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OBSERVATIONS ON THE ALKALINITY¹ OF ESTUARINE WATERS OF THE CHESAPEAKE BAY NEAR SOLOMONS ISLAND, MARYLAND*

By

HARRY F. BRUST AND CURTIS L. NEWCOMBE

*Chesapeake Biological Laboratory
and University of Maryland
College Park; Md.*

INTRODUCTION

Kolthoff (1926) without particular reference to sea water has defined buffer capacity (alkalinity, in the case of added strong base) of a solution quantitatively as the number of equivalents of added strong base or strong acid required to change the pH of one liter of solution one unit. Buch, in 1930, redefined this concept with reference to sea water as the number of moles of carbonic acid which must be added to one liter of the water in order to change its pH by one unit.

In the subsequent work of Thompson and Bonnar (1931) buffer capacity (alkalinity) is 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. This definition involves no assumptions with respect to the kind or concentration of buffers that may be present. In this procedure, an excess amount of hydrochloric acid is added to a known volume of sea water reducing the pH to about 3.80. Then, by the use of a formula, the number of millimoles of hydrogen ions per liter of sea water is obtained. This takes into consideration the alkalinity of all buffer salts. No allowance was made at that time for the amount of acid necessary to reduce the pH of that amount of sea water if free from buffers. Mitchell and Rakestraw (1933) have discussed this point. They consider the buffer capacity as determined by the equation of Thompson and Bonnar (1931) as apparent buffer capacity. They use neutral sea water free

¹The committee on Chemical Nomenclature and Procedures of the International Association of Physical Oceanography have recommended that the term "Alkalinity" be used, designating "buffer capacity of sea water," "titratable base," "excess base," etc.

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from carbonates and then reduce the pH to 3.80. The amount of acid required is subtracted from the apparent buffer capacity to give their buffer capacity. This obviously represents the buffering action of carbonates alone and leaves out of consideration other buffering salts including silicates, phosphates and borates which occur only in relatively small quantities.

In this study, the method of Thompson and Bonnar (1931) has been employed with the single exception that a glass electrode² was substituted for the colorimetric method of determining pH. No correction has been made for the amount of acid that would be necessary to reduce the pH of the sea water if free of buffers. Thompson and Bonnar, in considering the nature of the buffers in sea water, have clearly pointed out the principal importance of carbonates and the relatively minor role played by silicates, phosphates and borates. Mitchell and Rakestraw (1933) in making the aforementioned correction considered the buffer action as due to carbonates alone, while pointing out the relatively insignificant role played by additional buffer salts present.

Studies in progress at this laboratory are designed to prepare a comprehensive table along the lines of that of Mitchell and Rakestraw working in Narragansett Bay, which will provide corrections for the effects of salts upon the hydrogen ion activity and for the amount of acid necessary to reduce the carbonate free sea water to a pH of approximately 3.8. The preparation of this table will extend the use of the glass electrode for determining alkalinity.

EXPERIMENTAL

APPARATUS. In order to determine the pH of the sea water, after the addition of a known amount of standard hydrochloric acid from a burette, a Beckman pH meter equipped with a glass electrode was employed. A small electric motor provided with an efficient stirrer was used to insure thorough mixing of the solution.

METHOD. A known volume of 0.009745 N hydrochloric acid was added rapidly to 100 ml. of sea water until the pH was about 3.80. By using the motor driven stirrer it was found that the solution came rapidly to equilibrium after the acid had been added and did not change. The alkalinity, as described above, was determined immedi-

² Professor T. G. Thompson, Oceanographic Laboratory, University of Washington, has informed us, in a personal communication dated Feb. 5, 1940, that the satisfactory use of the glass electrode for this purpose has been demonstrated in his laboratory.

ately on board the boat. The chlorinity of each sample was determined by a standard procedure (Mohr's Method), and the chlorinity as found in parts per thousand was corrected to express as grams per liter at 20° C. Knowing the volume of hydrochloric acid used and the resulting pH, the alkalinity was calculated using the formula of Thompson and Bonnar (1931).

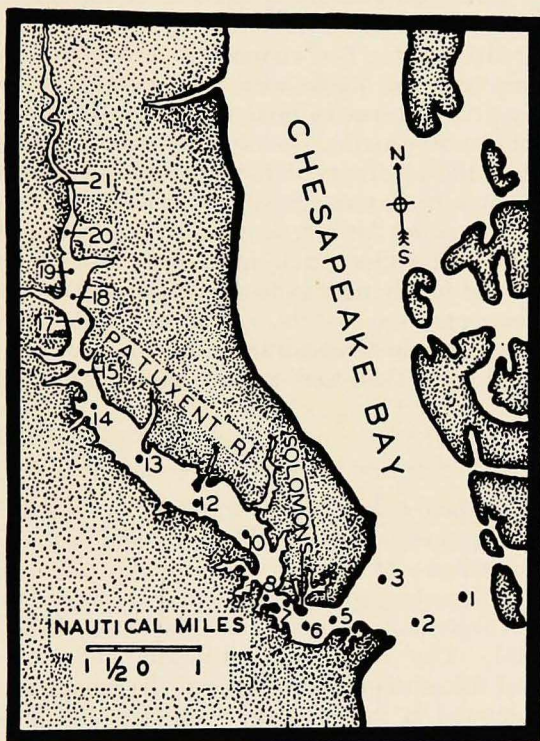


Figure 33. Location of principal sampling stations (numbered points) in the Patuxent River (2 = 102).

STANDARD USED. *Hydrochloric acid*: Two liters of about 0.1 N hydrochloric acid was made up in a pyrex flask and standardized against pure sodium carbonate. The acid was found to be 0.09745 N. From this stock solution a volumetric dilution was made with distilled water producing a 0.009745 N hydrochloric acid solution which was used in the work. The dilution was made in order to minimize titration errors in the standardization.

Sodium carbonate: Baker's C. P. sodium bicarbonate was recrystallized twice and dried. This purified bicarbonate was heated to constant weight at 280° C. The resulting pure sodium carbonate was cooled in a desiccator over calcium chloride and stored in a glass-stoppered bottle.

Standard pH solution: This standard buffered solution of known pH ($\pm .02$ pH unit) was constantly used to check the Beckman pH meter.

ACCURACY OF RESULTS. The volumetric measurements and gravimetric weighings were all made with an accuracy of two parts per thousand or less. The pipettes used were corrected for temperature variations in the sea water. The samples were collected in clean pyrex flasks, and the alkalinity determined within fifteen minutes of sampling. Silicates from soda glass can measurably raise the alkalinity if allowed to stand for any length of time, Mitchell and Rakestraw (1933). The Beckman pH meter had a temperature control which was adjusted for changes in temperature of the sea water. The accuracy of the meter was within ± 0.02 pH unit. Duplicate runs made on the same sample demonstrated that the amounts of acid used to produce a final pH of 3.80 were in each case within 0.02 ml. of each other.

RESULTS

Determinations have been made in waters of widely different chlorinities in the Bay proper—Stations 110 to 102 and in the lower reaches of the Patuxent River—Stations 5 to 18 (Figure 33). These waters show marked differences with respect to chlorinity, turbidity and nutrient salts (Newcombe, Horne and Shepherd, 1939; Newcombe and Lang, 1939). The conspicuous variations in turbidity following heavy rains and the seasonal differences in the amounts of suspended particles are reflected in the chemical equilibria that appear to exist. The alkalinity-chlorinity factor, called the specific buffer capacity by Mitchell and Rakestraw (1933), has not been found to be a constant one over the range of chlorinities studied. Table I is constructed on a basis of decreasing chlorinity 11.85 grams per liter to 4.39 grams per liter. Figure 34 shows more clearly the increase in the alkalinity-chlorinity factor with decrease in the chlorinity of estuarine waters. Thompson and Bonnar (1931), working with estuarine waters off the north Pacific coast, demonstrated this relationship. It was also shown to be true by Mitchell and Solinger (1934) of the estuarine waters of Narragansett Bay.

DISCUSSION

Mitchell and Rakestraw (1933) found the alkalinity-chlorinity factor of Atlantic water off Cape Cod to be about 0.119. The estuarine waters of Narragansett Bay gave a ratio of 0.175 at a chlorinity of 4.5 grams per liter, 0.154 at a chlorinity of 7 grams per liter and 0.137 at 11 grams per liter. Corresponding ratios for Chesapeake estuarine waters have been found to be 0.212, 0.183, and 0.143. These values, it is noted, are somewhat higher than those referred to above. As previously mentioned, our values are uncorrected. The corrected ratios probably would closely approximate those for the northern waters. That a pronounced difference has been shown to exist in the apparent buffer capacity between the typical Bay waters and the less saline river waters seems significant. Furthermore, the apparently close agreement with the results of Mitchell and Solinger (1934) is not necessarily to be expected. The modifying conditions of soil, land drainage, photosynthetic action, and pollution are obviously quite different in the Chesapeake Bay area from those in Narragansett Bay and might reasonably be expected to show significant differences in respect to buffering properties. Such differences have been found to exist between Bay waters having fairly similar chlorinities but of different origins.

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