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THE DETERMINATION OF THE ALKALINITY OF SEA WATER

By

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INTRODUCTION

In a previous paper one of us (*3*) described a method for the determination of the alkalinity of sea water—then termed the buffer capacity of sea water. This method was very rapid, eliminated the need for a titration process, and was particularly advantageous when working under rigorous field conditions. However considerable difficulty was sometimes experienced in the preparation of color comparison standards from base-free sea water. The method was later improved by Mitchell and Rakestraw (*2*). The present paper deals with a modification of the original method. The glass electrode is used for the measurement of excess acid and gives a precision greater than that obtained with color standards. If suitable shelter is available the method may be performed as readily in the field as in the laboratory. Following is a description of the apparatus and the method used.

DESCRIPTION OF APPARATUS

Potentiometer

A Leeds and Northrup pH potentiometer assembly was installed in the laboratory aboard ship in such a manner that it could be readily stowed when not in use. It was securely blocked and padded with sponge rubber and rested on cushions of the same material. The cushions aid in nullifying any vibrations that might affect the instrument.

The apparatus worked perfectly while the ship was under way and in moderate weather. In heavy swells the galvanometer needle oscillated slightly but by taking the midpoint of successive swings, as in making a weighing with an analytical balance, satisfactory results were obtained.

Automatic Pipets

A pair of 25 ml. automatic pipets made by Machlett and Son of New York was used to marked advantage in the measurement of the standard acid (Fig. 56, *Left*). They were more rapid than the common type of pipet and markedly reduced potential personal errors when a number of determinations were being made under rather adverse conditions. The pipets were adjusted and calibrated so that the delivery of the two did not vary by more than 0.02 ml.

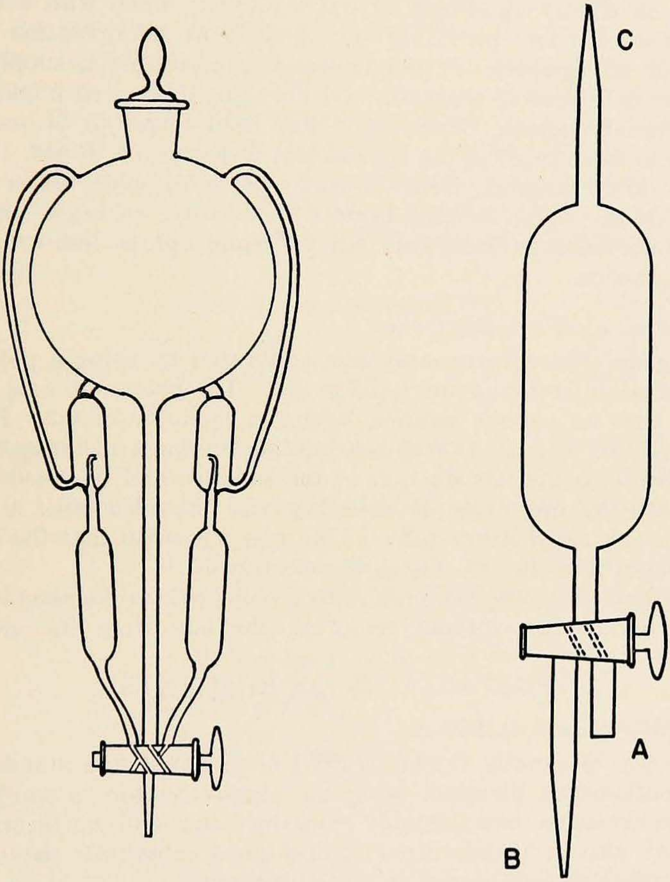

Figure 56. *Left:* Automatic pipet used for measuring the standard hydrochloric acid. *Right:* Sampling pipet. The pipet is filled by gravity from the water sampling bottle by means of a rubber tube connected at A. The pipet is filled partially after thorough rinsing. The stopcock is then turned so as to fill the tip B. When this has been done the stopcock is again turned and the pipet filled completely through A. This being done the sample is drained through B into the 135 ml. glass-stoppered bottle.

Sampling Pipet

It is important that the sample of sea water for the determination be secured from the sampling device as soon as practicable after its arrival on board. A sample of water may be taken with a 100 ml. graduated cylinder, providing the method of manipulation is the same for all samples. If ample water is available a supply may be taken in a suitable container and the sample pipetted immediately in the usual manner. However it has been found to be more expedient to use a pipet of the type shown in Figure 56, *Right.* Its use permits direct sampling from the water bottle sampler, conserves the supply of the water sample, insures an accurate measure when the boat is not on even keel, and reduces errors due to loss or gain of carbon dioxide.

Calibration of Glass Electrodes

The glass electrode assembly was calibrated by using a potassium acid phthalate buffer having a pH of 4.0. The potassium acid phthalate is kept as a stock solution having a molarity of 0.2. For use this is diluted in order to secure a solution having a molarity of 0.05.

To facilitate the introduction of the samples and to speed up the measurements, the electrode assembly was provided with a funnel sealed to a glass delivery tube. This was placed so that the sample as it flowed into the cup rinsed the electrodes.

The sample cup was equipped with a stop cock so the sample could be drained readily without removing the cup from the electrode assembly.

PREPARATION OF REAGENTS

Hydrochloric Acid, 0.1000 N

A supply of exactly 0.1000 N HCl is prepared and standardized by potentiometric titration, using the glass electrode in conjunction with the extension lead assembly made by Leeds and Northrup. The acid may also be standardized against pure anhydrous sodium carbonate, using methyl orange as an indicator.

Hydrochloric Acid, 0.0100 N

The 0.1000 N hydrochloric acid is prepared as described above and then aliquots of this solution are diluted to exactly 0.0100 N, preferably in 10-liter quantities. The latter solution is not standardized by titration.

PROCEDURE

25 ml. of 0.0100 N HCl are pipetted into a dry 135 ml.–150 ml. glass-stoppered bottle. (If the sample bottle has been used in a previous

determination for alkalinity, its contents are drained and the standard hydrochloric acid is then introduced for the next determination. Rinsing with distilled water should be avoided because of the dilution effect, drying of the sample bottle then being essential.) 100 ml. of the sea water sample are added and the resulting solution thoroughly mixed by shaking. After coming to the temperature of the laboratory, a portion of the solution is used to thoroughly rinse the cup of the potentiometer in which the glass electrode is suspended. The cup is finally filled with the solution and the pH determined

The alkalinity of the solution is expressed by the number of milligram atoms of hydrogen ions (millimols or millequivalents) that react with the anions in the sea water. This may be calculated from the following:

$$\mathrm{pH} = \log 1 - \log [\mathrm{H}^+] \qquad (1)$$

$$\mathrm{Alk} = \left[\frac{1000}{V_s}\right] [(V_1\mathrm{N}) - (V_s + V_1)[\mathrm{H}^+]] \quad \text{where,} \qquad (2)$$

V_s is the volume of the sample of sea water, V_1 the volume of HCl to which the water sample was added, N the normality of the acid, and $[\mathrm{H}^+]$ the hydrogen ion concentration after the addition of the sea water to the acid.

Example: If 25.00 ml. of acid having a normality of 0.0100 are added to 100 ml. of sea water, the resulting solution shows a pH of 3.65.

$$3.65 = \log 1 - \log [\mathrm{H}^+]$$

$$\log [\mathrm{H}^+] = \bar{4}.35$$

$$[\mathrm{H}^+] = 0.000224$$

Substituting in (2)

$$\mathrm{Alk} = \frac{1000}{100} [(25.00 \times 0.01) - (100 + 25)\, 0.000224$$

$$\mathrm{Alk} = 10\,(0.250 - 0.028)$$

$$\mathrm{Alk} = 2.22$$

THE ALKALINITY-CHLORINITY FACTOR

The alkalinity of a sample of sea water gives useful and desirable information. However for comparing the alkalinities of a series of samples of sea water whose concentrations vary, it is more expedient to express the value as a ratio to the chlorosity[1] of the water by

$$\frac{\text{Alk}}{{}^\circ/_{\circ\circ}\,\text{Cl}\left(\frac{\sigma_{20}}{1000}+1\right)} = K \text{ where,}$$

Alk is the alkalinity per liter of sea water at 20° C., ‰ Cl is the chlorinity per kilogram of sample, and $\left(\frac{\sigma_{20}}{1000}+1\right)$ is density of the water at 20° C.

The factor, *K,* is relatively constant but a deviation from an average value for it may indicate that important chemical changes have taken place in the water mass.

ACCURACY AND ERRORS OF THE METHOD

The pH measurements made with the glass electrode are readily duplicated and should never vary by more than 0.02 pH units. For average sea water samples this maximum variation is equivalent to 0.01 alkalinity unit (milligram atom of hydrogen). However in general routine determinations, the accuracies are equivalent to 0.005 alkalinity unit on duplicate determinations.

The volume of the sample should be measured with care. If an error of one per cent is made in the volume of a 100-ml. sample, it will produce a variation in the results by the procedure given above of 0.02 pH units.

At the pH range of the samples, 3.50–4.00, temperature changes were found to have little effect upon the actual determination. On three different samples run at various temperatures between 14° and 22°, the pH readings, while different for the samples, were constant. However, it is advisable that the determinations be made at laboratory temperature, because if the sample is below room temperature, there is a tendency for the condensation of atmospheric moisture on the electrode and the electrode assembly which may result in faulty readings.

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[1] The term "chlorosity" has been recommended by the Committee on Chemical Methods and Nomenclature of the International Association of Physical Oceanography. The chlorosity of a sample of sea water is defined as the chlorinity multiplied by the density of the water at a given temperature. By international agreement, the chlorinity designates the grams of halides in a kilogram of water and is determined by titration with a silver nitrate solution which has been standardized against the standard water of the Hydrographical Laboratories of Copenhagen.

The existence of a salt error need not be considered when a glass electrode is used in the presence of a concentration of sodium ions similar to that occurring in sea water at a pH of 3.50 to 4.00. Ball and Stock (1) have shown that there is practically no difference between measurements made in hydrochloric acid solutions to which sea salts have been added, when the hydrogen electrode was used and when the glass electrode was employed.

The glass surface of the electrode is highly adsorbtive; therefore errors may result in measurements made in solutions having very marked differences in pH. The error may be eliminated by thorough and careful rinsing between determinations. Thus if the glass electrode has been used for making determinations of the actual pH of a series of sea water samples, the glass electrode should be well washed and rinsed before making observations for the alkalinity determination. Then observations should always be checked with another portion of the sample.

The atmosphere aboard ship or near the sea shore has a high humidity and special precautions are necessary to keep the vacuum tube compartment of the potentiometer well desiccated. Frequent regeneration of the desiccant is advisable.

CONCLUSIONS

1. The alkalinity of sea water is easily determined by means of the glass electrode. The employment of the glass electrode instead of color standards, as previously recommended greatly increases the accuracy of the determination.

2. The glass electrode assembly available on the market has been modified to facilitate the filling and emptying of the sample cup.

3. The effect of temperature on the pH readings obtained in the procedure given is negligible and no appreciable salt error is obtained.

4. A special sampler has been devised to insure accurate measurement of the water sample when taken for analysis under field conditions.

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