THE BUFFER CAPACITY OF SEA WATER [1]

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The titration of sea water in order to measure its excess of base, or what may be called its buffer capacity for acids, is not only of interest from the standpoint of oceanography but also of practical value in the detection of acid wastes present in small quantities (Thompson and Bonnar, 1931). Several methods have been employed. Wattenberg (1930) has described a method in which an excess of acid is added to the sea water, CO_2-free air is drawn through the boiling mixture until all CO_2 is removed, and then the water is back-titrated with standard barium hydroxide solution, using a mixture of brom cresol green and methyl red as indicator. Greenberg, Moberg, and Allen (1932) use a method of direct titration with standard acid, using methyl orange as indicator. Both of these methods, and others of which they are typical, require the use of rather elaborate precautions and of more or less cumbersome apparatus.

Of recent methods, that of Thompson and Bonnar (1931) possesses certain distinct advantages. It is rapid and employs apparatus easily handled on board ship. It is especially good in that results are practically independent of the CO_2 tension of the sample.

The principle of the method is simple. A sufficient volume of standard HCl is added to a measured portion of the sample to produce an acidity near the middle of the useful range of brom phenol blue. From this the milliequivalents of hydrogen ion per liter remaining unneutralized are calculated. This value subtracted from the quantity of H ion added per liter gives what might be called the apparent buffer capacity of the water. This value, however, must be corrected for the effect of salts upon hydrogen ion activity and upon the dissociation of the indicator. The correction is made by carrying out the same procedure on a sample of carbonate-free, approximately neutralized sea water of the same salinity as the unknown sample. Subtracting the acid required by the carbonate-free water from that required by the sample gives the buffer capacity of the latter.

It seemed to us that if standard values for the amount of acid required to bring carbonate-free sea water of any given salinity to any

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given pH could be established, the method would be made much more useful, especially since the difficult part of Thompson and Bonnar's method is the preparation and preservation of neutral, carbonate-free water. Our experience has led to the conclusion that such standard values can be obtained. Sea waters from distinctly different regions, whether clear or cloudy (provided they are filtered before use) will yield the same results within the limits of observational error, when rendered truly carbonate-free.

The method of preparing the "neutralized" water has been slightly modified. Concordant and reproducible results can be obtained only when certain precautions are rigidly adhered to. Filtered sea water, sufficient to half fill a large Pyrex boiling flask, is treated with concentrated H_2SO_4, drop by drop, until a test portion gives a color with brom phenol blue approximately equivalent to that of a Clark and Lubs standard tube of pH 3.4. The water is then boiled for about six hours under a Pyrex reflux condenser, while a stream of CO_2-free air is rapidly drawn through it. The reflux condenser is then removed, and while the water is still boiling, carbonate-free NaOH of about 0.07N strength is added in small portions until a sample of the water quickly cooled to room temperature shows a pH of 6.6 with brom thymol blue. The approach to the condition of near neutrality is followed from time to time by titrating a cooled 25-ml. portion of the water with 0.01N NaOH, using brom thymol blue as indicator. As noted by Thompson and Bonnar, the occurrence of an alkaline condition in the water at any time during the approach to neutrality vitiates the preparation. CO_2 will be taken up so rapidly that the water, even though it is acidified as soon as the slight alkaline condition is discovered, will show acid requirements that are too high.

Measurements are made, after the preparation has been cooled to 20° C., upon various known dilutions with distilled water. The following series, for example, was used: 21, 18, 15, 12, 9, 6, and 3 grams per liter of halide, computed as chlorine. Approximate dilutions are prepared and the precise chlorinity later determined by titration with $AgNO_3$. Each of several 100-ml. portions of each dilution is treated with a suitable amount of 0.075N HCl added from a micro-burette permitting a precision of ± 0.001 ml. Each of the mixtures is then read at 20° C. with brom phenol blue as indicator in a pH bicolorimeter of the Hastings type. The precision of this instrument, provided its optical system is adjusted to give perfectly uniform illumination on both sides, is far beyond the expectations of one accustomed to older pH colorimetric methods. Differences corresponding to less than 0.01 of a pH unit can be recognised and measured by the experienced ob-

server. From the readings, pH values are computed, using 3.98 as the pK$_I$ of brom phenol blue. This "constant" varies, of course, with salinity, but if the same pK$_I$ of the indicator is used throughout, the so-called "salt-error" is automatically eliminated. The value 3.98 is convenient because it is the one established for brom phenol blue at 20° C. in Clark and Lubs' standard buffer solutions. From the pH value and the quantity of acid added are calculated the milliequivalents of H ion neutralized per liter, or the apparent buffer capacity of the carbonate-free water. The several values for each dilution are plotted

TABLE I

"Apparent" buffer capacity of carbonate-free, approximately neutralized sea water. Milliequivalents of H ion apparently neutralized per liter.

Cl after adding HCl	pH observed after adding HCl											
	4.10	4.05	4.00	3.95	3.90	3.85	3.80	3.75	3.70	3.65	3.60	3.55
gram/l.												
3	.048	.055	.061	.071	.080	.092	.105	.121	.139	.156	.179	.206
4	.058	.065	.075	.084	.095	.107	.123	.139	.158	.177	.203	.232
5	.067	.075	.087	.097	.110	.122	.140	.157	.177	.198	.226	.256
6	.076	.085	.098	.108	.127	.137	.155	.173	.196	.216	.247	.278
7	.083	.093	.109	.120	.135	.150	.171	.188	.209	.235	.267	.299
8	.090	.101	.116	.129	.146	.163	.182	.204	.224	.253	.285	.319
9	.096	.109	.125	.139	.155	.174	.194	.215	.239	.267	.302	.339
10	.103	.116	.132	.147	.167	.185	.205	.228	.251	.282	.317	.354
11	.109	.123	.140	.156	.176	.194	.215	.239	.264	.295	.332	.370
12	.114	.129	.146	.162	.179	.202	.225	.250	.277	.310	.345	.383
13	.120	.135	.151	.170	.190	.212	.236	.259	.288	.319	.358	.398
14	.124	.140	.158	.175	.197	.220	.243	.268	.298	.330	.369	.412
15	.128	.145	.164	.181	.201	.227	.250	.276	.307	.340	.380	.423
16	.133	.150	.168	.187	.210	.232	.259	.283	.316	.351	.390	.435
17	.137	.153	.173	.192	.215	.240	.266	.290	.324	.360	.400	.446
18	.141	.157	.178	.196	.222	.247	.273	.298	.333	.369	.410	.457
19	.145	.160	.184	.200	.225	.253	.280	.304	.340	.378	.419	.465
20	.149	.164	.186	.204	.229	.258	.283	.309	.347	.386	.429	.476
21	.152	.166	.190	.208	.234	.263	.292	.315	.354	.394	.336	.484

against the observed pH values, and when this is done for each of the several dilutions, a contour chart involving the three variables, pH, apparent buffer capacity, and chlorinity of the acidified water, is obtained. By interpolation, apparent buffer capacity for any given pH and chlorinity can be read off.

After this method had become standardized six different collections of sea water were used for extended sets of measurements. Their sources were: Woods Hole Harbor, two samples, and one each from Narragansett Bay, Atlantic Ocean near Newport, Atlantic Ocean south

of Martha's Vineyard, and Atlantic Ocean near Bermuda. From the resulting six contour charts, the mean value of the apparent buffer capacity was computed for each of 59 points distributed over the ranges of chlorinity and pH values which, when plotted, yield the contour chart shown in Fig. 1. The computed 59 points (in italics), together with others read off from Fig. 1, are given in Table I.

The precision of these values was tested by computation of the probable error of each of the mean values entered upon the contour chart. Of the 59 points 40 had a probable error of the mean not exceeding ± 0.003, 9 of them had a probable error less than ± 0.001 and the general order of the probable error was ± 0.002. In no case
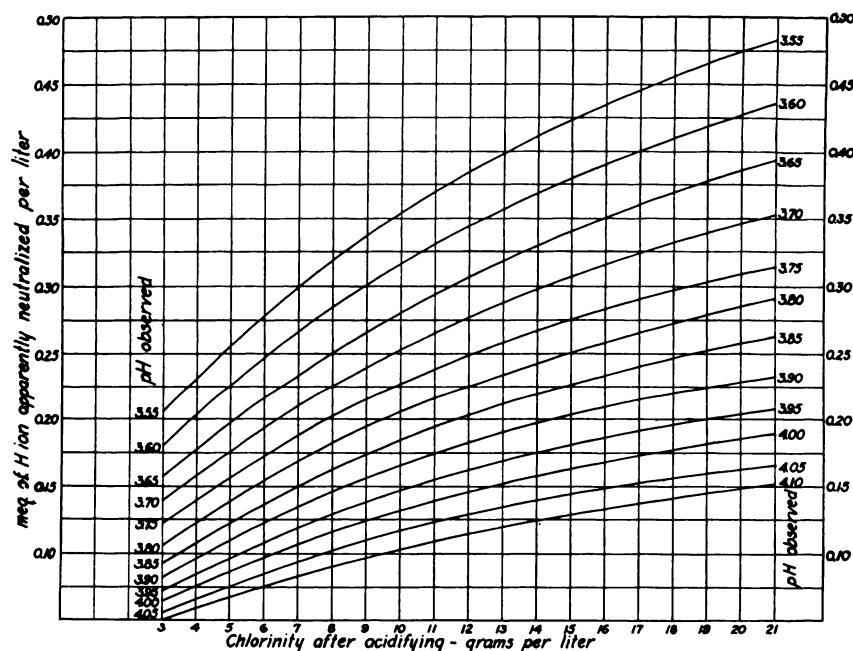

FIG. 1. The apparent buffer capacity of carbonate-free approximately neutralized sea water, used for standard correction values. Above the abscissa equal to the chlorinity of an acidified sea water sample, one selects by interpolation between the isohydric contour lines the pH observed with brom phenol blue as indicator and reads the corresponding ordinate as the correction to be subtracted from the apparent buffer capacity of the sample. These values are computed on the assumption that, for brom phenol blue,

$$pK_t = 3.98 - 0.007(t - 20°\text{ C.}).$$

did the probable error exceed ± 0.006 and the less consistent results were all in a range of pH values more acid than pH 3.70, a part of the chart not recommended for use in more precise measurements, for reasons to be discussed presently.

The final test of the accuracy of these values is their actual use as corrections for measurements of the buffer capacity of sea water. If accurate they should give results on any one sample of sea water, both with and without the addition of distilled water, and at any observed end-point of titration within the chosen pH range, such that the ratio of the buffer capacity (obtained with the use of the carbonate-free correction value) to the chlorinity of the water is constant. This has been found to be the case, in repeated trials, within the limits of observational error. An example of such a test of the method is shown by the results given in Table II.

TABLE II

Titrations of the same sea water sample undiluted and diluted with distilled water

Chloride content	Titration end point	Uncorrected buffer capacity	Correction from contour chart	Corrected buffer capacity	Ratio $\frac{BC}{Cl}$
gram/l.	*pH*	*meq./l.*	*meq./l.*	*meq./l.*	
17.38	3.77	2.394	0.280	2.114	0.1217
17.38	3.79	2.368	0.264	2.104	0.1210
11.98	3.75	1.707	0.247	1.460	0.1219
9.88	3.74	1.439	0.233	1.206	0.1219
5.94	3.87	0.846	0.128	0.718	0.1210
4.05	3.835	0.608	0.115	0.493	0.1217

The selection of an appropriate end-point for the titration of sea water, when brom phenol blue is the indicator, must be a compromise. Greenberg, Moberg and Allen (1932), applying the theory of titration to the problem of methyl orange titration of the total carbonates of sea water, compute the correct end-point as pH 4.35, and use 4.5 in practice. The steepest slope of the titration curve is in the region of pH 4 to 5. This we have found to be the case by the use of the glass electrode described by Taylor and Birnie (1933). This instrument was particularly suitable for the purpose because measurements are taken in a small closed chamber which prevents loss of CO_2. Two titration curves are shown in Fig. 2. They make it obvious that the most sharply defined end-point is at approximately 4.5. Here, however, the effects of carbonic acid are considerable, and loss of CO_2 makes the colorimetric pH estimation very difficult. Indeed, carbonic acid exerts a measurable effect upon the result unless the end-point is distinctly more acid. The true dissociation constant of H_2CO_3, though unknown, is of the general order of pK_a 3.5, according to several observers (Michaelis, 1926). But if the titration is arbitrarily carried to a pH of about 3.4–3.3, that is, beyond the possible effects of car-

bonic acid, the uncertainty of the colorimetric determination is greatly increased. Readings with brom phenol blue in this range show a comparatively large observational error.

A working compromise between these various objections is reached by selecting the end-point so as to be between pH 3.70 and 4.00, a
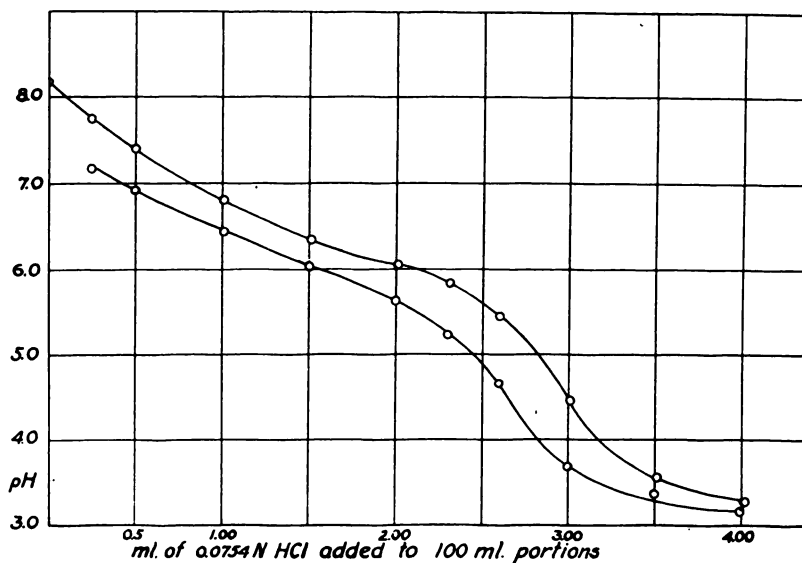

FIG. 2. Sea water titration curves. The pH measurements were taken with a glass electrode in a closed chamber. Each point was obtained with a separate 100-ml. portion of water to which was added the volume of 0.0754N HCl indicated. The pH measurements were made at 30° C.

Upper curve: water from near Newport; chlorinity, 18.10 gram/l.
Lower curve: Narragansett Bay water; chlorinity, 15.21 gram/l.

range within which the titration curve is fairly steep and the measurements can be made with a satisfactory degree of accuracy, while the effects of varying CO_2 tension in the sample are relatively small, affecting the result by an amount less than one per cent of the observed value. The latter fact was ascertained by measuring sea water samples which were equilibrated with laboratory air and then measuring the same samples after bubbling expired air through them. Using 3.98 as the pK_I of brom phenol blue in sea water, as we have proposed above, yields values which are somewhat higher than the *true* pH. In sea water of high salinity at 20° C., the pK_I is of the order of 3.78, as the work of Kolthoff (1930) on KCl solutions has indicated. Precise measurements in sea water of varied salinities and temperatures are desirable. Some preliminary work in this direction has been under-

taken in the laboratory of one of us, using the glass elecrode and the bicolorimeter. It is clear, however, that the end-point chosen for these titrations is sufficiently acid to avoid serious errors due to carbonic acid.

The following procedure is followed in taking the buffer capacity of a sample: It is collected in Pyrex glass, unless measurements can be made at once. Silicates from soda glass can measurably raise the buffer capacity. If it must await analysis for any length of time, it is preserved at a temperature not above 10° C. Fermentation acids can cause low results, in our experience. If any visible organic matter is present the sample is filtered. Protein and perhaps other organic matter raise the buffer capacity. Measurements are taken at or near 20° C. A 100-ml. portion is pipetted into a small Pyrex flask and HCl of about 0.075N strength is added in amount which, as estimated roughly from the salinity of the water, will bring it to the desired acidity as described above. Either preliminary trials or previous experience with water of the locality is necessary to determine the amount. The flask is stoppered and its contents thoroughly mixed and used for pH measurements in the bicolorimeter. The brom phenol blue can give reliable results only when of high purity, which can be ascertained by using it with Clark and Lubs' standard phthalate buffer solutions. Of five different manufacturers' products tested, only two were found to be within the limits of the accuracy of this method. For all the results reported here, brom phenol blue from Hynsonn, Westcott and Dunning was used.

The solution of the indicator must also be approximately isohydric with the solutions to be measured. This condition was sufficiently approximated by adding to the 0.04 per cent indicator solution, as commonly prepared with one molecular equivalent of NaOH, a further amount of 0.01N NaOH equal to one-third of a molecular equivalent. This solution gave the same pH readings in the sea water irrespective of the concentration of indicator. Indicator solutions containing either one or one and one-half molecular equivalents of NaOH failed to do so. An indicator solution containing more than one molecular equivalent of alkali is relatively unstable and should be prepared not more than three days before use.

It is not always feasible to secure temperature control at 20° C. during the pH observation. Although slight variations in temperature do not greatly alter the pH of the acidified sea water, they do affect the dissociation of the indicator to an extent exceeding the limits of accuracy otherwise attainable in this method. As an approximate correction for the temperature effect upon brom phenol blue, we have

used the formula, $pK_t = 3.98 - 0.007\ (t - 20°)$, where pK_t is the pK_I at temperature, t. This is taken from a few measurements with the use of the glass electrode and is subject to future correction.

The method of computation of results is shown by the following example. To 100 ml. of Woods Hole Harbor water was added 3.400 ml. of 0.07509N HCl, or 2.553 milliequivalents of H ion per liter of water. The resulting pH was 3.83, or 0.153 meq. of H ion in 1034 ml. of mixture. The apparent uncorrected buffer capacity is 2.553 − 0.153 = 2.400 meq./l. Interpolation from the contour chart of Fig. 1 or from Table I shows that at pH 3.83 and chlorinity of 17.8 grams/l (the value for this mixture), the correction is 0.260 meq./l.

TABLE III

Buffer capacity of surface water from the Cape Cod region

Date	Source of sample	Chloride content	Buffer capacity	Specific buffer capacity
		gram/l.	*meq./l.*	*BC/Cl*
12/19/30............	Near Woods Hole	18.31	2.204	0.1203
"	" " "	18.34	2.220	0.1210
"	" " "	18.28	2.188	0.1198
"	" " "	18.28	2.176	0.1189
"	" " "	18.27	2.171	0.1188
"	" " "	18.17	2.165	0.1192
"	" " "	18.21	2.188	0.1200
7/27/32............	" " "	18.05	2.161	0.1196
"	" " "	18.05	2.138	0.1183
8/30/32............	" " "	18.48	2.181	0.1181
"	" " "	18.48	2.162	0.1170
"	" " "	18.48	2.176	0.1177
9/10/32............	" " "	18.32	2.165	0.1182
9/12/32............	" " "	18.24	2.164	0.1186
"	" " "	18.35	2.159	0.1176
"	" " "	18.24	2.160	0.1182
1/29/33............	" " "	17.90	2.112	0.1181
9/16/32............	Buzzards Bay	18.48	2.223	0.1203
"	" "	18.27	2.191	0.1200
9/22/32............	Cape Cod Bay	18.11	2.183	0.1205
"	" " "	18.02	2.170	0.1203
"	" " "	18.05	2.187	0.1211
9/23/32............	East of Cape Cod	18.22	2.187	0.1200
"	" " " "	18.21	2.189	0.1202
"	" " " "	18.20	2.184	0.1200
"	" " " "	18.19	2.184	0.1201
"	" " " "	18.36	2.200	0.1198
"	" " " "	18.35	2.202	0.1200
8/11/32............	35 miles south of Martha's Vineyard	18.48	2.223	0.1203

The buffer capacity of the sample is, then, 2.400 − 0.260 = 2.140. The $AgNO_3$ titration of this water sample gave Cl 18.32 grams l, so that the ratio BC/Cl = 0.1168. The latter may be called the "specific buffer capacity."

Results of observations on various samples from the Cape Cod region and from parts of the Atlantic Ocean and the Caribbean Sea included in a recent cruise of the "Atlantis," are summarized in Tables

TABLE IV

Buffer capacity of sea water from the Gulf of Maine

Station	Depth	Chloride content	Buffer capacity	Specific buffer capacity
	meters	*gram/l.*	*meq./l.*	*BC/Cl*
1705	0	18.10	2.143	0.1184
	50	18.40	2.200	0.1196
	175	18.74	2.210	0.1179
1706	0	18.10	2.144	0.1185
	50	18.42	2.172	0.1179
	150	18.63	2.182	0.1171
1707	0	18.09	2.211	0.1222
	50	18.25	2.186	0.1198
	125	18.56	2.201	0.1186
1709	0	17.47	2.101	0.1203
	31	17.97	2.130	0.1185
1711	0	17.99	2.161	0.1201
	50	18.16	2.167	0.1193
	175	18.86	2.220	0.1177
1713	0	18.22	2.189	0.1201
	50	18.45	2.207	0.1196
	175	19.17	2.254	0.1176
1717	0	18.08	2.180	0.1206
	50	18.34	2.202	0.1201
	200	19.69	2.290	0.1163
1722	0	18.14	2.104	0.1160
	54	18.43	2.196	0.1192
	114	18.90	2.217	0.1173
	0	18.14	2.173	0.1198
	50	18.445	2.181	0.1182
	250	19.66	2.300	0.1170
1723	0	18.765	2.249	0.1199
	70	18.465	2.215	0.1200

III, IV, V, and VI.   (The results in Table VI were obtained by Mr.
Homer P. Smith, on board the "Atlantis.")   Figure 3 shows the loca-
tion of the principal stations in the investigation.

The specific buffer capacity, or the ratio of buffer capacity to the

TABLE V

Buffer capacity of Atlantic Ocean water

Station	Depth	Chloride content	Buffer capacity	Specific buffer capacity
	meters	*gram/l.*	*meq./l.*	*BC/Cl*
1462	0	20.90	2.420	0.1158
	0	20.90	2.452	0.1172
	100	20.90	2.450	0.1171
	2000	19.95	2.393	0.1199
	2000	19.95	2.371	0.1188
St. Georges Harbor, Bermuda	0	21.00	2.403	0.1144
1465	0	21.15	2.438	0.1152
	100	20.17	2.363	0.1171
1467	0	21.20	2.373	0.1120
	100	21.20	2.419	0.1140
	4500	20.17	2.378	0.1179
1469	0	21.20	2.402	0.1134
	100	21.15	2.419	0.1143
	600	20.83	2.386	0.1145
	800	20.45	2.380	0.1164
	1200	20.30	2.347	0.1157
	2000	20.22	2.338	0.1156
	3000	20.20	2.346	0.1161
	4000	20.20	2.346	0.1161
1473	0	21.22	2.384	0.1123
	100	21.20	2.374	0.1122
	500	21.07	2.367	0.1123
	1000	20.35	2.328	0.1144
	1600	20.20	2.317	0.1147
	2000	20.20	2.329	0.1153
	2500	20.20	2.329	0.1153
	3000	20.20	2.317	0.1147
1477	0	20.93	2.356	0.1125
	100	21.17	2.385	0.1126
	500	21.03	2.387	0.1135
	1000	20.27	2.319	0.1144
	1400	20.25	2.319	0.1145
	2000	20.25	2.295	0.1133
	3000	20.20	2.295	0.1136

TABLE VI

Buffer capacity of water from the Caribbean Sea

Station	Depth	Chloride content	Buffer capacity	Specific buffer capacity
	meters	*gram/l.*	*meq./l.*	*BC/Cl*
1482	100	20.855	2.406	0.1154
	500	20.375	2.367	0.1162
	1000	19.825	2.384	0.1203
	2000	19.845	2.384	0.1201
	3000	19.785	2.335	0.1180
1513	100	20.495	2.296	0.1120
	500	19.98	2.270	0.1136
	1000	19.745	2.245	0.1137
	2000	19.81	2.271	0.1146
	3000	19.81	2.271	0.1146
1527	0	20.65	2.355	0.1140
	100	20.755	2.389	0.1151
	500	19.77	2.310	0.1168
	1000	19.785	2.322	0.1174
	2000	19.82	2.335	0.1178
	3000	19.83	2.347	0.1184
1548	0	20.35	2.319	0.1140
	100	20.48	2.355	0.1150
	500	19.95	2.310	0.1158
	1000	19.74	2.298	0.1164
1581	0	20.425	2.355	0.1153
	100	20.435	2.368	0.1159
	500	20.07	2.309	0.1150
	1000	19.685	2.311	0.1174
	2000	19.755	2.298	0.1163
	3000	19.775	2.298	0.1162
	4000	19.76	2.258	0.1143
	5000	19.775	2.258	0.1142
	6000	19.775	2.229	0.1127
1598	0	20.38	2.391	0.1173
	100	20.36	2.381	0.1169
	500	20.00	2.346	0.1173
	1000	19.725	2.323	0.1178
	2000	19.77	2.310	0.1168
	3000	19.775	2.327	0.1177
			2.310	0.1168
1606	0	20.415	2.367	0.1159
	100	20.40	2.344	0.1149
	500	20.07	2.296	0.1144

chlorinity, is in general lower than that reported by Thompson and
Bonnar for Pacific water of the San Juan Archipelago and nearby
regions.   That this difference is not due merely to variations in method
is indicated by the results of measurements made by one of us on 48
samples from various bays in the Puget Sound region.   These measure-
ments were made by the same method as that used in this report and
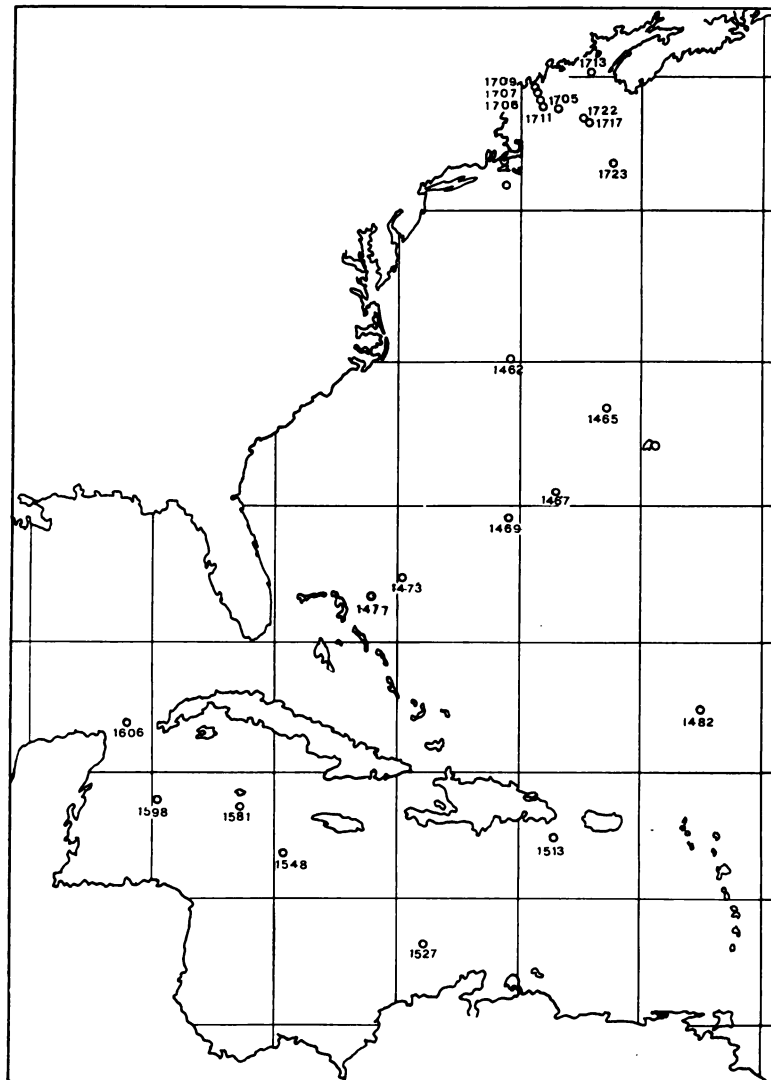the same correction values for salt effects were applied.   All the re-

FIG. 3.   Location of the principal stations.

sults fell within the range of specific buffer capacities reported by Thompson and Bonnar. It is hoped that the titratable alkalinity of Atlantic and Pacific waters can be more adequately compared in the near future. It would also be of interest to compare the ratios we have already found with those obtained in other parts of the world, but it is not yet certain in our opinion that results obtained by different methods are fairly comparable. So far as we are aware, the report of Thompson and Bonnar is the only one based upon the use of this method.

A comparison of our data with those of Wattenberg (1925–27), in the course of his extensive work in the South Atlantic on the "Meteor" expedition, shows very fair agreement. His values for the ratio of alkalinity to chloride fall mostly between 0.120 and 0.125, but using chloride per kilogram as a basis. When this is changed to chloride per liter (lowering the ratio about 2 per cent) very close agreement results with our average value of 0.119 + for water near Cape Cod.

Two general tendencies are to be seen in the above data: first, a lower specific buffer capacity in waters to the south than in those from the neighborhood of Cape Cod and the Gulf of Maine. This difference is especially noticeable in the western part of the Sargasso Sea and in the greater portion of the Caribbean. A full discussion of the significance of these differences must await further data, which we are endeavoring to obtain.

Were these variations due simply to a difference between coastal and mid-ocean water we should expect the results in the Caribbean to be similar to those in the Gulf of Maine, but it is precisely here that the difference is most marked. Wattenberg's values for "specific alkalinity" in the South Atlantic show a similar, but less pronounced, variation with respect to latitude. Averaging his results from stations in the neighborhood of 40° − 50° S. on the one hand, and those from stations 10° − 20° S. on the other, shows an increase of about 2 per cent, at corresponding depths, in the higher latitudes. A similar analysis of our more limited data reveals a difference of 4–5 per cent.

Second, there is a variation in specific buffer capacity with depth; in general, and especially at deep-sea stations, an *increase* with depth. (Wattenberg found the specific alkalinity to behave in the same manner.) In two widely separated areas, however, this variation is reversed. Both in the Gulf of Maine and in the western part of the Caribbean the buffer capacity consistently *decreases* with increasing depth. We are not yet in a position to discuss the full significance of these facts, beyond suggesting that mass movements of the water are concerned, as well as possible variations in the character of the land drainage.

It may be pointed out that the lowering of the specific buffer capacity resulting from the mixing of mid-ocean and coastal water has been apparent in several of our observations. For example, during a prolonged and violent easterly storm in April samples taken at Woods Hole had a higher chlorinity and correspondingly a lower ratio than any we had ever observed there, between 0.1138 and 0.1149.

In addition to the work here reported, many measurements have been made on samples from the Narragansett Bay region. Here, however, the buffer capacities are variable and of a different order from those observed in ocean water. The effects of land drainage, rainfall, tidal and other currents, etc., involved in a nearly land-locked body of water such as Narragansett Bay, are sufficiently complex to deserve special treatment, which will be undertaken in a later report.

SUMMARY

1. The method of Thompson and Bonnar for measuring the buffer capacity of sea water has been modified by the introduction of the use of standard correction values to make allowance for the effects of salts upon hydrogen ion activity and upon the dissociation of brom phenol blue. These values are reported in tabulated and graphic form.

2. Various sources of error in the method are discussed and corresponding refinements of technique suggested.

3. The specific buffer capacity of Atlantic waters according to these measurements is lower than that of Pacific waters, so far as yet investigated.

4. Lower specific buffer capacities were found in the Atlantic Ocean to the southward and in the Caribbean Sea than in the neighborhood of Cape Cod and the Gulf of Maine.

5. In general, an increase in buffer capacity with respect to depth was observed, but in the Gulf of Maine and the western part of the Caribbean this relation was distinctly reversed.

6. The effects of mass movements of ocean water upon the buffer capacity appear to be traceable.

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