

RAPID DETERMINATION OF THE “TITRATION ALKALINITY” OF SEA WATER BY EQUILIBRATION WITH CO₂

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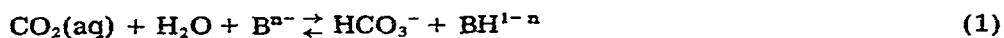
SUMMARY

Sea-water samples of salinities 31.88, 35.84, and 39.87‰ were acidified and then titrated with HCO₃⁻ under 1 atm. pressure of CO₂. The resulting pH–HCO₃⁻ titration plots were interpreted in terms of an ion pairing model, and an equation relating pH and alkalinity was derived. This expression was used to develop a rapid, volume-independent technique to measure alkalinity. The method has an accuracy of ±1% and a precision of ±0.35% (one σ), and lends itself to the analysis of flowing samples and to samples of small volume.

Studies of marine environments require rapid, precise determinations of the titration alkalinity of sea water [1], and such determinations should be amenable to continuous shipboard monitoring. Present methods [2, 3], which require titration of the sample with HCl, are not readily adaptable to continuous flow analysis because sample and acid volumes need to be known accurately. Titration with CO₂, however, is volume-independent, and lends itself readily to the analysis of flowing samples. Although this method is inherently less precise than the HCl titration, it may be useful in the study of estuaries where variable surface alkalinities require collection of numerous data. Additionally, the method may be used for samples of very small volume. This paper describes the CO₂ titration method and discusses the pH–alkalinity titration curve of sea water using a model of the Garrels and Thompson type [4].

THEORY

“Titration alkalinity” can be defined as the number of equivalents of hydrogencarbonate plus the equivalents of bases stronger than hydrogencarbonate in 1 l of sea water at constant temperature [3]. When sea water is equilibrated with CO₂ at 1 atm. pressure the equilibrium



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where B is any base stronger than hydrogencarbonate, is shifted far to the right. The pH of the resulting solution at constant temperature is a function of the hydrogencarbonate concentration. Hence, the "titration alkalinity" can be measured by equilibrating sea water at constant temperature with 1 atm. pressure of CO₂ and measuring the pH.

For a sea-water solution in equilibrium with 1 atm. pressure of CO₂ at 25°C, the hydrogencarbonate range of 0–4.5 meq l⁻¹ corresponds to a pH range of 3.7–5.2. In this pH range, the free ion species which exist in significant amounts are H⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, HCO₃⁻, SO₄²⁻, Cl⁻, and F⁻. To solve for the hydrogencarbonate concentration as a function of pH, the above ions are considered in equilibrium with H₂O, CO₂, HSO₄⁻, HF and the possible ion pairs formed by association of the above ions. The ion pairs present are considered to be NaSO₄⁻, KSO₄⁻, MgSO₄, CaSO₄, NaHCO₃, MgHCO₃⁺, CaHCO₃⁺, MgF⁺, and CaF⁺. This sea-water solution can be represented by a model system composed of a solution of NaCl, NaHCO₃, KCl, KF, MgCl₂, MgSO₄, and CaCl₂. The relationship between pH and titration alkalinity can then be derived on the basis of this model by use of appropriate equilibrium expressions, mass balances, and the electroneutrality condition. These equations are listed in Table 1.

Reaction (1) shows that C_{HCO₃} = A, the titration alkalinity, and in the model system under consideration C_{HCO₃} = C_{NaHCO₃}. Substituting the appropriate mass balance equations into the electroneutrality expression gives

$$A = [\text{HCO}_3^-] + [\text{NaHCO}_3] + [\text{MgHCO}_3^+] + [\text{CaHCO}_3^+] \\ - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}^+] \quad (2)$$

Insertion of the equilibrium expressions into eqn. (2) yields

$$A = \frac{\alpha P_{\text{CO}_2} K'_{\text{CO}_2}}{[\text{H}^+]} \left\{ 1 + \frac{[\text{Na}^+]}{K'_{\text{NaHCO}_3}} + \frac{[\text{Mg}^{2+}]}{K'_{\text{MgHCO}_3^+}} + \frac{[\text{Ca}^{2+}]}{K'_{\text{CaHCO}_3^+}} \right\} \\ - \left\{ \frac{C_{\text{SO}_4}}{1 + \frac{K'_{\text{HSO}_4^-}}{[\text{H}^+]}} \left\{ 1 + \frac{[\text{Na}^+]}{K'_{\text{NaSO}_4^-}} + \frac{[\text{K}^+]}{K'_{\text{KSO}_4^-}} + \frac{[\text{Mg}^{2+}]}{K'_{\text{MgSO}_4}} + \frac{[\text{Ca}^{2+}]}{K'_{\text{CaSO}_4}} \right\} \right\} \\ - \left\{ \frac{C_{\text{F}}}{1 + \frac{K'_{\text{HF}}}{[\text{H}^+]}} \left\{ 1 + \frac{[\text{Mg}^{2+}]}{K'_{\text{MgF}^+}} + \frac{[\text{Ca}^{2+}]}{K'_{\text{CaF}^+}} \right\} \right\} - [\text{H}^+] \quad (3)$$

Equation (3) can then be expressed in terms of the apparent dissociation constant which is defined as $K''_{\text{HL}} = a_{\text{H}}[\text{L}]_{\text{T}}/[\text{HL}]$, where L = HCO₃⁻, SO₄²⁻, or F⁻; a_H = hydrogen ion activity (as measured by the pH electrode, here); and [L]_T is the sum of the free ligand and metal ion pair concentrations [5]. K''_{HL} can also be written as

$$K''_{\text{HL}} = \gamma_{\text{H}} K'_{\text{HL}} \left\{ 1 + \sum_i \frac{[\text{M}_i]}{K'_{\text{M}_i\text{L}}} \right\}$$

TABLE 1

Equilibria, mass balances and electroneutrality conditions
(Square brackets denote molar concentrations.)

Equilibria

$$K'_{\text{CO}_2} = \frac{[\text{H}^+][\text{HCO}_3^-]}{\alpha P_{\text{CO}_2}}$$

where α is the solubility of CO_2 in sea water.

$$K'_{\text{ML}} = \frac{[\text{M}][\text{L}]}{[\text{ML}]}$$

where K'_{ML} is the stoichiometric equilibrium constant for ML with free ions M (H^+ , Na^+ , Mg^{2+} , or Ca^{2+}) and L (HCO_3^- , SO_4^{2-} , or F^-).

Mass balances (Salts: NaCl , NaHCO_3 , KCl , KF , MgCl_2 , MgSO_4 , CaCl_2 . C_i denotes total concentration.)

$$C_{\text{Na}} = C_{\text{NaCl}} + C_{\text{NaHCO}_3} = [\text{Na}^+] + [\text{NaHCO}_3] + [\text{NaSO}_4^-]$$

$$C_{\text{K}} = C_{\text{KCl}} + C_{\text{KF}} = [\text{K}^+] + [\text{KSO}_4^-]$$

$$C_{\text{Mg}} = C_{\text{MgCl}_2} + C_{\text{MgSO}_4} = [\text{Mg}^{2+}] + [\text{MgHCO}_3^+] + [\text{MgSO}_4] + [\text{MgF}^*]$$

$$C_{\text{Ca}} = C_{\text{CaCl}_2} = [\text{Ca}^{2+}] + [\text{CaHCO}_3^+] + [\text{CaSO}_4] + [\text{CaF}^*]$$

$$C_{\text{Cl}} = C_{\text{NaCl}} + C_{\text{KCl}} + 2C_{\text{MgCl}_2} + 2C_{\text{CaCl}_2} = [\text{Cl}^-]$$

$$C_{\text{SO}_4} = C_{\text{MgSO}_4} = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{KSO}_4^-] + [\text{NaSO}_4^-] + [\text{MgSO}_4] + [\text{CaSO}_4]$$

$$C_{\text{F}} = C_{\text{KF}} = [\text{F}^-] + [\text{HF}] + [\text{MgF}^*] + [\text{CaF}^*]$$

Electroneutrality condition

$$[\text{H}^+] + [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{MgHCO}_3^+] + [\text{CaHCO}_3^+] + [\text{MgF}^*] \\ + [\text{CaF}^*] = [\text{Cl}^-] + [\text{F}^-] + 2[\text{SO}_4^{2-}] + [\text{HCO}_3^-] + [\text{HSO}_4^-] + [\text{NaSO}_4^-] + [\text{KSO}_4^-]$$

where γ_{H} is the free hydrogen ion activity coefficient and $M_i = \text{Na}^+$, K^+ , Mg^{2+} and Ca^{2+} . When written in terms of the apparent dissociation constants, eqn. (3) becomes

$$A = \frac{\alpha P_{\text{CO}_2} K''_{\text{CO}_2}}{a_{\text{H}}} - a_{\text{H}} \left\{ \frac{1}{\gamma_{\text{H}}} + \frac{C_{\text{SO}_4}}{a_{\text{H}} + K''_{\text{HSO}_4^-}} + \frac{C_{\text{F}}}{a_{\text{H}} + K''_{\text{HF}}} \right\} \quad (4)$$

This equation describes the pH-alkalinity curve of sea water in the range pH 3-5 and can be simplified as follows. The term in parentheses can be considered as a constant (k); it varies by less than 1% over the pH range

$$3.7-5.2 \text{ because } [2] K''_{\text{HSO}_4^-} \gg a_{\text{H}} \text{ and } \frac{1}{\gamma_{\text{H}}} + \frac{C_{\text{SO}_4}}{a_{\text{H}} + K''_{\text{HSO}_4^-}} \gg \frac{C_{\text{F}}}{a_{\text{H}} + K''_{\text{HF}}}$$

Hence eqn. (4) can be rewritten as

$$A = \frac{\alpha P_{\text{CO}_2} K''_{\text{CO}_2}}{a_{\text{H}}} - k a_{\text{H}} \quad (5)$$

When $k a_H \ll \alpha P_{CO_2} K''_{CO_2} / a_H$, eqn. (5) reduces to $A = \alpha P_{CO_2} K''_{CO_2} / a_H$, or

$$\log A = \text{pH} + \log (\alpha P_{CO_2} K''_{CO_2}) \quad (6)$$

Thus at constant temperature and high alkalinity, a linear relationship exists between \log (alkalinity) and pH. The line has unit slope and an intercept equal to $\log \alpha P_{CO_2} K''_{CO_2}$. Because α and K''_{CO_2} vary with salinity, a family of parallel lines is needed to describe fully the \log (alkalinity)–pH field at all salinities. As \log (alkalinity) approaches infinity, the plot becomes curvilinear. Competition for H^+ by SO_4^{2-} and F^- will shift this portion of the plot toward higher pH values.

EXPERIMENTAL

Equipment and chemicals

A diagram of the apparatus is shown in Fig. 1. A Corning combination electrode (No. 476050) was connected to an Orion 801 digital pH meter. The electrode was calibrated before each determination with Beckman buffers.

A Gilmont microburette, 2.5-ml capacity, was used for all titrations. A stock HCO_3^- solution was made by drying A.R. sodium carbonate [6], dissolving ca. 1.3 g (accurately weighed) in distilled water and diluting to 100 ml. The CO_2 employed was of at least 99.5% purity.

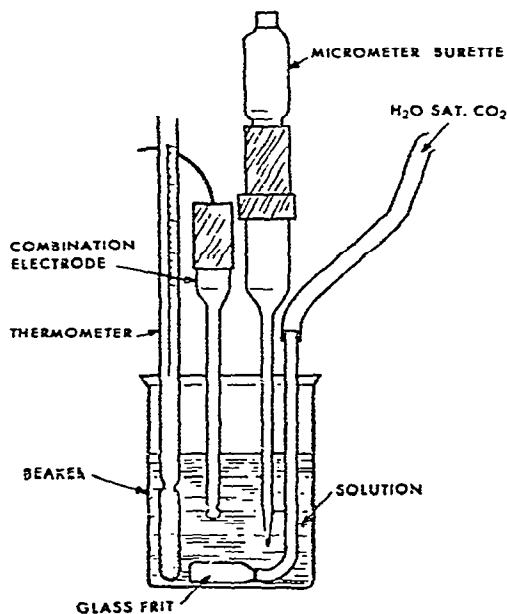


Fig. 1. Diagram of apparatus.

Determination of pH—log (alkalinity) standard curve

Alkalinity-free sea-water was prepared from San Diego Bay water which had been filtered (0.47- μ m Millipore filter), acidified with HCl to pH 2 to remove HCO_3^- , and evaporated to give a stock solution with a salinity of 41.2 ‰. This stock was subsequently diluted with distilled water to give samples of 39.87, 35.84, and 31.88 ‰ salinity. To obtain a titration curve for each salinity, a 50-ml sample was placed in the thermostated cell (25°C) and water-saturated CO_2 was bubbled continuously through it at a rate of ca. 1.2 l min^{-1} . Increments (0.005 ml) of the standardized Na_2CO_3 solution were then added with the microburette. The volume of standard and the potential of the electrode were recorded. The equivalence point (i.e. $A = 0$) was determined from a derivative plot of $\Delta mV/\Delta \text{ml}$ vs. ml of standard carbonate. A was then calculated from $A = (V - V_0)N/50 \text{ ml} + V$, where $V = \text{ml}$ of standard carbonate added, $V_0 = \text{ml}$ of carbonate added to equivalence point, and $N = \text{meq l}^{-1}$ of the standard carbonate. The pH was calculated from $\text{pH} = 4.008 + [(E_{\text{cell}} - E_{4.008})/\Delta mV/\Delta \text{pH}]$ where E_{cell} = potential produced by electrode, $E_{4.008}$ = potential of the 4.008 pH buffer, and $\Delta mV/\Delta \text{pH}$ = experimentally determined electrode response.

RESULTS

Figure 2 presents the obtained log (alkalinity) vs. pH plots with the 35.84 ‰ curve omitted for clarity. An enlargement of the plots for alkalities between 1.7 and 2.7 meq l^{-1} is shown in Fig. 3. The slopes and intercepts of these plots were calculated by linear regression (Table 2). Table 2 also shows the values of $\alpha K''_{\text{CO}_2}$, calculated from the values tabulated in Riley and Skirrow [7]. A quick inspection of the data shows that the values of $\alpha K''_{\text{CO}_2}$, obtained by the proposed method are only approximations of the literature values. The proposed technique fails to yield good absolute values because there is too much experimental error in the slopes to yield good intercepts at pH 0 and because the true value of P_{CO_2} in the solution is unknown. However, in the alkalinity range 1.7–2.7 meq l^{-1} the technique yields a good linear correlation between log (alkalinity) and pH ($r^2 = 0.999$) and is suitable for quantitative analysis. Thus it is possible to bracket a sample with appropriately prepared standards and then analyse a large number of samples by titration with CO_2 (if a salinity correction is to be avoided, standards should be within 0.05 ‰ of the sample). The accuracy of this method was determined by preparing three sets of five standard solutions of known alkalities by the procedure described for the preparation of the titration curves. The solutions were made up at salinities 38.92, 36.71, and 33.51 ‰, and for each salinity, the solutions of lowest and highest alkalinity were considered as "standards". All fifteen solutions were titrated with CO_2 in random order. For each sample, a stable pH was reached within 2 min and then the equilibrium pH values were plotted vs. log (alkalinity). For each salinity, a straight line was drawn between the "standards" and

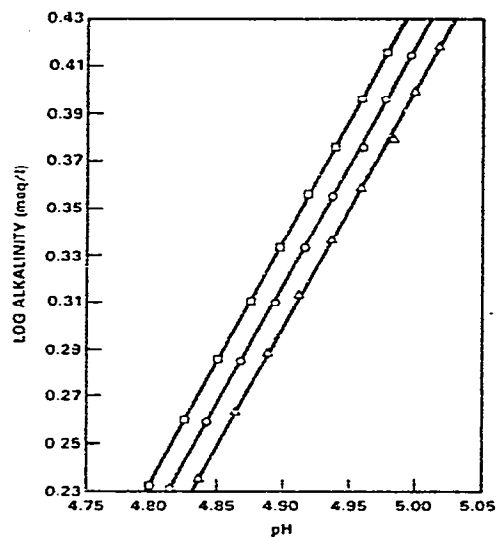
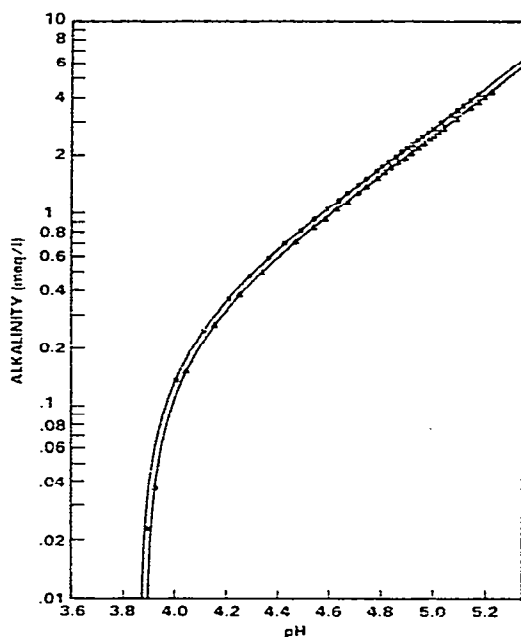


Fig. 2. Experimental log A vs. pH plot for $S = 31.88 \text{ ‰}$ (Δ) and $S = 39.87 \text{ ‰}$ (\square).

Fig. 3. Experimental log A vs. pH plots for alkalinities between 1.7 and 2.7 meq l^{-1} at three salinities. Δ 31.88 ‰, \circ 35.84 ‰, \square 39.87 ‰.

TABLE 2

Values of $\log \alpha K''_{CO_2}$ obtained by titration with CO_2 and from the literature

Salinity (‰)	$\log A - \log \alpha K''_{CO_2}$	$\log \alpha K''_{CO_2}$ at 1 atm. and 25°C	
	pH	Experimental	Ref. 7
31.88	1.003	-4.615	-4.545
35.84	1.018	-4.669	-4.531
39.87	1.019	-4.658	-4.515

the alkalinities of the 3 remaining solutions were computed from the plots. The results are presented in Table 3. Although the average recovery was 99.9%, the error was ± 0.96 (one σ). Similarly, the relative precision of the technique — established by titrating 10 replicate samples of filtered San Diego Bay water — was found to be $\pm 0.36\%$ (one σ).

TABLE 3

Accuracy of the CO₂ titration

Salinity (‰)	Expected	Found	Recovery (%)
38.92	2.404	2.388	99.3
	2.188	2.200	100.5
	1.968	1.949	99.0
35.71	2.404	2.366	98.4
	2.188	2.205	100.8
	1.968	1.959	99.5
33.51	2.404	2.409	100.2
	2.188	2.221	101.5
	1.968	1.969	99.9

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