alkalinity, millimoles:						
With methyl red	1.82	1.84	1.92	1.89	1.84	1.74
With methyl orange	1.99	1.95	2.01	1.97	1.89	1.80
With bromophenol blue (cold)	2.23	2.24	2.24	2.25	2.13	1.99
With bromophenol blue (hot)	2.65	2.48	2.72	2.62	2.56	2.25

[a] Boiled before and after with various samples and same results obtained as on fresh samples.

The high oxygen content indicates processes of photosynthesis, and a low *Bc/Cl* might thus be predicted. The alkalinity was determined by titration, using different indicators. The data under alkalinity show that in some cases methyl red may give a fair indication of the total carbon dioxide, but noticeable variations may be obtained. With methyl orange as the indicator, the results are higher, and bromophenol blue gives still higher results. In all the data reported, duplicate and ofttimes triplicate determinations were run on the samples. In all the alkalinity determinations the greatest variation on the same sample was 0.03 millimole. For values obtained by titration no corrections were made for the salt errors of the indicators.

To insure concordant results in the alkalinity determinations, boiling of the solutions was essential. This process is very inconvenient aboard ship, and as the buffer capacity does not show any variation whether or not the samples are heated to boiling, it thus serves as an excellent means for arriving at values that lend themselves readily to interpretation. Comparison of the titrable values with bromophenol blue and the buffer capacity emphasize the differences that may be produced by excess acid.

Neither the buffer capacity nor the titration values show a constant and concordant relationship with the total carbon dioxide nor with the dissolved oxygen.

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