Alkalinity measurement:
Part 1 - A 4 pH point titration method to determine the carbonate weak acid/base in an aqueous carbonate solution

RE Moosbrugger, MC Wentzel*, GA Ekama and GvR Marais
Department of Civil Engineering, University of Cape Town, Rondebosch 7700, South Africa

Abstract

Theory of a 4 pH point acid titration method is presented to measure the $H_2CO_3^*$ alkalinity and the total carbonate species (C_T) in aqueous solutions containing only the carbonate weak acid/base. The influence of a systematic pH measurement error (due to faulty calibration, residual liquid junction effect, temperature) on the calculation of C_T and $H_2CO_3^*$ alkalinity is examined, and methods presented to minimise the influence of the error. The influence of CO_2 loss during titration on C_T and $H_2CO_3^*$ alkalinity estimates is shown to be negligible provided the titration is completed within 10 min with gentle stirring. Comparative tests using the 4 pH point titration and First Gran Function methods, on aqueous $NaHCO_3$ solutions ranging from 10 to 50 mg/ℓ as $CaCO_3$ gave closely equal results with r = 0,99. For $NaHCO_3$ solutions ranging from 100 to 1 750 mg/ℓ as $CaCO_3$, the 4 pH point titration method has high accuracy, and a standard deviation of < 2 per cent.

Introduction

Reviewing weak acid/bases and pH control in anaerobic systems, Moosbrugger et al. (1993) identified the importance of measuring one parameter relating to the carbonate and one to the short-chain fatty acid (SCFA) weak acid/bases. Parameters identified for measurement were total species concentration (C_T) or $H_2CO_3^*$ alkalinity for the carbonate weak acid/base, and total species concentration for the SCFA weak acid/bases (A_T). An evaluation of techniques available to measure these parameters indicated that:

- For determination of C_T, inorganic carbon analysers are available. However, with this instrument C_T is very likely to be in error due to CO_2 loss on sampling anaerobic digester liquid.
- The $H_2CO_3^*$ alkalinity has the merit that its reference specie is $H_2CO_3^*$ and hence CO_2 loss does not affect its value. For determination of $H_2CO_3^*$ alkalinity in solutions containing only the carbonate weak acid/base or mixtures of weak acid/bases, the Gran and Extended Gran methods respectively (Loewenthal et al., 1989) are available. Both Gran methods are relatively complex and tedious and for the Extended Gran method the required independent accurate determination of A_T is not a simple task. For routine monitoring, the Gran and the Extended Gran methods would not find ready application.
- For determination of A_T distillation/titration, colorimetric and chromatographic methods are available. These methods are time-consuming and involve considerable analytical skill and/or expensive equipment.
- For determination of $C_T/H_2CO_3^*$ alkalinity or A_T, or $C_T/H_2CO_3^*$ alkalinity and A_T, simplified titration methods are available. These methods are either too cumbersome, or provide only approximations of the parameters of interest.

With the increased understanding of mixed weak acid/base chemistry (Loewenthal et al., 1989;1991), a study of the basic theory indicated that, by using an alternative approach, it should be possible to evaluate one or more weak acid/bases by a simple titration procedure. The development of this approach and the titration procedure is detailed in this series of papers, dealing with estimation of: Part 1 (this paper) - $C_T/H_2CO_3^*$ alkalinity in an aqueous solution containing only the carbonate weak acid base; Part 2 - $C_T/H_2CO_3^*$ alkalinity in an aqueous solution also containing other weak acid/bases of known concentration; and Part 3 - $C_T/H_2CO_3^*$ alkalinity and SCFA in an aqueous solution also containing other weak acid/bases of known concentration.

Theory

To completely characterise a weak acid/base in solution, the total species concentration and pH are required (Loewenthal and Marais, 1976). With the carbonate weak acid/base in solution, the practical difficulties in measuring total species concentration (C_T) have led to the development of a substitute parameter, "alkalinity" (Loewenthal and Marais, 1976; Loewenthal et al., 1989). Alkalinity is defined as the proton accepting capacity of the solution relative to a reference state; quantitatively the alkalinity equals the mass of H^+ (or OH^-) that must be added to titrate from the solution pH to the reference state pH (called the equivalence point), where the reference state pH is the pH established on addition of a reference species to pure water. For example, CO_2 reference species (equivalently $H_2CO_3^*$) addition to pure water gives the $H_2CO_3^*$ equivalence point, and titration to this pH gives the $H_2CO_3^*$ alkalinity. However, measurement of alkalinity itself is not a simple task due to the problem of identifying the equivalence point in the titration. Techniques are available to overcome this problem (Gran and Extended Gran titrations, Loewenthal et al., 1989), but as noted earlier, these are complex and tedious.

In general, a proton accepting capacity exists between any two pH points and quantitatively equals the mass of H^+ (or OH^-) ions that must be added to titrate from the one pH to the other. For a particular weak acid/base in solution, theoretically measurement of the proton accepting capacity between any two pH points allows the total species concentration to be determined. This approach has received little attention in the past. The theory for this approach now will be developed to determine C_T in an aqueous solution containing only the carbonate weak acid/base.

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*To whom all correspondence should be addressed.

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Carbonate system equilibrium equations

Following Loewenthal et al. (1989;1991) an aqueous solution containing only the carbonate weak acid/base constitutes the carbonate system. The carbonate system is made up of two subsystems, the carbonate subsystem and the water subsystem. The equilibrium equations defining the carbonate subsystem are:

$$\frac{[HCO_3^-](H^+)}{[H_2CO_3^*]} = K_{ac1}/f_m = K'_{ac1} \qquad (1)$$

$$\frac{[CO_3^{2-}](H^+)}{[HCO_3^-]} = K_{ac2}\, f_m/f_d = K'_{ac2} \qquad (2)$$

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \qquad (3)$$

The equilibrium equation defining the water subsystem is:

$$(H^+)[OH^-] = K_w/f_m = K'_w \qquad (4)$$

where:

(H^+), $[H^+]$ = hydrogen ion activity (measured via pH) and hydrogen ion concentration respectively (mol/ℓ)

K_{ac1},K'_{ac1} = first thermodynamic and apparent dissociation constants respectively for the carbonate subsystem (mol/ℓ) (Loewenthal et al., 1989)

K_{ac2},K'_{ac2} = second thermodynamic and apparent dissociation constants respectively for the carbonate subsystem (mol/ℓ) (Loewenthal et al., 1989)

K_w,K'_w = thermodynamic and apparent ionic product constants respectively for water subsystem $(mol/ℓ)^2$ (Loewenthal et al., 1989)

f_m,f_d = mono- and divalent activity coefficients (determined from μ in the Davies equations, see Loewenthal et al., 1989)

$[H_2CO_3^*]$ = sum of molecularly dissolved carbon dioxide $[CO_2]_{aq}$, and carbonic acid, $[H_2CO_3]$, (mol/ℓ), these two having a virtually fixed ratio with regard to each other thereby allowing expression in terms of the composite $H_2CO_3^*$ (Loewenthal et al., 1986)

[ ], ( ) = molar mass and active mass (activity) respectively (mol/ℓ)

C_T = carbonate total species concentration (mol/ℓ)

Relationship between carbonate system parameters

System and subsystem alkalinities

The carbonate system and subsystem alkalinities for the $H_2CO_3^*$ reference species are related as follows (Loewenthal et al., 1991):

$$H_2CO_3^* \text{ alkalinity} = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+] \qquad (5)$$

$$= \text{Alk } H_2CO_3^* + \text{Alk } H_2O \qquad (6)$$

where:

$H_2CO_3^*$ alkalinity = carbonate system alkalinity with $H_2CO_3^*$ as reference species

Alk $H_2CO_3^*$ = carbonate subsystem alkalinity $= [HCO_3^-] + 2\,[CO_3^{2-}]$ (7)

Alk H_2O = water subsystem alkalinity $= [OH^-] - [H^+]$ (8)

The species $[HCO_3^-]$ and $[CO_3^{2-}]$ and hence Alk $H_2CO_3^*$ can be expressed as functions of C_T and pH, and Alk H_2O as a function of pH, as follows:

HCO_3^- as function of C_T and pH

Rearranging Eq. (3):

$$C_T = [HCO_3^-]\left[\frac{[H_2CO_3]}{[HCO_3^-]} + 1 + \frac{[CO_3^{2-}]}{[HCO_3^-]}\right] \qquad (9)$$

Inserting Eqs. (1) and (2) in Eq. (9), letting

$$A = \left[\frac{(H^+)}{K'_1} + 1 + \frac{K'_2}{(H^+)}\right] \qquad (10)$$

and solving for $[HCO_3^-]$ gives:

$$[HCO_3^-] = \frac{C_T}{A} \qquad (11)$$

CO_3^{2-} as a function of C_T and pH

Rearranging Eq. (3):

$$C_T = [CO_3^{2-}]\left[\frac{[H_2CO_3]}{[HCO_3^-]}\,\frac{[HCO_3^-]}{[CO_3^{2-}]} + \frac{[HCO_3^-]}{[CO_3^{2-}]} + 1\right] \qquad (12)$$

Inserting Eqs. (1 and 2) in Eq (12), letting

$$B = \left[\frac{(H^+)^2}{K'_1K'_2} + \frac{(H^+)}{K'_2} + 1\right] \qquad (13)$$

and solving for $[CO_3^{2-}]$ gives:

$$[CO_3^{2-}] = \frac{C_T}{B} \qquad (14)$$

Alk $H_2CO_3^*$ as a function of C_T and pH

Substituting Eqs. (11) and (14) into Eq. (7) gives the carbonate subsystem alkalinity (Alk $H_2CO_3^*$) at any pH as a function of C_T and pH:

$$\text{Alk } H_2CO_3^* = \frac{C_T}{A} + 2\,\frac{C_T}{B} \qquad (15)$$

Alk H_2O as a function of pH

From Eq. (8), the alkalinity contribution of the water subsystem (Alk H_2O) is:

$$\text{Alk } H_2O = [OH^-] - [H^+] \qquad (16)$$

From Loewenthal et al. (1991)

$$[H^+] = 10^{-pH}/f_m \qquad (17)$$

$$[OH^-] = \frac{K'_w}{(H^+)} = 10^{pH-pK'_w} \qquad (18)$$

where:

$pH = -\log (H^+)$

$pK'_w = -\log K_w$

From Eqs. (17) and (18), inserting for $[H^+]$ and $[OH^-]$ in Eq. (16):

$$\text{Alk } H_2O = 10^{pH-pK'_w} - \frac{10^{-pH}}{f_m} \qquad (19)$$

$H_2CO_3^*$ alkalinity in terms of C_T and pH

Inserting in Eq. (6) for Alk $H_2CO_3^*$ and Alk H_2O from Eqs. (15) and (19) respectively:

$$H_2CO_3^* \text{ alkalinity} = \frac{C_T}{A} + 2\frac{C_T}{B} + 10^{pH-pK'_w} - \frac{10^{-pH}}{f_m} \qquad (20)$$

Determination of C_T in a sample by titration between two pH points

Equation (20) expresses the proton accepting capacity of the solution between the sample pH and the $H_2CO_3^*$ reference state pH (i.e. $H_2CO_3^*$ alkalinity) in terms of C_T and pH. The problem is in the measurement of either C_T or $H_2CO_3^*$ alkalinity. It will now be shown that, provided there is no CO_2 loss from a sample during titration, C_T can be determined from the titration data between any two pH points. Then, knowing the initial pH of the sample, the state of the carbonate system (i.e. carbonate + water subsystems) is completely defined in the sample being titrated.

Assume the sample is acid titrated between two pH points. Since $H_2CO_3^*$ alkalinity is defined as a proton accepting capacity, the addition of H^+ will cause a decrease in $H_2CO_3^*$ alkalinity. The mass of H^+ required to titrate from the first pH point (pH_1) to the second pH point (pH_2) equals the decrease in the mass of $H_2CO_3^*$ alkalinity, or alternatively, the sum of the decreases in the masses of Alk $H_2CO_3^*$ and Alk H_2O. From this decrease in mass of $H_2CO_3^*$ alkalinity and the two pH points, C_T can be calculated as follows:

The $H_2CO_3^*$ alkalinities before and after the titration are $H_2CO_3^*$ alk_1 and $H_2CO_3^* alk_2$ respectively. The magnitude of the decrease in $H_2CO_3^*$ alkalinity ($\Delta H_2CO_3^*$ $alk_{1,2}$) due to addition of the specific amount of H^+ is therefore:

$$\Delta H_2CO_3^* \text{ alk}_{1,2} = H_2CO_3^* \text{alk}_1 - H_2CO_3^* \text{alk}_2 \qquad (21)$$

$$= \Delta \text{Alk}_{1,2} H_2CO_3^* + \Delta \text{ Alk}_{1,2} H_2O \qquad (22)$$

where:

$$\Delta \text{Alk}_{1,2} H_2CO_3^* = \text{Alk}_1 H_2CO_3^* - \text{Alk}_2 H_2CO_3^* \qquad (23)$$

$$\Delta \text{Alk}_{1,2} H_2O = \text{Alk}_1 H_2O - \text{Alk}_2 H_2O \qquad (24)$$

If Ca is the normality of the strong acid and $V_{x1,2}$ the volume of strong acid added, the molar mass of H^+ added to the sample is:

$$\text{Molar mass of } H^+ \text{ added} = \text{Ca } V_{x1,2} \qquad (25)$$

The molar mass of H added in titrating from pH_1 to pH_2 equals the mass decrease in $H_2CO_3^*$ alkalinity (Δ $MH_2CO_3^* alk_{1,2}$):

$$\text{Ca } V_{x1,2} = \Delta\, MH_2CO_3^* \text{alk}_{1,2} \qquad (26)$$

$$= \Delta \text{ MAlk}_{1,2} H_2CO_3^* + \Delta \text{MAlk}_{1,2} H_2O \qquad (27)$$

Now the two terms in the right hand side of Eq. (27) need to be determined:

$\Delta MAlk_{1,2} H_2CO_3^*$

The mass decrease (mol) in $H_2CO_3^*$ alkalinity on acid titration due to the carbonate subsystem can be written as:

$$\Delta \text{MAlk}_{1,2} H_2CO_3^* = \text{MAlk}_1 H_2CO_3^* - \text{MAlk}_2 H_2CO_3^* \qquad (28a)$$

$$= V_{s1} \text{ Alk}_1 H_2CO_3^* - (V_{s1}+V_{x1,2}) \text{ Alk}_2 H_2CO_3^* \qquad (28b)$$

where:

V_{s1} = the sample size at pH_1 (ℓ)

$V_{x1,2}$ = the volume of strong acid added to the sample from pH_1 to pH_2 (ℓ)

From Eq. (15), $Alk_1 H_2CO_3^*$ and $Alk_2 H_2CO_3^*$ can be expressed in terms of C_{T1} and pH_1, and C_{T2} and pH_2 respectively; inserting in Eq. (28b):

$$\Delta \text{MAlk}_{1,2} H_2CO_3^* = V_{s1}\, C_{T1} \left(\frac{1}{A_1} + 2\frac{1}{B_1}\right) - (V_{s1} + V_{x1,2})\, C_{T2} \left(\frac{1}{A_2} + 2\frac{1}{B_2}\right) \qquad (28c)$$

In the titration, provided adequate precautions are taken to minimise CO_2 loss, the mass of C_T (MC_T) in the sample remains constant and equals the masses of C_T at pH_1 (V_s C_{T1}) and pH_2 [$(V_{s1} + V_{x1,2})$ C_{T2}] i.e.

$$MC_T = (V_{s1} + V_{x1,2})\, C_{T2} = V_{s1}\, C_{T1}$$

Rearranging Eq. (28c), and substituting:

$$\Delta \text{MAlk}_{1,2} H_2CO_3^* = MC_T \left[\left(\frac{1}{A_1} + 2\frac{1}{B_1}\right) - \left(\frac{1}{A_2} + 2\frac{1}{B_2}\right)\right] \qquad (29)$$

where subscripts 1 and 2 refer to the condition at the first and second pH respectively.

Letting

$$X_{1,2} = \left(\frac{1}{A_1} + 2\frac{1}{B_1} - \frac{1}{A_2} - 2\frac{1}{B_2}\right) \qquad (30)$$

then Eq. (29) becomes

$$\Delta \text{MAlk}_{1,2} H_2CO_3^* = MC_T\, X_{1,2} \qquad (31)$$

Note that MC_T is the total carbonate species mass in the sample provided adequate precautions are taken to minimise CO_2 loss during titration.

$\Delta MAlk\ H_2O$

The mass decrease of $H_2CO_3^*$ alkalinity due to the water subsystem is:

$$\Delta MAlk_{1,2}H_2O \;=\; V_{s1}\,Alk_1H_2O - (V_{s1} + V_{x1,2})\,Alk_2H_2O \qquad (32)$$

From Eq. (19):

$$\begin{aligned}\Delta MAlk_{1,2}H_2O \;=\; & V_{s1}\,(10^{pH_1 - pK'_w} - 10^{-pH_1}/f_m) \\ & -(V_{s1}+V_{x1,2})\,(10^{pH_2 - pK'_w} - 10^{-pH_2}/f_m)\end{aligned} \qquad (33)$$

In Eq. (27), substitute for $\Delta MAlk_{1,2}H_2CO_3^*$ from Eq. (31) and solve for MC_T (mass of C_T in the sample):

$$MC_T = (Ca\,V_{x1,2} - MAlk_{1,2}H_2O)/\,(X_{1,2}) \qquad (34a)$$

From MC_T, the carbonate total species concentration in the initial sample can be calculated:

$$C_T = MC_T/V_s \qquad (34b)$$

where:

C_T = sample carbonate total species concentration prior to titration (mol/ℓ); very likely this C_T will not equal the *in situ* C_T due to loss/gain of CO_2 in sampling (see later)

V_s = sample volume prior to titration (ℓ)

Equations (34a) and (34b) are the fundamental ones to calculate the sample C_T from the titration results between any two pH points. The calculation algorithm is as follows:

> Calculate $\Delta MAlk_{1,2}H_2O$ and $X_{1,2}$ from Eqs. (33) and (30) respectively utilising pH_1, pH_2, V_{s1} and $V_{x1,2}$. Insert in Eq. (34a) the term $(Ca\,V_{x1,2})$ which is obtained from the titration and is the measured molar mass of H^+ required to change the pH from pH_1 to pH_2, and calculate MC_T in the sample. From MC_T and V_s using Eq. (34b) calculate C_T. Knowing C_T and the initial pH of the sample (pH_O), the carbonate subsystem in the sample is completely defined. Since the carbonate subsystem in the sample is completely defined, the $H_2CO_3^*$ alkalinity for the sample can be calculated from C_T and pH_O, via Eq. (20).

Very likely the sample C_T will not be equal to the C_T in the *in situ* solution from which the sample was taken (e.g. underground water supply) due to loss/gain of CO_2 in sampling. The parameter $H_2CO_3^*$ alkalinity has the advantage in that it is not influenced by loss/gain of CO_2 (Loewenthal et al., 1986); accordingly, taking due account of any dilution, the sample $H_2CO_3^*$ alkalinity equals the *in situ* $H_2CO_3^*$ alkalinity (from where the sample was obtained). This provides the means to calculate the *in situ* C_T from $H_2CO_3^*$ alkalinity and the *in situ* pH, by rearranging Eq. (20).

Errors in sample C_T determination

Two potential sources of errors are of importance when carrying out a titration between two pH points:

- A systematic pH measurement error from poor calibration of the pH probe, residual liquid junction potential (caused by the difference in ionic strength and ionic constitution between the calibration solution and that of the sample when using a glass electrode), and other effects, Linder et al. (1984).
- Exchange of CO_2 during titration between the liquid and gas at the interface of the sample surface: Such exchange of CO_2 would cause a change in MC_T as the titration proceeds. From Eq. (29), calculation of MC_T is based on the assumption that MC_T in the sample remains constant at the two pH points. Consequently, the titration has to be carried out in a way that minimises exchange of CO_2.

Effect of systematic pH errors on the C_T determination

From Eq. (34a), a systematic error in pH will cause an error in calculation of the terms $\Delta MAlk_{1,2}H_2O$ and $X_{1,2}$. Between pH 7 and pH 4 the error induced in $\Delta MAlk_{1,2}H_2O$ is negligible because the buffer index of the water subsystem remains very small in this pH range (Moosbrugger et al., 1993). With regard to the error in $X_{1,2}$, this induces an error in $\Delta MAlk_{1,2}H_2CO_3^*$ (Eq. 31) and gives rise to an error in calculation of MC_T (Eq. 34a). Accordingly, the effect of a systematic pH error on the calculation of $\Delta MAlk_{1,2}H_2CO_3^*$ requires further investigation:

From Eqs. (29) and (28a):

$$\Delta MAlk_{1,2}H_2CO_3^* = MC_T\left[\left(\frac{1}{A_1} + 2\,\frac{1}{B_1}\right) - \left(\frac{1}{A_2} + 2\,\frac{1}{B_2}\right)\right]$$

$$= \Delta MAlk_1H_2CO_3^* - \Delta MAlk_2H_2CO_3^* \qquad (35)$$

An error in $\Delta MAlk_{1,2}H_2CO_3^*$ arises from an error in either $MAlk_1H_2CO_3^*$ or $MAlk_2H_2CO_3^*$, or both of these terms. Hence, it is necessary to investigate the effect of a systematic pH error on the calculation of $MAlk\,H_2CO_3^*$ at any pH in the pH titration range. At any pH point $MAlk\,H_2CO_3^*$ can be written as:

$$MAlk\,H_2CO_3^* = MC_T\left[\frac{1}{A} + 2\,\frac{1}{B}\right] \qquad (36)$$

A deviation of the observed pH from its true value can be written as:

$$\Delta pH \;=\; pH_{true} - pH_{obs} \qquad (37)$$

$$\text{i.e. } pH_{true} \;=\; pH_{obs} + \Delta pH \qquad (38)$$

Hence, $MAlk\,H_2CO_3^*$ can be expressed in terms of Eq. (36) for two cases:

- at pH_{obs} giving $MAlk\,H_2CO_3^*\,(pH_{obs})$
- at pH_{true} giving $MAlk\,H_2CO_3^*\,(pH_{true})$

Subtracting these two alkalinities:

$$\begin{aligned}\Delta MAlk\,H_2CO_3^*\,(\Delta pH) = & \;MAlk\,H_2CO_3^*\,(pH_{obs}) \\ & - MAlk\,H_2CO_3^*\,(pH_{true})\end{aligned} \qquad (39)$$

where:

$MAlk\,H_2CO_3^*\,(\Delta pH)$ = error introduced in $MAlk\,H_2CO_3^*$ by an error in pH measurement, ΔpH

For the purpose of demonstrating the effect of ΔpH on $MAlk\,H_2CO_3^*$, in Fig. 1 $\Delta MAlk\,H_2CO_3^*\,(\Delta pH)$ is shown plotted versus

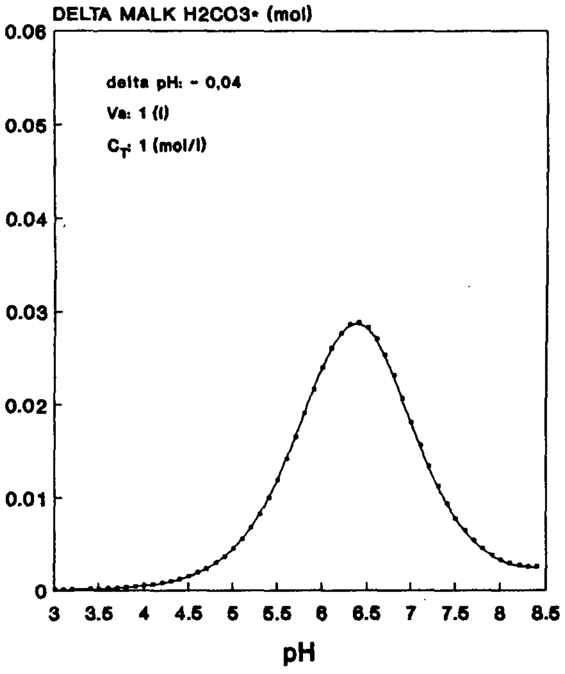

Figure 1
Theoretical error in MAlk H_2CO_3 (mass of Alk H_2CO_3* of sample) at any pH over the pH range 3,0 to 8,5 due to a systematic pH measurement error (ΔpH), ΔMAlk H_2CO_3* (ΔpH), calculated for a specific $\Delta pH = -0{,}04$ with C_T and V_s equal to unity*

pH assuming MC_T (i.e. C_T and V_s) equal to unity and $\Delta pH = -0{,}04$ at temperature = 20° C, $\mu = 0{,}01$ to give $pK'_{ac1} = 6{,}34$ (Loewenthal et al., 1989). The plot illustrates the following points:

- The magnitude of ΔMAlk $H_2CO_3^*$ (ΔpH) is dependent on ΔpH, and on pH
- The bell shaped curve has a maximum at pH = $pK'_{ac1} = 6{,}34$
- ΔMAlk $H_2CO_3^*$ (ΔpH) decreases sharply on either side of pK'_{ac1}
- If $\Delta pH = 0$, then ΔMAlk $H_2CO_3^*$ (ΔpH) = 0, and MAlk $H_2CO_3^*$ is at its true value
- The shape and pH location of the ΔMAlk $H_2CO_3^*$ (ΔpH) curve is the same as for the buffer index curve (Moosbrugger et al., 1993).

When titrating a sample between pH_1 and pH_2, if the measured pH differs from the true pH, the error, ΔpH, at these two pH points respectively are not known. Hence, only $MAlk_1H_2CO_3^*$ (pH_{1obs}) and $MAlk_2H_2CO_3^*$ (pH_{2obs}) can be calculated. Assuming that the ΔpH is the same at pH_1 and pH_2 (i.e. a systematic pH error is present), both the MAlk $H_2CO_3^*$ (pH_{obs}) terms deviate from their respective true values as follows:

$$MAlk_1H_2CO_3^*\,(pH_{1true}) = MAlk_1H_2CO_3^*\,(pH_{1obs}) - \Delta MAlk_1H_2CO_3^*\,(\Delta pH) \qquad (40)$$

$$MAlk_2H_2CO_3^*\,(pH_{2true}) = MAlk_2H_2CO_3^*\,(pH_{2obs}) - \Delta MAlk_2H_2CO_3^*\,(\Delta pH) \qquad (41)$$

In Eqs. (40) and (41) neither $\Delta MAlk_1H_2CO_3^*$ (ΔpH) nor $\Delta MAlk_2H_2CO_3^*$ (ΔpH) can be calculated. Hence, the titration points have to be chosen such that the effect of ΔpH on the calculation of $\Delta MAlk_{1,2}H_2CO_3^*$ is minimised. From Eq. (35) it can be seen that $MAlk_2H_2CO_3^*$ is subtracted from $MAlk_1H_2CO_3^*$ to calculate $MAlk_{1,2}H_2CO_3^*$ from which MC_T is finally obtained. Subtracting Eq. (40) and (41):

$$\begin{aligned}\Delta MAlk_{1,2}H_2CO_3^* &= MAlk_1H_2CO_3^*\,(pH_{1true}) \\ &\quad - \Delta MAlk_2H_2CO_3^*\,(pH_{2true}) \\ &= \Delta MAlk_1H_2CO_3^*\,(pH_{1obs}) \\ &\quad - \Delta MAlk_2H_2CO_3^*\,(pH_{2obs}) \\ &\quad - \Delta MAlk_1H_2CO_3^*\,(\Delta pH) \\ &\quad + \Delta MAlk_2H_2CO_3^*\,(\Delta pH) \end{aligned} \qquad (42)$$

From Fig. 1, if pH_1 and pH_2 are chosen symmetrical around pK'_{ac1} their respective ΔMAlk $H_2CO_3^*$ (ΔpH) values are equal, and, if inserted in Eq. (42), cancel out to give the correct $\Delta MAlk_{1,2}H_2CO_3^*$, and, consequently, also the correct MC_T. However, the value of pK'_{ac1} changes with temperature and ionic strength (Loewenthal et al., 1989). To obtain a correct MC_T, theoretically it would be necessary first to determine the appropriate pK'_{ac1} for the temperature and ionic strength of the solution, and then select pH_1 and pH_2 symmetrical around the pK'_{ac1} value. From a practical point of view, such a procedure would not be viable. A solution to this problem is presented below.

Estimate of systematic pH error

Despite the fact that with a strictly symmetrical pH pair the estimate of MC_T and C_T may be error free, the estimate of $H_2CO_3^*$ alkalinity which is derived via Eq. (20) from the initial sample pH (pH_O) and C_T will not be error free, because pH_O will contain the systematic pH error, ΔpH. It is necessary therefore to form an estimate of ΔpH; then the initial pH can be corrected for ΔpH and $H_2CO_3^*$ alkalinity calculated more accurately.

For a solution with temperature = 20°C and $\mu = 0{,}01$ (i.e. $pK'_{ac1} = 6{,}34$, Loewenthal et al., 1989), consider a titration from any pH point, say $pH_1 = 7{,}9$, to $pH_2 = 6{,}0$ to $pH_3 = 4{,}8$. To determine ΔpH, its effect on the calculation of $\Delta MAlk_{1,2}H_2CO_3^*$ from Eq. (42) is examined using the symmetrical pH pair (7,9;4,8) and the unsymmetrical pH pair (7,9;6,0) assuming MC_T unity.

Symmetrical pH pair (7,9;4,8): Since ΔpH is unknown the terms $\Delta MAlk_1H_2CO_3^*$ (ΔpH) and $\Delta MAlk_2H_2CO_3^*$ (ΔpH) in Eq. (42) cannot be calculated. However, from Fig. 1 note that for this particular pH pair these two terms cancel out; from this it follows that $\Delta MAlk_{1,2}H_2CO_3^{*}$* for pH pair (7,9;4,8) theoretically is error free. From Eq. (31) for MC_T equal to unity, $\Delta MAlk_{1,2}H_2CO_3^*$ is equal to $X_{1,2}$. Hence for titration between pH pair (7,9;4,8), $X_{1,2}$ can be obtained error free (despite the fact that ΔpH is unknown) and, hence, an error free MC_T and C_T can be calculated via Eq. (34).

Unsymmetrical pH pair (7,9;6,0): C_T can be obtained analogously to pH pair (7,9;4,8). In this case, however, the terms $\Delta MAlk_1H_2CO_3^*$ (ΔpH) and $\Delta MAlk_2H_2CO_3^*$ (ΔpH) do not cancel out in Eq. (42); this leads to an incorrect estimate of $X_{1,2}$ and, consequently, the MC_T and C_T calculated via this pH pair will contain an error due to ΔpH.

From the above: (1) To eliminate the error in the calculation of MC_T the pH pair must be selected such that the terms $\Delta MAlk_1H_2CO_3^*$ (ΔpH) and $\Delta MAlk_2H_2CO_3^*$ (ΔpH) are equal and cancel out in Eq. (45); this was done by selecting a pH pair symmetrical around pK'_{acl} (pH_1;pH_2). (2) If an estimate of ΔpH is required, we make use of the fact that ΔpH causes different MC_T values ($MC_{T1,2}$; $MC_{T1,3}$) for the symmetrical pH pair (pH_1;pH_2 = 7,9;4,8 say) and the unsymmetrical pH pair (pH_1;pH_3 = 7,9;6,0 say) respectively. $MC_{T1,2}$ represents the true MC_T value (to the first order of magnitude) because the effect of ΔpH cancels out. By adjusting the pH measurements and recalculating the MC_T values until $MC_{T1,3}$ equals $MC_{T1,2}$, the difference between the observed pH and the adjusted (true) pH equals ΔpH.

In the method above the pH pair (pH_1;pH_2) was strictly symmetrical about pK'_{acl}. However, as noted earlier, pK'_{acl} changes with temperature and ionic strength (Loewenthal et al., 1989) so that it would be necessary to determine pK'_{acl} and select the symmetrical pH pair each time a determination is made. This would seriously inhibit application of the method, for example, the titration may need to be done before the ionic strength (or TDS, see Loewenthal et al., 1989) data for calculating pK'_{acl} are available. However, if an approximately symmetrical pH pair and a strongly unsymmetrical pH pair are selected in the titration, then with the ΔpH adjustment procedure described above applied to all the pH points, both $MC_{T1,2}$ and $MC_{T1,3}$ are adjusted until $MC_{T1,2} = MC_{T1,3} \rightarrow MC_{T(true)}$. Consequently, ($pH_1$;$pH_2$) can be selected *a priori* symmetrical to some approximate pK'_{acl} value. The pK'_{acl} values for 20°C could range from 6,3 to 6,4, or wider and (pH_1;pH_2) can be selected symmetrical around any pK'_{acl} value in this range, say 6,3.

Titration procedure

From the above, the following procedure is used to estimate ΔpH, C_T and $H_2CO_3^*$ alkalinity:

- Titrate the sample from its initial pH (pH_O) to three appropriately selected pH points pH_1, pH_2 and pH_3, such that pH pair (pH_1, pH_2) is approximately symmetrically located, and pH pair (pH_1, pH_3) is unsymmetrically located around pK'_{acl}. Via Eq. (34a) calculate $MC_{T1,2}$ and $MC_{T1,3}$ respectively for these two data pairs. (Optimal selection of pH points will be considered later).
- Compare $MC_{T1,2}$ and $MC_{T1,3}$; if different, pH_1, pH_2, pH_3 are all adjusted by ΔpH and the MC_T values again recalculated from Eq. (34). This is repeated by progressively changing ΔpH until $MC_{T1,3}$ equals $MC_{T1,2}$. When $MC_{T1,3}$ equals $MC_{T1,2}$, the adjusted pH values should closely equal their respective true pH values. The difference between the true and observed pH gives ΔpH, Eq. (37).
- From $MC_{T1,2}$ and the initial sample volume (V_s) calculate C_T using Eq. (34b).
- With pH_O corrected for ΔpH, calculate the sample $H_2CO_3^*$ alkalinity from C_T (Eq. 20); taking due account of any dilution, the sample $H_2CO_3^*$ alkalinity equals the *in situ* $H_2CO_3^*$ alkalinity.
- From the *in situ* $H_2CO_3^*$ alkalinity and the *in situ* pH corrected for ΔpH, calculate the *in situ* C_T if required, Eq. (20).

This calculation procedure can be readily incorporated in a computer program with the measured pHs and titration data as input (Source code listing (Turbo Pascal) and executable file of a program are available from the Water Research Commission, PO Box 824, Pretoria, 0001, South Africa).

Error due to CO_2 loss during titration

The algorithm for calculating C_T and the $H_2CO_3^*$ alkalinity, set out above, assumes that the mass of C_T in the sample (MC_T) remains constant during titration, implying that there is no exchange of CO_2 between the sample being titrated and the atmosphere. Such CO_2 exchange depends primarily on the difference in partial pressure of CO_2 in the water and the air and on mixing conditions. Loss of CO_2 from the sample decreases MC_T and from the basic theory of the carbonate system this gives rise to an increase in pH (Loewenthal and Marais, 1976), and *vice versa* for a gain in CO_2. Through Eq. (34), MC_T is linked to pH_1 and pH_2. If CO_2 is lost while titrating with a strong acid from pH_1 to pH_2, this will cause that pH_2 is attained with more titrant than if there was no CO_2 loss and will result in an error in calculation of MC_T (the calculated MC_T will show a higher value than the true value of the sample). There is no theoretical basis whereby this error can be minimised, only by following an appropriate experimental procedure.

Experimental investigation

The objectives of the experimental investigation were to:

- Verify experimentally the existence of a systematic pH measurement error
- Quantify ΔpH
- Investigate possible causes for ΔpH
- Investigate the effect of CO_2 loss during titration
- Select pH pairs for 4 pH point titration
- Evaluate the accuracy and precision of the 4 pH point titration method.

All experiments were done at 20°C and all titrations were on undiluted samples.

Existence of systematic pH error

To enquire experimentally into the existence of a systematic pH error a set of aqueous solutions with increasing concentrations of $NaHCO_3$ (250, 500, 750 and 1 000 mg/ℓ as $CaCO_3$) were made up. Each concentration was titrated from the initial pH (approximately 8,3) to lower pH values, i.e. from 8,3 to 6,0; 5,8; 5,6; 5,4; 5,2; 5,0 and 4,8. Each test was repeated five times. The pH probe (GK 2401C combined glass electrode, Radiometer, Copenhagen) was calibrated against Radiometer NBS buffers (0,05 M potassium hydrogen phthalate for pH 4,00 at 25°C; 0,0275 M disodium hydrogen phosphate and 0,025 M potassium dihydrogen phosphate for pH 7,00 at 25°C).

For each titration 7 pH pairs were formed, i.e. (8,3; 6,0), (8,3; 5,8), (8,3; 5,6) etc. From each pH pair C_T and $H_2CO_3^*$ alkalinity values were determined, using Eqs. (34) and (20) respectively. When plotted against pH, the data for the different $NaHCO_3$ solutions all exhibited similar trends. Furthermore, the C_T and $H_2CO_3^*$ alkalinity plots for each $NaHCO_3$ concentration were virtually identical. Hence, for the purpose of illustration only the results for C_T of the $NaHCO_3$ solution of 1 000 mg/ℓ as $CaCO_3$, μ = 0,02, are shown in Fig. 2. As the second (lower) pH of the titration decreases from 6,0 to 4,8 so the value of C_T decreases to approach the known (expected) value. Theoretically each of the pH pairs should have given the same C_T equal to the expected C_T. The deviation of the measured C_T from the expected value and the variation in measured C_T for different pH pairs was

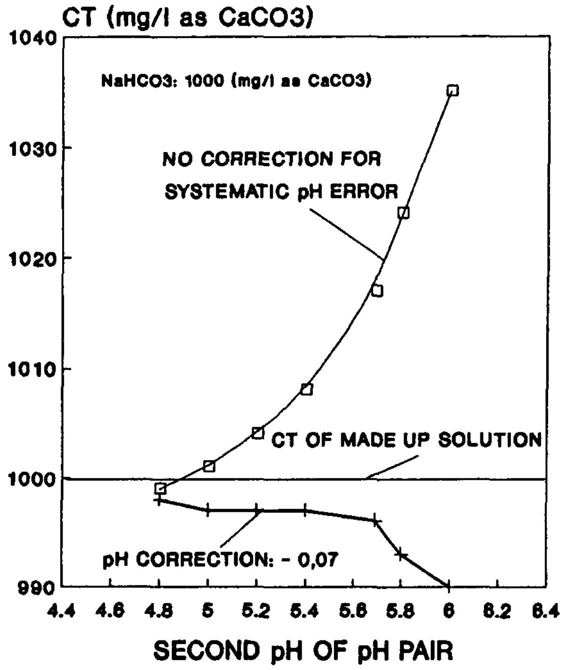

Figure 2

Error in determining C_T in aqueous solutions containing only the carbonate subsystem (made up $NaHCO_3$ solutions) using pH pairs (8,3; 6,0...4,8) for (1) without correcting for systematic pH measurement error, ΔpH, and, (2) correcting for an estimated systematic pH measurement error of ΔpH = -0,07. The first pH of all pH pairs, pH = 8,3

postulated to be due to a systematic error in the observed pH.

On the basis that the errors in C_T had arisen from a systematic pH error, a pH correction factor, ΔpH, was applied to each pH of the pH titration set: Starting with ΔpH = - 0,01, a new set of values for C_T and $H_2CO_3^*$ alkalinity was calculated; ΔpH was increased incrementally until all the C_T and $H_2CO_3^*$ alkalinity values were approximately equal. For the pH pairs in Fig. 2, with ΔpH = - 0,07, the C_T values remained approximately constant and close to the expected C_T value. It was concluded that the error in C_T for each pH pair was due to some consistent error in the pH observation.

Quantification of pH error

In a previous section a theory was developed to quantify ΔpH from two pH pairs, one approximately symmetrical and one unsymmetrical around pK'_{acl}. In the titrations described in the section above the only approximately symmetrical pH pair is (8,3; 4,8) but a number of unsymmetrical pH pairs of (8,3; 6,0), (8,3; 5,8) (8,3; 5,6) etc. can be formed. From the symmetrical pH pair and for each of the unsymmetrical pH pairs, a ΔpH was derived, as set out in the theory described earlier. The results are given in Table 1.

Clearly using the approximate symmetrical/unsymmetrical pH pair approach, ΔpH can be quantified and, correcting the measured pH values, all the sets of pH pairs give close estimates of the known added true C_T and $H_2CO_3^*$ alkalinity.

The presence of the systematic pH error raises the question as to its cause. Great care had been taken in the calibration of the pH probe using NBS buffer solutions and in frequently renewing the buffer solution. Consequently, a pH measurement error from faulty calibration was unlikely. This left the possibility that the systematic pH error was caused by the residual liquid junction potential (RLJP). This possibility was investigated.

pH error and residual liquid junction potential (RLJP)

If the error in pH was due to a RLJP then, since the RLJP arises from a difference in ionic concentration and composition between two solutions, such a difference must have been present between the pH standard buffer solution and the sample. To investigate the RLJP effect, a stock solution of $NaHCO_3$ in distilled water was made to give $C_T = H_2CO_3^*$ alkalinity = 1 000 mg/ℓ (as $CaCO_3$). Five solutions of different ionic strength were made up by adding the following masses of NaCl: 0,0; 3,5; 7,0; 10,5 and 14 g NaCl/ℓ, to different samples of the stock solution to give respective ionic strengths (μ) of the samples of 0,02, 0,09, 0,14, 0,20 and 0,26. Each sample was titrated from pH $\simeq$ 8,3 to pH $\simeq$ 5,4 and thereafter to pH $\simeq$ 4,8 and the approximately symmetrical pH pair (8,3; 4,8) and the unsymmetrical pH pair (8,3;5,4) were used to determine ΔpH, C_T and $H_2CO_3^*$ alkalinity. For each of the five solutions average ΔpH, and corrected C_T and $H_2CO_3^*$ alkalinity values were determined from three replicated tests; these are plotted in Fig. 3. The ΔpH adjusted C_T and $H_2CO_3^*$ alkalinity values do not change significantly with changing ionic

TABLE 1

C_T, $H_2CO_3^*$ ALKALINITY AND ΔpH FOR APPROXIMATE SYMMETRICAL AND UNSYMMETRICAL pH PAIRS AROUND pK'_{acl} FOR $NaHCO_3$ SOLUTION ($CT = H_2CO_3^*$ ALKALINITY = 1 000 mg/ℓ as $CaCO_3$)

Sym. pH pair	Unsym. pH pair	$H_2CO_3^*$ alk (mg/ℓ as $CaCO_3$)	C_T (mg/ℓ as $CaCO_3$)	ΔpH
8,38;4,82	8,38;5,98	1 000	994	- 0,06
	;5,78	1 003	997	- 0,06
	;5,59	1 004	998	- 0,06
	;5,38	1 004	998	- 0,07
	;5,20	1 004	998	- 0,07
	;5,01	1 003	998	- 0,08

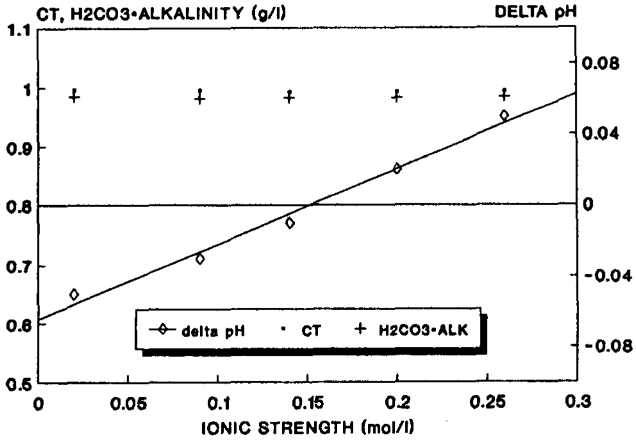

Figure 3

Estimation of systematic pH measurement error, ΔpH, C_T and H_2CO_3 alkalinity at different levels of ionic strengths in aqueous $NaHCO_3$ solutions (1 000 mg/ℓ as $CaCO_3$) also containing additions of 0, 3,5; 7,0; 10,5 and 14 g/ℓ of NaCl to give respective ionic strengths of the solutions of 0,02, 0,09, 0,14, 0,20 and 0,26; ΔpH was estimated using an approximately symmetrical and an unsymmetrical pH pair located around pK'_{acl} of the carbonate subsystem*

strength and deviate from their input values by less than two per cent. However, clearly ΔpH is influenced by the change in ionic strength of the sample due to addition of NaCl.

The activity coefficients (f_m,f_d) required to obtain the pK'_{acl} values at the different ionic strengths were calculated using the Davies equation in which the value of ionic strength (μ) was determined from $\mu = 0,5 \sum C_i Z_i^2$ (see Loewenthal et al., 1989). The Davies equation is valid for low salinity waters with TDS < 2 500 mg/ℓ (Loewenthal et al., 1989). However, the solutions tested in this experiment exceeded this TDS limit, up to ± 15 000 mg/ℓ; this raised the possibility that the effect of ionic strength on ΔpH was due to misapplication of the Davies equation. Accordingly, ΔpH, C_T and $H_2CO_3^*$ alkalinity were recalculated using a more elaborate method to determine μ and the activity coefficients for medium salinity waters, i.e. taking into account ion pairing effects (Loewenthal and Marais, 1983). The resulting values of ΔpH, C_T and $H_2CO_3^*$ alkalinity were very close to those obtained using the activity coefficients derived for low salinity waters. It was concluded that there is little merit in including ion pairing effects in the calculation of the activity coefficients for medium salinity waters, that is, C_T and $H_2CO_3^*$ alkalinity can be derived accurately over a wide range of ionic strength values even when using the low salinity water approach to determine the activity coefficients for medium salinity waters. Clearly, the effect of μ on ΔpH was not due to the exclusion of ion pairing effects in calculating activity coefficients. That ΔpH changes monotonically with μ would implicate a RLJP. However, from this experiment it cannot be established if the estimated ΔpH is exclusively caused by the RLJP; other undefined factors may also have contributed to ΔpH. Hence, the results do not necessarily represent a quantitative analysis of the RLJP.

CO_2 loss during titration

Loss of CO_2 from an aqueous solution containing the carbonate subsystem leads to an increase of the solution pH and a decrease in MC_T and accordingly C_T. It has been stated earlier that if CO_2 is lost during a titration with strong acid from, say, pH_1 to pH_2, then C_T will be overestimated if this measured pH pair is used for its calculation. To investigate the effect of CO_2 loss from solution during titration on the calculation of C_T the following experiment was carried out:

Twelve different Na_2CO_3 solutions were made up to provide a range of expected C_T values from 50 to 1 700 mg/ℓ as $CaCO_3$. Each solution was titrated from its initial pH_0 (pH ≃ 11) to pH_1 ≃ 8,3 and then to pH_2 ≃ 4,8. It was hypothesised that prolonged stirring at pH_2 ≃ 4,8 would cause loss of CO_2 from the sample and consequently the second pH reading of the pH pair should increase.

Each of the above Na_2CO_3 solutions was tested using the following procedure: Gentle stirring for 1 min at initial pH (pH_0 ≈ 11) before recording the reading; titrating to pH_1 ≃ 8,3 and recording of pH reading after 1 min of stirring; titrating to pH_2 ≃ 4,8 where pH readings were recorded after 1, 10, 20 and 30 min of stirring. From the recorded pH readings the following pH data pairs were formed: pH-pair$_1$ (8,3; pH_2 after 1 min stirring); pH-pair$_2$ (8,3; pH_2 after 10 min stirring); pH-pair$_3$ (8,3; pH_2 after 20 min stirring) and pH-pair$_4$ (8,3; pH_2 after 30 min stirring). For each pH pair a C_T value was calculated, to give C_{T1} from pH-pair$_1$, C_{T2} from pH-pair$_2$, C_{T3} from pH-pair$_3$ and C_{T4} from pH-pair$_4$ respectively.

In Fig. 4, the measured C_{T1} values (i.e. after 1 min stirring) for the different Na_2CO_3 solutions are plotted against their expected (known) values. The plot indicates that C_{T1} closely equals the known C_T value, i.e. negligible CO_2 loss occurred at all concentrations of C_T with 1 min stirring. Therefore it was concluded that C_{T1} could serve as a basis to assess the effect of CO_2 loss under prolonged stirring conditions: By subtracting C_{T1} from C_{T2}, C_{T3} and C_{T4} three ΔC_T values were obtained (Fig. 5). From Figs. (4) and (5) the following conclusions were drawn:

For all the tests, with gentle stirring for stirring periods of ≃ 1 min the effect of CO_2 loss on the calculation of C_T is insignificant. From a practical point of view, only when the stirring times exceed 10 min would the effect of CO_2 loss on calculation of C_T become significant.

Selection of pH data pairs for 4 pH point titration

To provide the best estimate for C_T, titration data for a pH pair approximately symmetrical around pK'_{acl} ≈ 6,3 (pH_1;pH_2) and for a pH pair unsymmetrical around pK'_{acl} (pH_1;pH_3) are required. In the section above, the approximately symmetrical pH pair selected was (8,3;4,8) and the unsymmetrical pair (8,3;5,4). In practice, the initial pH of the sample very likely will lie below 8,3 which means that the pH would have to be raised to 8,3 before the titration procedure could be commenced, clearly an undesirable requirement. To resolve this problem, the best practical symmetrical (pH_1;pH_2) and unsymmetrical (pH_1;pH_3) pH pairs need to be selected. From experience, for high sensitivity in estimating ΔpH:

- pH_1, pH_2 and pH_3 should be covered by the pH buffer solutions used for calibration of the pH probe.
- The difference between pH_2 and pH_3 should be sufficiently large to ensure that any difference in $MC_{T1,2}$ and $MC_{T1,3}$ (due to ΔpH) is shown up; pH_2 and pH_3 must differ by at least 0,6 pH units.
- The lowest pH, pH_3 should not be less than about the $H_2CO_3^*$ equivalence point, say pH = 4,8.

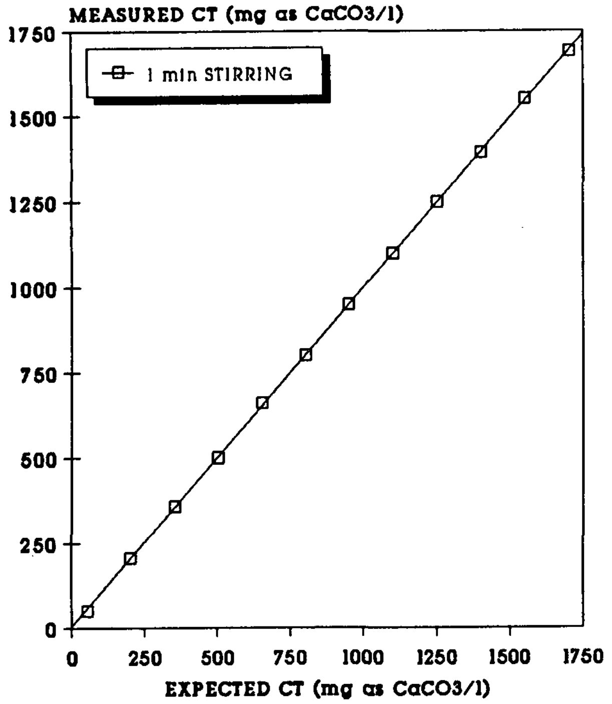

Figure 4
Comparison of calculated versus expected total carbonate species concentrations, C_T, for aqueous Na_2CO_3 solutions; pH pair used for calculation (8,3; 4,8); stirring time of 1 min before taking pH reading at pH ≃ 4,8

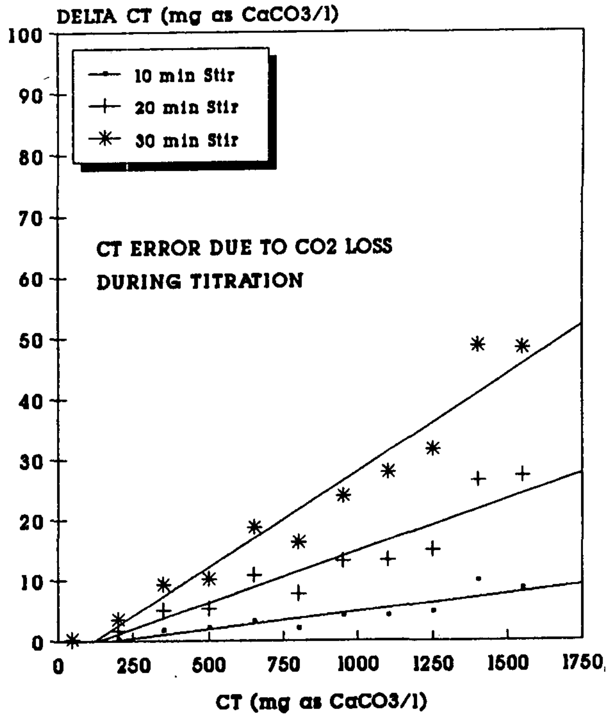

Figure 5
Effect of CO_2 loss on calculation of total carbonate species concentration, C_T, in titrating from pH_1 = 8,3 to pH_2 = 4,8 in 1 min, and thereafter recording pH_2 for different periods of stirring; delta C_T by subtracting results after 1 min stirring from all other results

- The highest pH, pH_1 must be at least 0,4 pH units above pK'_{acl} otherwise random titration errors arising from the small difference between pH_1 and pH_2 give rise to estimates of low precision.

If pH_3 is selected at the lowest point of the pH range, i.e. at 4,8, then pH_2 will be at pH 4,8 + 0,6 = 5,4 which is the lowest possible value for pH_2. Hence, in order to establish a pH pair (pH_1;pH_2) equidistant about pK'_{acl} ≃ 6,3, pH_1 will be located at approximately 7,2 (see Fig. 1) which is the highest possible value for pH_1. Alternatively, if pH_1 is selected at the lower limit, i.e. pH_1 ≃ 6,3 + 0,4 = 6,7 the corresponding pH_2 is fixed at 5,9 and pH_3 should be located at 5,9 − 0,6 = 5,3. Accordingly, pH_1 is limited to the range of 6,7 and 7,2. These give the following limiting sets of titration ranges of pH values:

- pH_1 = 6,7; pH_2 = 5,9 and pH_3 = 5,3; and
- pH_1 = 7,2; pH_2 = 5,4 and pH_3 = 4,8.

Once a set of pH values is selected from these ranges, the titration to each pH point can be ± 0,1 pH units without introducing additional errors in the estimates provided the actual pH values and titration data are used. The titration from pH_1 to pH_2 to pH_3 (actual values) supplies the data to obtain ΔpH and C_T of the titrated sample. Using ΔpH, the initial pH of the sample (pH_0) is corrected and $H_2CO_3^*$ alkalinity calculated.

In the above procedure, if $pH_0 < pH_1$ then for the titration the pH is first raised to pH_1 by adding a strong base; it is not necessary to know the normality of strong base added, but the volume added must be recorded, to determine the sample volume at pH_1 for Eq. (33). If $pH_0 > pH_1$ then in effect the reverse applies, with reduction of pH to pH_1 first and then measured titration pH_1 to pH_2 to pH_3. Here the same titrant can be used for lowering pH_0 to pH_1 and for the pH pairs titration.

Evaluation of accuracy and precision of the 4 pH point titration method

The accuracy and precision of the 4 pH point method using the pH values (pH_1 = 6,7; pH_2 = 5,9; pH_3 = 5,3) was tested separately for low and high $C_T/H_2CO_3^*$ alkalinity concentration ranges. Test solutions were made with $NaHCO_3$ in distilled water so that theoretically C_T = $H_2CO_3^*$ alkalinity (both as $CaCO_3$). The 4 pH point method results were to be compared with the known (expected) values.

Low $C_T/H_2CO_3^*$ alkalinity concentration solutions

At low $C_T/H_2CO_3^*$ alkalinity concentrations, the effects of impurities in the distilled water, particularly contamination by CO_2, become important and may significantly influence pH_0 and C_T so that $C_T \neq H_2CO_3^*$ alkalinity. This will cause that comparison of the results from the 4 pH point method with the input values will show deviations. Accordingly, it was decided to compare the 4 pH point method results also with results using the Gran method, a method which is reputed to provide accurate estimates in pure carbonate systems of $H_2CO_3^*$ alkalinity and the (derived) C_T value down to very low concentrations. A set of $NaHCO_3$ solutions were made up in distilled water to give C_T =

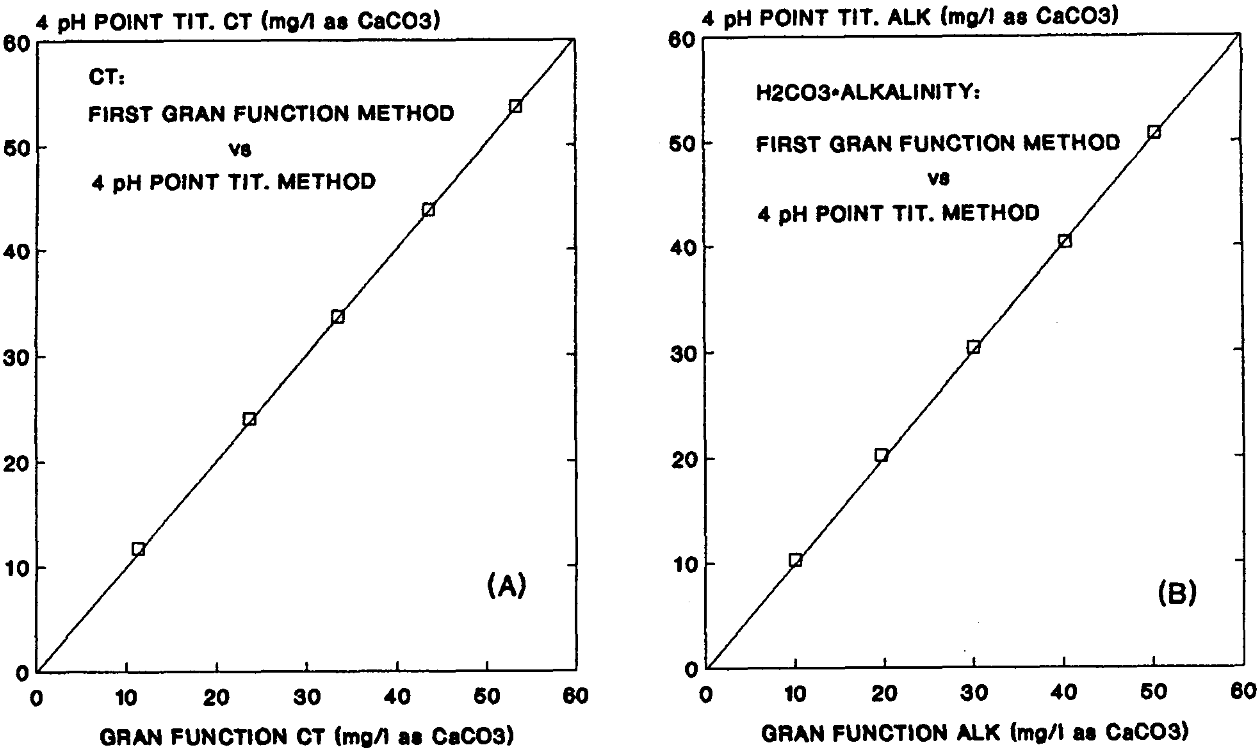

Figure 6

Low concentrations of H_2CO_3 alkalinity and total carbonate species concentrations, C_T: Comparison of results obtained from Gran Function and 4 pH point titration methods on aqueous $NaHCO_3$ solutions for (a) C_T and (b) H_2CO_3* alkalinity*

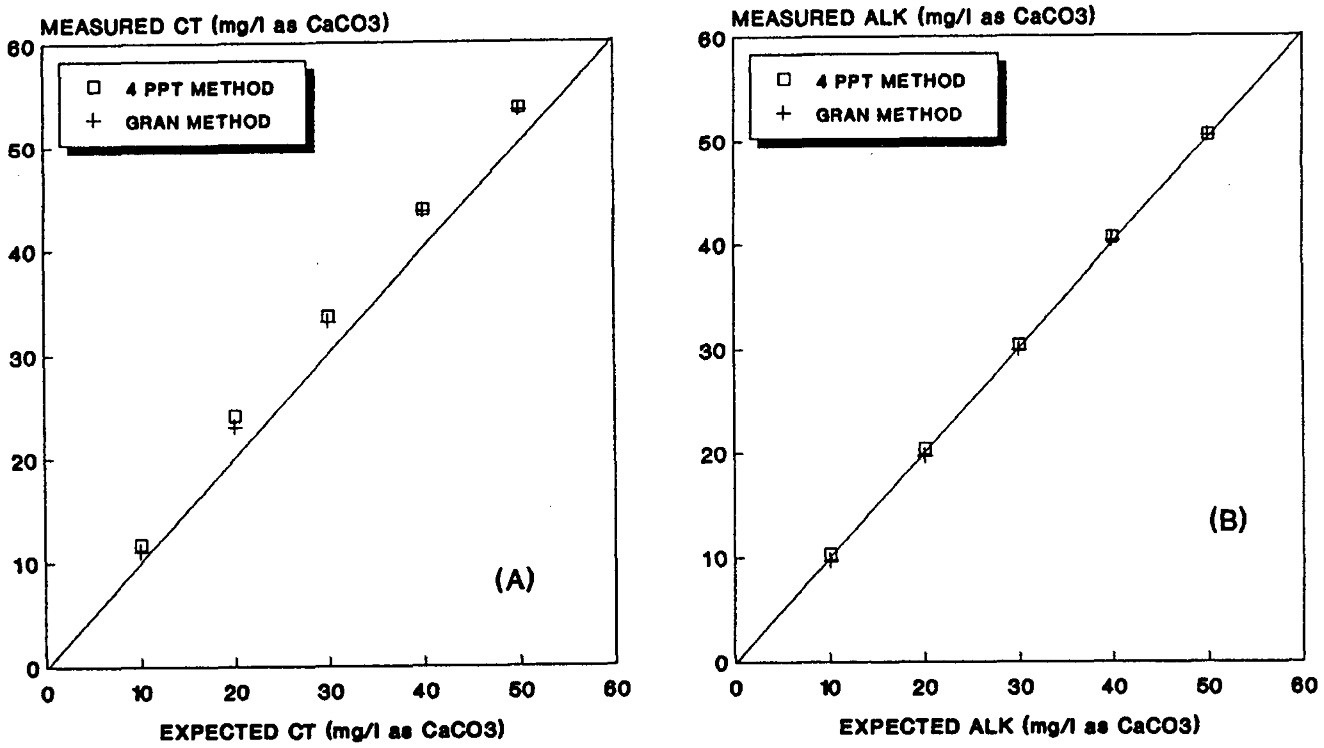

Figure 7

Low concentrations of H_2CO_3 alkalinity and total carbonate species concentrations, C_T: Comparison of (a) C_T and (b) H_2CO_3* alkalinity measured by the Gran Function and 4 pH point titration methods with their respective expected values. The various aqueous solutions were made up from $NaHCO_3$ and distilled water*

$H_2CO_3^*$ alkalinity = 10, 20, 30, 40 and 50 mg/ℓ (as $CaCO_3$). The solutions were tested using the complete first Gran Function method (Loewenthal et al., 1989), and the 4 pH point method. In Figs. 6a and 6b the results for C_T and $H_2CO_3^*$ alkalinity obtained from the Gran and 4 pH point titration methods are plotted against each other; evidently the two methods give values very close to each other (correlation coefficient = 0,99). In Fig. 7a and 7b the results for C_T and the $H_2CO_3^*$ alkalinity obtained from the Gran Function and 4 pH point titration method are plotted versus their respective expected values. Comparing the measured $H_2CO_3^*$ alkalinity with the expected values, the measured values for both 4 pH point titration and the Gran methods show errors less than two per cent of the expected values (Fig. 7b). With regard to C_T the results from both methods deviate from their respective expected values in that the measured values are consistently higher, by approximately 3 mg/ℓ as $CaCO_3$ (Fig. 7a). Since the error in C_T is virtually the same in both methods and consistent for all C_T values, it is likely that a C_T additional to the $NaHCO_3$ input was present in the sample, very likely through CO_2 contamination of the distilled water from contact with the air. That this was present is supported by noting that the initial pH values of the solutions ranged from 7,2 to 7,6 whereas the expected pH value for pure $NaHCO_3$ in CO_2 free water is about 8,3.

High C_T, $H_2CO_3^*$ alkalinity concentration solutions

A set of $NaHCO_3$ solutions were made up to give C_T = $H_2CO_3^*$ alkalinity = 100, 200, 300, 400 and 500 mg/ℓ (as $CaCO_3$). C_T and $H_2CO_3^*$ alkalinity were estimated using only the 4 pH point method. These estimates were compared with their respective expected values; the small errors introduced by CO_2 contamination of the solutions became insignificant because of the high input concentrations of C_T and $H_2CO_3^*$ alkalinity so that cross checking with the Gran Function was not required. The measured results for C_T and $H_2CO_3^*$ alkalinity are plotted for each solution against their respective expected values, in Figs. 8 and 9. In all instances the measured average values of the various solutions, for both C_T and $H_2CO_3^*$ alkalinity, deviated by less than two per cent from their respective expected values.

Discussion

In this paper, a 4 pH point titration method is developed to determine the carbonate total species concentration (C_T) in a sample containing only the carbonate and water subsystems and to derive the $H_2CO_3^*$ alkalinity from C_T and the sample initial pH.

The proposed method involves little, if any, extra effort over the conventional $H_2CO_3^*$ alkalinity titration to a selected pH endpoint (*Standard Methods*, 1984), but is free of the problem of endpoint identification/selection and has the advantage of providing an assessment of systematic pH measurement error. The estimate of systematic pH error enables reasonable estimates of C_T and $H_2CO_3^*$ alkalinity to be made even though the pH meter may be poorly calibrated. The indications are that the 4 pH point method has an accuracy near that of the Gran method (Gran, 1952), yet it is much simpler. The method should lend itself readily to automation.

The 4 pH point method can be readily extended to measure C_T and $H_2CO_3^*$ alkalinity when non-carbonate weak acid/bases (e.g. phosphate, ammonium) also are present in solution at known concentrations (derived in the next paper of this series).

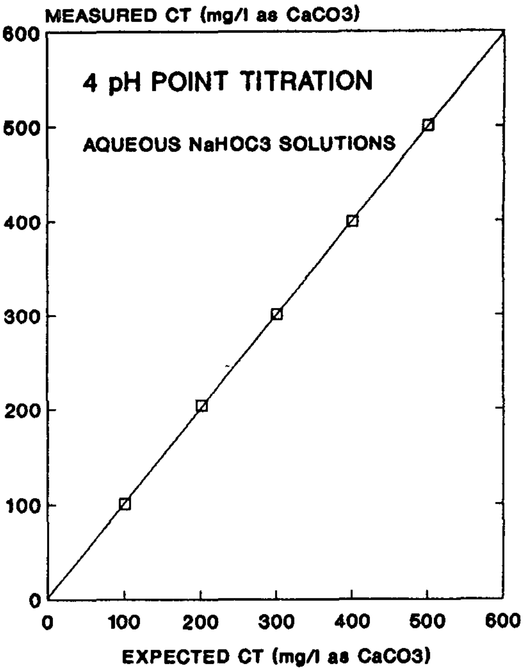

Figure 8
High concentrations of total carbonate species concentration, C_T: Results derived from 4 pH point titration method for total carbonate species concentration, C_T, plotted versus their respective expected values; solutions made up with $NaHCO_3$ and distilled water

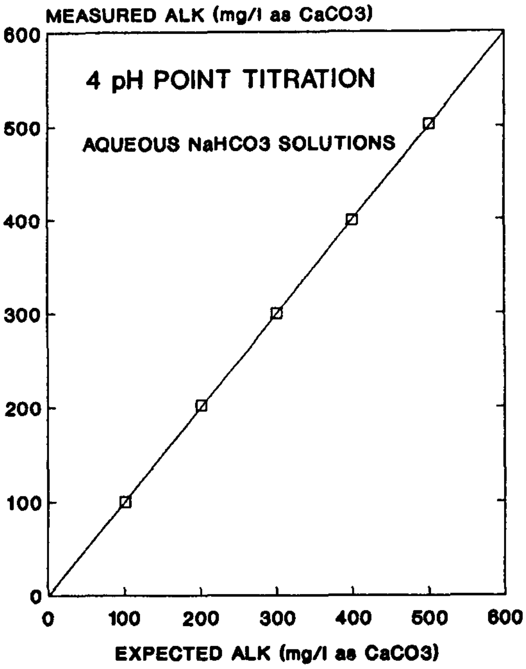

Figure 9
High concentrations of $H_2CO_3^*$ alkalinity: Results derived from 4 pH point titration method for $H_2CO_3^*$ alkalinity plotted versus their respective expected values; solutions made up with $NaHCO_3$ and distilled water

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