

Alkalinity measurement: Part 2 - A 4 pH point titration method to determine the carbonate weak acid/base in aqueous solutions containing other weak acid/bases of known concentrations

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Abstract

In this paper the 4 pH point titration method (see **Part 1**) is extended to determine the carbonate total species concentration (C_T) and $H_2CO_3^*$ alkalinity in aqueous solutions containing other weak acid/bases of known concentrations. Two typical other weak acid/bases are selected, ammonium with a pK_a far from, and inorganic phosphate with a pK_a near to, the 4 pH point titration range of 7,2 to 4,8. The influence of the phosphate and ammonium on the 4 pH point titration is examined theoretically and experimentally. Knowing the total species concentrations of the ammonium and phosphate, their respective effects on the 4 pH point titration are assessed and corrected for, to isolate C_T and $H_2CO_3^*$ alkalinity. With regard to the effect of ammonium, this is negligible for most practical applications of the 4 pH point titration and normally requires no correction. However, the effect of phosphate can be significant and should be corrected for by the proposed method.

Introduction

In a previous paper (**Part 1**) Moosbrugger et al. (1993b) proposed a 4 pH point titration method to determine the carbonate total species concentration (C_T) and $H_2CO_3^*$ alkalinity in aqueous solutions, provided the carbonate weak acid/base is the only one present. In practice this method can be applied only where the carbonate weak acid/base is dominant, to such a degree that other non-carbonate weak acid/bases can be neglected. However, in many practical situations in addition to the carbonate, other weak acid/bases may be present in such concentrations that they contribute significantly to the proton accepting capacity in the pH range covered by the 4 pH point titration method (see **Part 1**). This will lead to an error in the determination of C_T and $H_2CO_3^*$ alkalinity from the titration data. For example, in anaerobic systems the phosphate, sulphide, ammonium and short-chain fatty acids (SCFA) weak acid/bases may be present in appreciable concentrations. Consequently, in these systems the effect of the non-carbonate weak acid/bases no longer can be neglected.

In this paper, the 4 pH point method is extended to determine C_T and $H_2CO_3^*$ alkalinity in aqueous solutions that include known-total species concentrations of non-carbonate weak acid/bases.

Theory

In the 4 pH point titration proposed by Moosbrugger et al. (1993b), the sample is titrated from its initial pH (pH_0) to pH_1 to pH_2 [pH_1 and pH_2 situated approximately equidistant around the first apparent dissociation constant of the carbonate weak acid/base (pK_{a1})], and to a lower pH point (pH_3). Two equations for sample mass of C_T (MC_T) are formed, for the approximately symmetrical ($pH_1;pH_2$) and unsymmetrical ($pH_1;pH_3$) pH pairs respectively. By successive approximation, all the pH values are

adjusted until MC_T for both equations is the same; this constitutes the best estimate for MC_T and accordingly C_T , and the magnitude of the pH adjustment (ΔpH) gives an estimate of the systematic error in pH, i.e. $pH_{\text{observed}} + \Delta pH = pH_{\text{true}}$. Knowing ΔpH , the initial pH of the sample is adjusted which allows a more accurate calculation of the sample $H_2CO_3^*$ alkalinity, from the corrected C_T and corrected initial pH.

Moosbrugger et al. (1993b) concluded that if the carbonate weak acid/base is the only one present, the pH data points in the 4 pH point method would range from $pH_1 \approx 7,2$, $pH_2 \approx 5,4$ and $pH_3 \approx 4,8$ to $pH_1 \approx 6,7$, $pH_2 \approx 5,9$ and $pH_3 \approx 5,3$, i.e. the maximum titration range is from $pH \approx 7,2$ to $\approx 4,8$. In a mixture of weak acid/bases, if the pK_a values of the non-carbonate weak acid/bases are near or within this pH range, the proton accepting capacity (PAC) contributions of these weak acid/bases to the titration must be isolated and removed in order to determine the correct value for C_T . If the total species concentrations of the non-carbonate weak acid/bases are known it is possible to calculate the PAC for each of these in the pH region covered by the 4 pH point titration and take account of these in the determination of C_T and $H_2CO_3^*$ alkalinity. An approach to achieve this will now be presented for a mixture of the carbonate and a general monoprotic weak acid/base.

Determination of C_T in a mixture of the carbonate and a monoprotic weak acid/base

The basic equations defining the carbonate weak acid/base have been presented in **Part 1**. The basic equations defining a monoprotic weak acid/base are:

$$\frac{(H^+) [A^-]}{[HA]} = K_a / f_m = K'_a \quad (1)$$

$$A_t = [HA] + [A^-] \quad (2)$$

where:

$(H^+) =$ hydrogen ion activity (mol/l)

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

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Received 5 February 1992; accepted in revised form 16 July 1992.

[A⁻] = concentration of the salt of the weak acid/base (mol/l)
 [HA] = concentration of the undissociated weak acid/base (mol/l)
 A_t = total species concentration of weak acid/base (mol/l)
 K_a, K'_a = thermodynamic and apparent dissociation constants respectively of the monoprotic weak acid/base (mol/l)
 f_m = monovalent activity coefficient

These two equations contain four unknowns, hence to completely characterise the weak acid/base two unknowns need to be measured; of these A_t and (H⁺) usually are measured; [HA] and [A⁻] then can be expressed in terms of A_t and (H⁺):

A⁻ as function of A_t and pH

From Eq. (2):

$$[HA] = A_t - [A^-] \quad (3)$$

Inserting Eq. (3) in Eq. (1) and rearranging:

$$[A^-] = \frac{A_t K'_a}{(H^+) + K'_a} \quad (4)$$

HA as function of A_t and pH

Inserting Eq. (4) in Eq. (3):

$$[HA] = A_t \left(1 - \frac{K'_a}{(H^+) + K'_a}\right) \quad (5)$$

Subsystem alkalinity of monoprotic weak acid/base

Consider a mixture of the carbonate and monoprotic weak acid/bases in an aqueous medium. From Loewenthal et al. (1989), a solution alkalinity (solution proton accepting capacity) can be defined for the mixture relative to its solution reference state, and can be measured by titration as the molar mass of H⁺ (or OH⁻) that must be added to the solution to move from the initial pH to the pH of the reference solution state. The reference solution state is defined as the state established on addition to pure water of one reference species each for the carbonate (H₂CO₃^{*}, HCO₃⁻ or CO₃²⁻) and for the monoprotic (HA or A⁻) weak acid/bases. Selecting the most protonated species as reference species (H₂CO₃^{*} and HA), the solution alkalinity at any pH relative to this solution reference state can be written as follows (see Loewenthal et al., 1989;1991):

$$H_2CO_3^*/HA \text{ alk} = \{[HCO_3^-] + 2[CO_3^{2-}]\} + \{[A^-]\} + \{[OH^-] - [H^+]\} \quad (6)$$

The right hand side of Eq. (6) can be written as the sum of subsystem alkalinity of the weak acid/bases and water (for definition of a subsystem and a subsystem alkalinity see Part 1 or Loewenthal et al. (1991)):

$$H_2CO_3^*/HA \text{ alk} = \text{Alk } H_2CO_3^* + \text{Alk } HA + \text{Alk } H_2O \quad (7)$$

where:

$$\text{Alk } HA = [A^-] \quad (8a)$$

$$\text{Alk } H_2CO_3^* = [HCO_3^-] + 2 [CO_3^{2-}] \quad (8b)$$

$$\text{Alk } H_2O = [OH^-] - [H^+] \quad (8c)$$

Hence, substituting Eq. (4) into Eq. (8a), the alkalinity contribution of the HA weak acid/base subsystem can be written as a function of A_t and pH:

$$\text{Alk } HA = \frac{A_t K'_a}{(H^+) + K'_a} \quad (9)$$

The alkalinity contributions of the carbonate (Alk H₂CO₃^{*}) and water (Alk H₂O) subsystems have been set out in Part 1.

Subsystem alkalinity contribution of monoprotic HA weak acid/base between two pHs

From Eq. (9), the mass of the monoprotic weak acid/base subsystem alkalinity, MAlk HA, at any pH₁ is:

$$MAlk_1 HA = V_{s1} \frac{A_{t1} K'_a}{(H^+)_1 + K'_a} \quad (10a)$$

$$= MA_{t1} \frac{K'_a}{(H^+)_1 + K'_a} \quad (10b)$$

where:

V_{s1} = volume of sample at pH₁ (l)

A_{t1} = total species concentration of monoprotic weak acid/base at pH₁ (mol/l)

MA_{t1} = mass of A_t at pH₁ (mol)

Consider an acid titration from pH₁ to pH₂. Since Alk HA is defined as a proton accepting capacity, addition of H⁺ will cause a decrease in Alk HA. The mass decrease in HA subsystem alkalinity from pH₁ to pH₂ is:

$$\begin{aligned} \Delta MAlk_{1,2} HA &= MAlk_1 HA - MAlk_2 HA \\ &= MA_{t1} \frac{K'_a}{(H^+)_1 + K'_a} - MA_{t2} \frac{K'_a}{(H^+)_2 + K'_a} \end{aligned}$$

In the titration, the mass of A_t (MA_t) remains constant, and equals the mass of A_t at pH₁ (MA_{t1}) and the mass of A_t at pH₂ (MA_{t2}):

$$\Delta MAlk_{1,2} HA = MA_t \left[\frac{K'_a}{(H^+)_1 + K'_a} - \frac{K'_a}{(H^+)_2 + K'_a} \right] \quad (11a)$$

$$= MA_t Y_{1,2} \quad (11b)$$

where:

MA_t = mass of A_t in the sample; this remains constant during the titration (mol)

$$= A_t V_s \quad (11c)$$

- A_1 = monoprotic weak acid/base total species concentration in sample prior to titration (mol/l)
 V_s = volume of sample prior to titration (mol/l)

C_T and $H_2CO_3^*$ alkalinity in a mixture of weak acid/bases

In an acid titration, Eq. (11) allows calculation of the magnitude of the decrease in subsystem alkalinity (subsystem proton accepting capacity) of any monoprotic weak acid/base from pH_1 to pH_2 , provided its total species concentration is known. In a mixture of the carbonate and a monoprotic weak acid/base, when endeavouring to determine C_T and $H_2CO_3^*$ alkalinity this additional proton accepting capacity must be removed in order to determine C_T and $H_2CO_3^*$ alkalinity correctly. The mass decrease in solution alkalinity of the sample equals the molar mass of H^+ added ($Ca V_{x1,2}$) and can be written as the sum of the mass changes in subsystem alkalinities of the individual weak acid/bases:

$$\begin{aligned} Ca V_{x1,2} &= \Delta MH_2CO_3^* / HA \text{ alk}_{1,2} \\ &= \Delta MAlk_{1,2}H_2CO_3^* + \Delta MAlk_{1,2}HA + \Delta MAlk_{1,2}H_2O \end{aligned} \quad (12)$$

where:

- $V_{x1,2}$ = volume of titrant added to titrate from pH_1 to pH_2 (l)
 Ca = normality of strong acid added (mol/l)

Rearranging Eq. (12) and noting from **Part 1** Eq. (31) that $\Delta MAlk_{1,2}H_2CO_3^* = MC_T X_{1,2}$ gives:

$$MC_T X_{1,2} = Ca V_{x1,2} - \Delta MAlk_{1,2}HA - \Delta MAlk_{1,2}H_2O \quad (13)$$

In Eq. (13), ($Ca V_{x1,2}$) is known from the titration, $\Delta MAlk_{1,2}HA$ is calculated from Eq. (11); from **Part 1** Eqs. (33) and (30), $\Delta MAlk_{1,2}H_2O$ and $X_{1,2}$ respectively are calculated; hence, MC_T can be calculated. This procedure yields the same MC_T for any two pH points provided that no error in the pH (ΔpH) is present. If a ΔpH exists, from **Part 1**, the procedure is duplicated for titration data from two pH pairs, one approximately symmetrical and one strongly unsymmetrical around pK'_{ac1} , ($pH_1;pH_2$) and ($pH_1;pH_3$) respectively. This gives two values for MC_T , $MC_{T1,2}$ and $MC_{T1,3}$ respectively. By successive approximation all the pH values are adjusted until the two MC_T values are equal; this constitutes the best estimate for MC_T and the magnitude of the pH adjustment provides an estimate of ΔpH . The calculation algorithm is as follows:

- Adjust pK_a for temperature and ionic strength to give pK'_a ; calculate K'_a from $pK'_a = -\log K'_a$.
- Calculate MA_1 from the measured A_1 and V_s using Eq. (11c).
- In Eq. (11a) insert MA_1 , K'_a and $(H^+)_1$ and $(H^+)_2$ from pH_1 and pH_2 , and calculate $\Delta MAlk_{1,2}HA$. Now insert $\Delta MAlk_{1,2}HA$, together with ($Ca V_{x1,2}$), $\Delta MAlk_{1,2}H_2O$ (Eq. (33) of **Part 1**) and $X_{1,2}$ (Eq. (30) of **Part 1**) in Eq. (13) and calculate $MC_{T1,2}$.
- Duplicate the above with pH_1 and pH_3 , to calculate $MC_{T1,3}$.
- Compare $MC_{T1,2}$ and $MC_{T1,3}$; if different, adjust all pH values by ΔpH and recalculate $\Delta MAlk_{1,2}HA$, $\Delta MAlk_{1,3}HA$, $MC_{T1,2}$ and $MC_{T1,3}$. This step is repeated until $MC_{T1,3} = MC_{T1,2}$ which gives the best estimate for the sample MC_T and ΔpH .
- From MC_T and V_s calculate the sample C_T (Eq. (34b) of **Part 1**).
- With pH_0 corrected for ΔpH , calculate the sample $H_2CO_3^*$

alkalinity from C_T (**Part 1**, Eq. (20)).

The approach above is now applied to two types of weak acid/base mixtures in aqueous solutions, one in which the non-carbonate weak acid/base has a pK_a value far from the titration range and the other in which it has a pK_a value near the titration range, ammonium and phosphate respectively.

C_T in a mixture of the carbonate and ammonium weak acid/bases

Substituting the ammonium weak acid/base for the HA weak acid/base in Eq. (7), the solution alkalinity can be written in terms of the subsystem alkalinities as follows:

$$H_2CO_3^*/NH_4^+ \text{ alk} = \text{Alk } H_2CO_3^* + \text{Alk } NH_4^+ + \text{Alk } H_2O \quad (14)$$

where:

$$\text{Alk } NH_4^+ = [NH_3] \quad (15)$$

In an acid titration from pH_1 to pH_2 , substituting the ammonium weak acid/base for the HA weak acid/base in Eq. (11a) gives:

$$\Delta MAlk_{1,2}NH_4^+ = MN_T \left[\frac{K'_{an}}{(H^+)_1 + K'_{an}} - \frac{K'_{an}}{(H^+)_2 + K'_{an}} \right] \quad (16a)$$

$$= MN_T Y_{N1,2} \quad (16b)$$

where:

$$\begin{aligned} MN_T &= \text{mass of ammonium weak acid/base total species in the sample (mol)} \\ &= N_T V_s \end{aligned} \quad (16c)$$

$$N_T = \text{total species concentration of the ammonium weak acid/base prior to titration (mol/l)}$$

$$V_s = \text{sample volume prior to titration (l)}$$

$$K'_{an} = \text{apparent dissociation constant of the ammonium weak acid/base (mol/l)}$$

From Eq. (16), the mass change in ammonium subsystem alkalinity, $\Delta MAlk_{1,2}NH_4^+$, can be calculated. Consequently, the algorithm set out earlier to determine C_T can be appropriately modified, by substituting $\Delta MAlk_{1,2}NH_4^+$ for $\Delta MAlk_{1,2}HA$ [Eq. (16) for Eq. (11)].

C_T in a mixture of the carbonate and phosphate weak acid/bases

The phosphate subsystem is triprotic with $pK_{ap1} \approx 2.1$, $pK_{ap2} \approx 7.2$, $pK_{ap3} \approx 12.0$. These pK_{ap} values are so far apart that the dissociation around each pK_{ap} can be considered as arising from a monoprotic weak acid/base. pK_{ap1} and pK_{ap3} are situated far from the 4 pH point titration range (7.2 to 4.8) so that the proton accepting capacity contribution centered around these two pK_a values is extremely small and can be neglected. This leaves pK_{ap2} as the only one of importance in the 4 pH point titration range. Accordingly, the phosphate system can be considered as a monoprotic weak acid/base, with a single dissociation constant $pK_{ap2} \approx 7.2$ and dissociation species $H_2PO_4^-$ and HPO_4^{2-} . Substituting the phosphate subsystem for the HA weak acid/base subsystem in Eq. (7), the solution alkalinity can be written in terms of the subsystem alkalinities as follows:

$$H_2CO_3^*/H_2PO_4^- \text{ alk} = \text{Alk } H_2CO_3^* + \text{Alk } H_2PO_4^- + \text{Alk } H_2O \quad (17)$$

In Eq. (17) the reference species for the “monoprotic” phosphate weak acid/base is $H_2PO_4^-$, consequently:

$$\text{Alk } H_2PO_4^- = [HPO_4^{2-}] \quad (18)$$

In an acid titration from pH_1 to pH_2 , substituting the “monoprotic” phosphate weak acid/base for the HA weak acid/base in Eq. (11a) gives:

$$\Delta \text{MALK}_{1,2} H_2PO_4^- = MP_T \left[\frac{K'_{ap2}}{(H^+)_{1,2} + K'_{ap2}} - \frac{K'_{ap2}}{(H^+)_{2,2} + K'_{ap2}} \right] \quad (19a)$$

$$= MP_T Y_{p1,2} \quad (19b)$$

where:

$$\begin{aligned} MP_T &= \text{mass of phosphate weak acid/base total species in the sample (mol)} \\ &= P_T V_s \quad (19c) \\ P_T &= \text{total species concentration of the phosphate weak acid/base prior to titration (mol/l)} \\ V_s &= \text{sample volume prior to titration (l)} \\ K'_{ap2} &= \text{second apparent dissociation constant of the phosphate subsystem (mol/l)} \end{aligned}$$

From Eq. (19), the mass decrease in phosphate subsystem alkalinity for an acid titration between pH_1 and pH_2 , $\Delta \text{MALK}_{1,2} H_2PO_4^-$, can be calculated. Consequently, the algorithm set out earlier to determine C_T can be appropriately modified, by substituting $\Delta \text{MALK}_{1,2} H_2PO_4^-$ for $\Delta \text{MALK}_{1,2} HA$ [Eq. (19) for Eq. (11)].

Experimental investigation

To check the theoretical method for the determination of C_T and $H_2CO_3^*$ alkalinity in mixtures containing other weak acid/bases, two additional weak acid/bases were selected:

- ammonium having a $pK_{an} \approx 9,25$, well away from the carbonate subsystem $pK'_{ac1} \approx 6,3$
- phosphate having a $pK_{ap2} \approx 7,20$, near pK'_{ac1}

The effect of each of these weak acid/bases was investigated separately. For the test solution, the C_T , N_T and P_T values were selected as those common in anaerobic systems. All tests were done at approximately 20° C.

Effect of ammonium weak acid/base

A set of solutions was made up: Addition to distilled water of $NaHCO_3$ to give $C_T = H_2CO_3^*$ alkalinity = 2 985 mg/l as $CaCO_3$, and NH_4Cl to give $N_T = 0, 100, 200, 300, 400$ or 500 mg N/l. The solutions were titrated with standardised HCl. For each mixture, three replica titrations were performed from the initial pH of 8,0 to 7,4 to 5,4 to 4,8, except for the solution containing only carbonate where five replica titrations were done. Two titration sets of pH pairs were selected: pH pair (8,0;4,8) approximately symmetrical and pH pair (8,0;5,4) unsymmetrical around pK'_{ac1} , and pH pair (7,4;5,4) approximately symmetrical and pH pair (7,4;4,8) unsymmetrical around pK'_{ac1} . The pH symmetrical pair (8,0;4,8) was selected rather than the pH pairs recommended in Part 1 (6,7;5,9 or 7,2;5,4) in order to move the first pH of the pH pair closer to $pK_{an} \approx 9,3$ and thereby increase the effect of the ammonium weak acid/base in the titration. The

second symmetrical pH pair (7,4;5,4) was tested to demonstrate the effect of “moving” the first pH of the pH pair further away from $pK_{an} \approx 9,3$.

The algorithm employed to take account of the ammonium in determining C_T was as set out for the general monoprotic weak acid/base, but with the appropriate modifications (see earlier). From the measured titration data, two values for C_T were derived: taking into account the presence of the ammonium subsystem by setting $N_T =$ (input value) in the algorithm above, giving the corrected C_T , C_{T1} ; and neglecting the presence of the ammonium subsystem by setting $N_T = 0$ in the algorithm, giving an uncorrected C_T , C_{T2} . To estimate the error introduced by not correcting for the presence of the ammonium weak acid/base, the tests in which zero ammonium was added (5 tests) were averaged and accepted as the best estimate for C_T . This C_T value was subtracted from the corrected C_{T1} to give ΔC_{T1} and from the uncorrected C_{T2} value to give ΔC_{T2} . ΔC_{T1} and ΔC_{T2} are plotted against N_T in Fig. 1 for pH pair set (8,0;4,8) and (8,0;5,4), and in Fig. 2 for pH pair set (7,4;5,4) and (7,4;4,8). These plots give the following information:

- ΔC_T values not corrected for presence of the ammonium subsystem (ΔC_{T2}) are higher for the pH set with the symmetrical pH pair (8,0;4,8) than for the set with symmetrical pH pair (7,4;5,4).
- ΔC_{T2} values increase linearly with the increase in ammonium concentrations.
- For both pH sets, ΔC_T values corrected for ammonium (ΔC_{T1}) are insignificantly small and virtually independent of the ammonium concentration.

From the above, should the approximately symmetrical pH pair be selected even closer around pK'_{ac1} than pH pair (7,3;5,4), the uncorrected ΔC_T values would be even smaller. This would indicate that in a practical situation, should it not be possible to determine N_T the error in C_T induced by the presence of the ammonium subsystem can be minimised by selecting the symmetrical pH pair close around pK'_{ac1} . From Part 1, the closest possible symmetrical pH pair around pK'_{ac1} is (6,7;5,9). Tests using this pH pair gave a percentage error in C_T of less than two per cent for 1 990 mg C_T/l as $CaCO_3$ and 500 mg N/l when the presence of the ammonium subsystem was neglected.

Effect of phosphate weak acid/base

A set of solutions was made up: Addition to distilled water of $NaHCO_3$ giving $C_T = H_2CO_3^*$ alkalinity = 2 985 mg/l as $CaCO_3$, and K_2HPO_4 to give $P_T = 0, 16, 33, 49, 65$ or 81 mg P/l. The solutions were titrated with standardised HCl. One of the symmetric and unsymmetric pH pair sets used for the ammonium-carbonate mixtures was selected, pH pairs (7,4;5,4) and (7,4;4,8) respectively. For each phosphate concentration, three replica titrations were performed together with five replica titrations on the solution with zero addition of K_2HPO_4 . The symmetrical pH pair (7,4;5,4) is widely spaced around pK'_{ac1} . A second set of solutions was prepared with addition to distilled water of $NaHCO_3$ to give $C_T = H_2CO_3^*$ alkalinity = 1 990 mg/l as $CaCO_3$, and K_2HPO_4 to give $P_T = 0, 33, 65$ and 98 mg P/l, in order to determine the effect with a symmetrical pH pair closely spaced around pK'_{ac1} , i.e. symmetrical pH pair (6,7;5,9) with unsymmetrical pH pair (6,7;5,1).

The algorithm used to take account of the phosphate weak acid/base was as set out for the general monoprotic weak

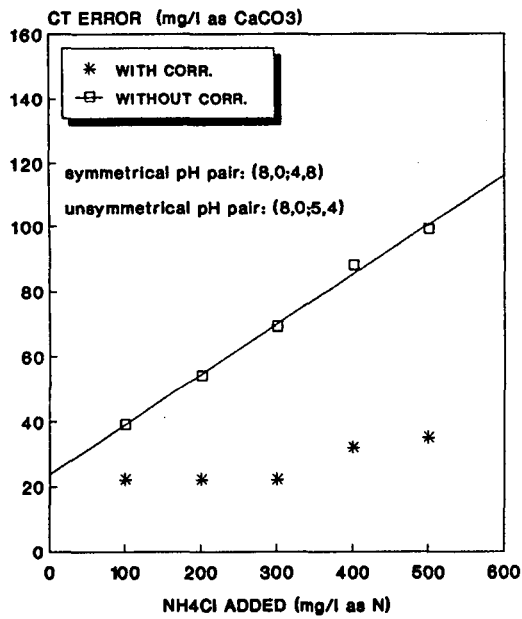


Figure 1

Influence of total species concentration of ammonium weak acid/base on determination of C_T (with/without correction) by the 4 pH point titration method [using pH pairs (8,0;4,8) and (8,0;5,4)]. Test solutions were made up of distilled water, NaHCO_3 (2 985 mg/l as CaCO_3) and various concentrations of NH_4Cl

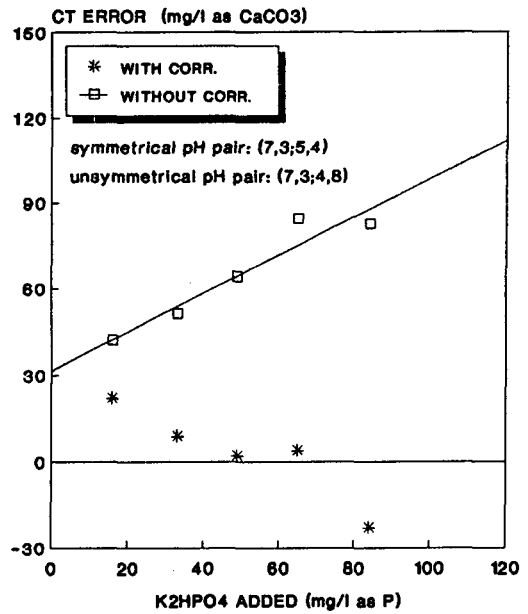


Figure 3

Influence of total species concentration on determination of C_T by the 4 pH point titration method [using pH pairs (7,4;5,4) and (7,4;4,8)]. Test solutions were made up of distilled water, NaHCO_3 (2 985 mg/l as CaCO_3) and various concentrations of K_2HPO_4

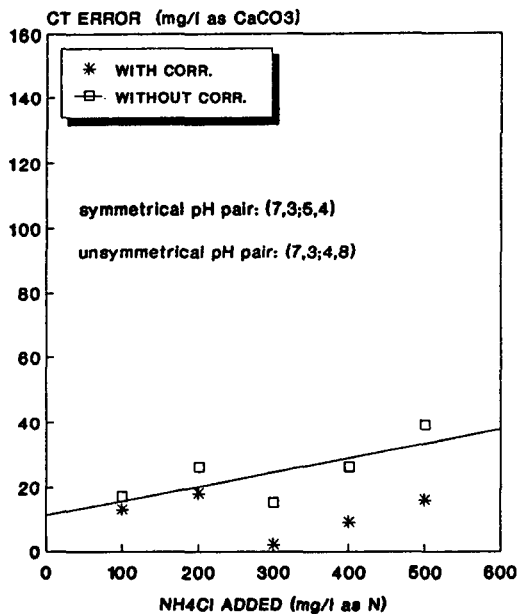


Figure 2

Influence of total species concentration of ammonium weak acid/base on determination of C_T (with/without correction) by the 4 pH point titration method [using pH pairs (7,4;5,4) and (7,4;4,8)]. Test solutions were made up of distilled water, NaHCO_3 (2 985 mg/l as CaCO_3) and various concentrations of NH_4Cl

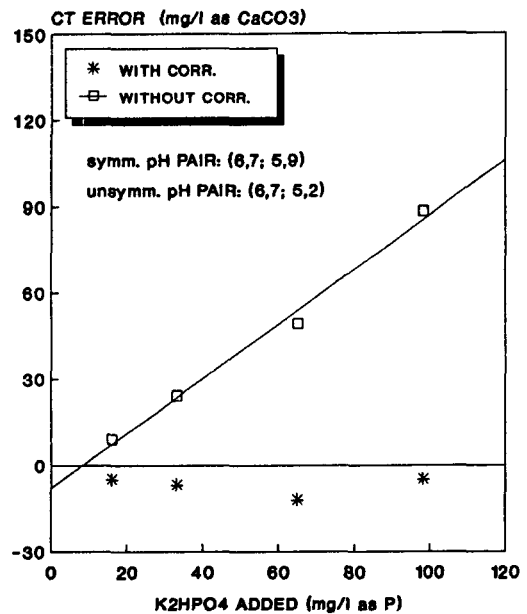


Figure 4

Influence of total species concentration on determination of C_T by the 4 pH point titration method [using pH pairs (6,7;5,9) and (6,7;5,1)]. Test solutions were made up of distilled water, NaHCO_3 (1 990 mg/l as CaCO_3) and various concentrations of K_2HPO_4

acid/base, but with the appropriate modifications (see earlier). Two values for C_T were calculated: taking into account the presence of phosphate by setting $P_T =$ (input value) to give the corrected C_T , C_{T1} ; and neglecting the presence of phosphate by setting $P_T = 0$ to give an uncorrected C_T , C_{T2} . To estimate the error introduced by not correcting for the presence of phosphate, the results for the tests in which zero phosphate was added were averaged and accepted as the best estimate for C_T . This value was subtracted from the corrected C_{T1} to give ΔC_{T1} and from the uncorrected C_{T2} to give ΔC_{T2} . ΔC_{T1} and ΔC_{T2} are plotted against P_T in Fig. 3 for pH set (7,4;5,4) and (7,4;4,8), and in Fig. 4 for pH set (6,7;5,9) and (6,7;5,1). From these plots the following information is obtained:

- In a mixture of the carbonate and phosphate weak acid/bases in aqueous solutions, the errors induced in the determination of C_T using a set of pH pairs with the symmetrical pH pair closely spaced around pK'_{ac1} (symmetrical 6,7;5,9; unsymmetrical 6,7;5,1) are only slightly reduced compared to the set of pH pairs with the symmetrical pH pair spaced further around pK'_{ac1} (symmetrical 7,4;5,4; unsymmetrical 7,4;4,8).
- Should the phosphate subsystem not be accounted for, the presence of phosphate can give rise to an appreciable error in the determination of C_T irrespective of the spacing of the approximately symmetrical pH pair around pK'_{ac1} .
- Knowing the P_T and including its effect in the 4 pH point titration method, the corrected C_T and $H_2CO_3^*$ alkalinity are virtually error-free.

Discussion

In this paper we investigated the effect of a non-carbonate weak acid/base of known concentration on the determination of carbonate weak acid/base total species concentration (C_T) and $H_2CO_3^*$ alkalinity using the 4 pH point titration method. Theoretically, and verified experimentally, it was shown that, if proton accepting capacity contribution of the non-carbonate weak acid/base is calculated (from its total species concentration) and this contribution subtracted from the titration, C_T and $H_2CO_3^*$ alkalinity can be determined largely error-free.

The method can be adapted readily with more than one non-carbonate weak acid/base present in solution, provided that the total species concentrations are known for each of the non-carbonate weak acid/bases. In this fashion, for example, the

effects of the phosphate, ammonium, sulphide and SCFA weak acid/bases in anaerobic digester liquors can be removed and C_T and $H_2CO_3^*$ alkalinity determined. The total species concentrations of the phosphate, ammonium and sulphide weak acid/bases can be readily measured by independent wet chemical techniques. However, measurement of total SCFA species concentrations can present difficulties in many practical situations (Moosbrugger et al., 1993a); in the next paper of this series the 4 pH point titration will be extended to a 5 pH point titration to obtain estimates of both the SCFA and carbonate total species concentrations in solutions which contain other non-carbonate weak acid/bases of known concentrations.

Closure

For the more practically inclined reader the method set out above may appear too complex for routine use. However, despite the rather elaborate theory the experimental procedure for the 4 pH point titration method requires little experimental effort and skill and the calculation procedures can be readily coded into a computer program (Source code (Turbo Pascal) and executable version of such a computer program are available from Water Research Commission, PO Box 824, Pretoria 0001, South Africa).

Acknowledgements

This research was supported jointly by the Water Research Commission and the Foundation for Research Development and this paper is published with their permission.

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