Alkalinity measurement:
Part 3 - A 5 pH point titration method to determine the carbonate and SCFA weak acid/bases in aqueous solution containing also known concentrations of other weak acid/bases

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Abstract

The theoretical basis for a 5 pH point acid titration method is described that allows the determination of $H_2CO_3^*$ alkalinity, total carbonate species concentration (C_T) and total short-chain fatty acid (SCFA) concentration in anaerobic digestor liquids also containing known concentrations of other weak acid/bases, e.g. ammonium and phosphate. The known concentrations of the other weak acid/bases are incorporated in the algorithm employed to calculate the $H_2CO_3^*$ alkanity, C_T and SCFA, i.e. their alkalinity contributions are removed from the measurements in the 5 pH point acid titration to give C_T, $H_2CO_3^*$ alkalinity and SCFA. The method also provides an estimate of any systematic pH measurement error, provided the carbonate subsystem dominates over the SCFA subsystem, i.e. C_T as $CaCO_3 > 2$ SCFA as acetic acid.

Introduction

In **Part 1** of this series (Moosbrugger et al., 1993a), a 4 pH point titration method was described that allows determination of the carbonate weak acid/base in aqueous solutions containing only the carbonate weak acid/base. In **Part 2** (Moosbrugger et al., 1993b), the 4 pH point titration method was extended to determine the carbonate weak acid/base in a mixture of weak acid/bases, provided the total species concentration of all the non-carbonate weak acid/bases is known. This would apply also if one of the non-carbonate weak acid/bases in the mixture is a short-chain fatty acid (SCFA). However, measurement of the total species concentration of the SCFA (A_T) by conventional methods involves considerable analytical skills and expensive equipment. In this paper the theory of the 4 pH point titration method is extended to a 5 pH point method, to obtain estimates of carbonate total species concentration (C_T), $H_2CO_3^*$ alkalinity, and A_T in mixtures of the carbonate and SCFA weak acid/bases with other weak acid/bases of known concentrations.

Theory

The theory of the 5 pH point titration method will be considered for two cases: Mixtures of carbonate and SCFA weak acid/bases only in aqueous solution, and mixtures of carbonate and SCFA plus phosphate and ammonium weak acid/bases where the last two are known quantitatively by their total species concentrations.

Mixture of carbonate and SCFA acid/bases

Consider a mixture of the carbonate and acetate (representing the SCFA) weak acid/bases in an aqueous medium. Selecting the most protonated species as reference species ($H_2CO_3^*$ and HAc respectively) the solution or system alkalinity at any pH relative to the solution reference state pH (Loewenthal et al., 1989) is:

$$H_2CO_3^*/HAc \ alk = \{[HCO_3^-]+2[CO_3^{2-}]\}+\{[Ac^-]\}+\{[OH^-]-[H^+]\} \tag{1}$$

The solution reference state pH (or the equivalence point pH) is that pH established when the molar masses of the weak acid/bases (say C_T and A_T) are dissolved in the solution in their reference state species, i.e. in this case $H_2CO_3^*$ and HAc.

Following Loewenthal et al. (1991), $H_2CO_3^*/HAc$ alk can be written as the sum of the subsystem alkalinities of the weak acid/bases and water:

$$H_2CO_3^*/HAc \ alk = Alk \ H_2CO_3^* + Alk \ HAc + Alk \ H_2O \tag{2}$$

where:

$$Alk \ HA = [Ac^-] \tag{3a}$$

$$Alk \ H_2CO_3^* = [HCO_3^-] + 2 \ [CO_3^{2-}] \tag{3b}$$

$$Alk \ H_2O = [OH^-] - [H^+] \tag{3c}$$

From Eq. (2), the masses of solution alkalinity and subsystems alkalinities contained in a sample at pH_1 are:

$$MH_2CO_3^*/HAc \ alk_1 = MAlk_1H_2CO_3^* + MAlk_1HAc + MAlk_1H_2O \tag{4}$$

With acid titration from pH_1 to pH_2, from Eq. (4) the molar mass decrease of the solution alkalinity and the subsystem alkalinities are:

$$\Delta MH_2CO_3^*/HAc \ alk_{1,2} = \Delta MAlk_{1,2}H_2CO_3^*+\Delta MAlk_{1,2}HAc+\Delta MAlk_{1,2}H_2O \tag{5}$$

where:

$$\Delta MH_2CO_3^*/HAc \ alk_{1,2} = MH_2CO_3^*/HAc \ alk_1 - MH_2CO_3^* /HAc \ alk_2 \tag{6a}$$

$$\Delta MAlk_{1,2}H_2CO_3^* = MAlk_1H_2CO_3^* - MAlk_2H_2CO_3^* \tag{6b}$$

$$\Delta MAlk_{1,2}HAc = MAlk_1HAc - MAlk_2HAc \tag{6c}$$

$$\Delta MAlk_{1,2}H_2O \qquad = MAlk_1H_2O - MAlk_2H_2O \qquad (6d)$$

The molar mass of H^+ added in titrating from pH_1 to pH_2 equals the molar mass decrease in solution alkalinity:

$$Ca\,V_{x1,2} = \Delta MH_2CO_3*/HAc\,alk_{1,2} \qquad (7)$$
$$= \Delta MAlk_{1,2}H_2CO_3*+\Delta MAlk_{1,2}HAc + \Delta MAlk_{1,2}H_2O \qquad (8)$$

where:

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

In Eq. (8), the water subsystem term ($\Delta MAlk_{1,2}H_2O$) can be calculated as set out in **Part 1** Eq. (33) (Moosbrugger et al., 1993a). The carbonate and acetate subsystem terms ($\Delta MAlk_{1,2}H_2CO_3*$ and $\Delta MAlk_{1,2}HAc$ respectively) remain as two unknowns. In **Part 1** Eq. (31), $\Delta MAlk_{1,2}H_2CO_3*$ is expressed as:

$$\Delta MAlk_{1,2}H_2CO_3* = MC_T\,X_{1,2} \qquad (9a)$$

where:

MC_T	= mass of carbonate total species in the sample (mol)
	= $C_T\,V_s$ (9b)
C_T	= carbonate total species concentration prior to titration (mol/ℓ)
V_s	= sample volume prior to titration (ℓ)
$X_{1,2}$	= function of pH_1 and pH_2 [see **Part 1** Eq. (30)].

Similarly, in **Part 2** Eq. (11) (Moosbrugger et al., 1993b), $\Delta MAlk_{1,2}HAc$ is expressed as:

$$\Delta MAlk_{1,2}HAc = MA_T\,Y_{1,2} \qquad (10a)$$

where:

MA_T	= mass of SCFA total species in the sample (mol)
	= $A_T\,V_s$ (10b)
A_T	= SCFA total species concentration prior to titration (mol/ℓ)
$Y_{1,2}$	= function of pH_1 and pH_2 [see **Part 2**, Eq. (11)].

In Eq (8), substituting for $\Delta MAlk_{1,2}H_2CO_3*$ and $\Delta MAlk_{1,2}HAc$ from Eqs. (9a) and (10a) respectively, and rearranging gives:

$$(Ca\,V_{x1,2} - \Delta MAlk_{1,2}H_2O) = MC_T\,X_{1,2} + MA_T\,Y_{1,2} \qquad (11)$$

This equation contains two unknowns (MC_T and MA_T) and hence cannot be solved - a second independent equation can be formed by titrating to a further pH point, say pH_3. Considering a titration between pH_2 and pH_3, Eq. (11) can be expressed as:

$$(Ca\,V_{x2,3} - \Delta MAlk_{2,3}H_2O) = MC_T\,X_{2,3} + MA_T\,Y_{2,3} \qquad (12)$$

where:

$V_{x2,3}$	= volume of strong acid added from pH_2 to pH_3 (ℓ).

From Eqs. (11) and (12), MC_T and MA_T, and accordingly C_T and A_T can be calculated. Thus by titrating between 3 pH points, from pH_1 to pH_2 to pH_3 (in effect a 4 pH point titration) to form the data pairs (pH_1; pH_2) and (pH_2; pH_3), theoretically it is possible to determine C_T and A_T. This approach would be valid

provided there is no systematic error in the pH measurement. However, if there is a systematic error in pH (ΔpH) then, for every different pH_1, pH_2, pH_3 selected, different values for C_T and A_T will be obtained. It is necessary therefore to develop a procedure which will:

- minimise the error in C_T and A_T with ΔpH present; and
- estimate ΔpH to further correct C_T and A_T, to give the most accurate estimates of C_T and A_T.

Minimising the error in C_T and A_T with ΔpH present

In **Part 1** (Moosbrugger et al., 1993a), the systematic error in pH measurement is expressed as:

$$\Delta pH = pH_{true} - pH_{obs} \qquad (13)$$

From **Part 1** Eq. (39), the error due to ΔpH in the carbonate subsystem alkalinity at any pH, $\Delta MAlkH_2CO_3*$ (ΔpH), is:

$$\Delta MAlkH_2CO_3* (\Delta pH) = MAlkH_2CO_3* (pH_{obs}) - MAlkH_2CO_3* (pH_{true}) \qquad (14)$$

Similarly, for the acetate subsystem:

$$\Delta MAlkHAc (\Delta pH) = MAlkHAc (pH_{obs}) - MAlkHAc (pH_{true}) \qquad (15)$$

These errors cannot be corrected for because ΔpH is not known. However, the behaviour of the error at any selected pH can be demonstrated as follows: Assume $\Delta pH = -0,04$ and MC_T and MA_T are unity. For a range of pH_{obs} values, calculate pH_{true} using Eq. (13) with $\Delta pH = -0,04$. In Eq. (9a), set $pH_1 = pH_{obs}$ and $pH_2 = pH_{true}$ and with MC_T unity, calculate $\Delta MAlk_{1,2}H_2CO_3* = \Delta MAlkH_2CO_3*$ (ΔpH). Similarly, in Eq. (10a) set $pH_1 = pH_{obs}$ and $pH_2 = pH_{true}$ and with MA_T unity calculate $\Delta MAlk_{1,2}HAc = \Delta MAlkHAc$ (ΔpH). Plots of $\Delta MAlkH_2CO_3*(\Delta pH)$ and $\Delta MAlkHAc(\Delta pH)$ are shown in Fig. 1.

4 pH point titration

From Fig. 1, the importance of selection of pH pairs in the 4 pH point titration to calculate $\Delta MAlk_{1,2}H_2CO_3$ and $\Delta MAlk_{1,2}HAc$ becomes apparent; the pH pairs need to be selected in such a way that the influence of ΔpH is minimised in Eqs. (11) and (12). This can be achieved by selecting one pH pair (pH_1;pH_2) approximately symmetrical around pK'_{ac1} and the other (pH_2;pH_3) approximately symmetrical around pK'_{aa}. This implies that pH_2 must lie midway between pK'_{ac1} ($\approx 6,3$) and pK'_{aa} ($\approx 4,75$), pH_3 must lie the same distance below pK'_{aa} as pH_2 is above it, and pH_1 must lie the same distance above pK'_{ac1} as pH_2 is below it, i.e. $pH_1 \approx 7,1$, $pH_2 \approx 5,5$ and $pH_3 \approx 4,0$ (see Fig. 1). A problem with this procedure is that the pH values are fixed, with the maximum pH, $pH_1 = 7,1$, so high that for many purposes one will have to add a strong base from pH_0 to give $pH_1 = 7,1$ before the titration can commence, an undesirable requirement.

With regard to the errors due to ΔpH, with the first data pair (pH_1;pH_2) the error due to ΔpH in the carbonate subsystem is virtually eliminated [calculation of $X_{1,2}$ in Eq. (11)], but the error due to ΔpH in the acetate subsystem is retained [calculation of $Y_{1,2}$ in Eq. (11)] . With the second pH data pair (pH_2;pH_3) the error due to ΔpH in the acetate subsystem is virtually eliminated [calculation of $Y_{2,3}$ in Eq. (12)], but the error due to ΔpH in the
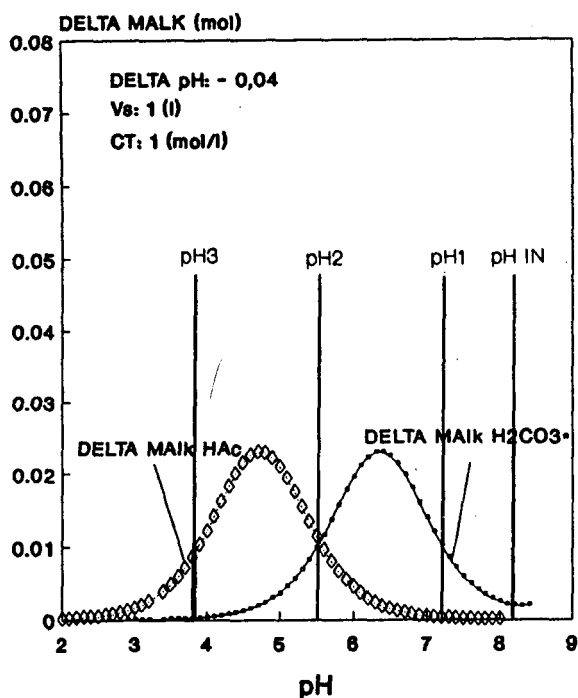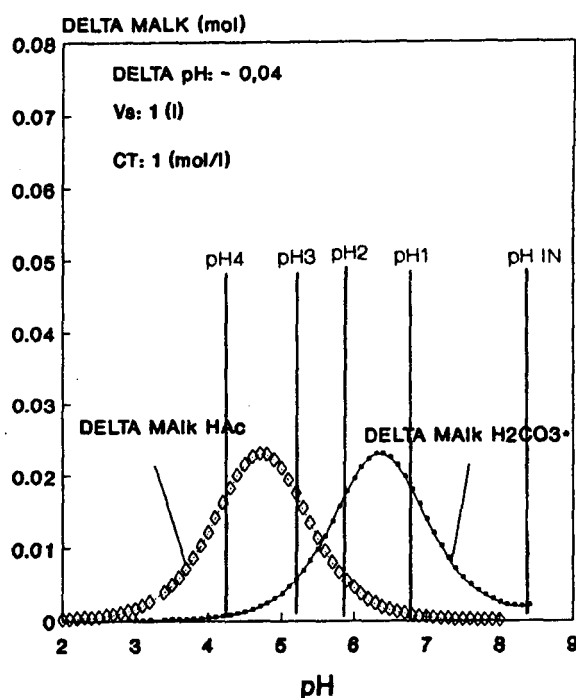
Figure 1

Theoretical implications of a systematic pH measurement error, ΔpH, on calculation of subsystem alkalinities: Error in calculation of MAlk H_2CO_3* and MAlk HAc over pH range, pH = 2,0 to pH = 8,5, caused by ΔpH = - 0,04 and MC_T equal to unity. Approximate location of pH points for 4 pH point titration

Figure 2

Theoretical implications of a systematic pH measurement error, ΔpH, on calculation of subsystem alkalinities: Error in calculation of MAlk H_2CO_3* and MAlk HAc over pH range, pH = 2,0 to pH = 8,5, caused by ΔpH = - 0,04 and MC_T equal to unity. Approximate location of pH points for 5 pH point titration

carbonate subsystem is retained [calculation of $X_{2,3}$ in Eq. (12)].

Reducing these remaining errors and providing greater freedom in selection of the pH points can be achieved by a titration from pH_0 to 4 pH points, pH_1, pH_2, pH_3, pH_4, a 5 pH point titration.

5 pH point titration

In the 5 pH point titration method (Fig. 2), pH_2 is replaced by two pH points between pK'_{ac1} and pK'_{aa}, pH_2 and pH_3; this gives greater freedom to selecting the symmetrical pH pairs around these two pK_a values. The first pH pair is approximately symmetrical around pK'_{ac1} (pH_1; pH_2) and the second approximately symmetrical around pK'_{aa} (pH_3; pH_4). From the two symmetrical pH pairs, the following set of equations can be established from Eqs. (11) and (12):

First set: (pH_1, pH_2) and (pH_3, pH_4), giving MC_{T1} and MA_{T1}

$$(Ca\ V_{x1,2} - \Delta MAlk_{1,2}H_2O) = MC_{T1}\ X_{1,2} + MA_{T1}\ Y_{1,2} \qquad (16)$$

$$(Ca\ V_{x3,4} - \Delta MAlk_{3,4}H_2O) = MC_{T1}\ X_{3,4} + MA_{T1}\ Y_{3,4} \qquad (17)$$

where:

Ca = normality of titrant added (moles/ℓ)
$V_{x1,2}$ = volume of titrant added between pH_1 and pH_2 (ℓ)
$V_{x3,4}$ = volume of titrant added between pH_3 and pH_4 (ℓ)

With regard to the errors in Eqs. (16) and (17) due to ΔpH, Eq.

(16) contains the virtual error free $X_{1,2}$, but ΔpH not being equal to zero, an error in $Y_{1,2}$ is retained. Equation (17) contains the virtually error free $Y_{3,4}$, but ΔpH not being equal to zero, an error in $X_{3,4}$ is retained. Hence, MC_{T1} and MA_{T1} calculated from Eqs. (16) and (17) still contain errors due to the terms $Y_{1,2}$ and $X_{3,4}$. Thus, by changing from the 4 to 5 pH point titration, greater freedom in selection of pH points is achieved, but the errors in C_T and A_T due to ΔpH are not eliminated (A detailed evaluation of these errors is given by Moosbrugger et al., 1992). To eliminate these errors, ΔpH needs to be evaluated. An estimate of ΔpH also is required to adjust pH_0 in order to calculate the H_2CO_3* alkalinity accurately.

Evaluation of ΔpH in the 5 pH point titration

With the 5 pH point titration, to evaluate ΔpH the focus is on the carbonate subsystem because invariably it dominates over the SCFA subsystem and will be affected by ΔpH to a greater extent than the SCFA subsystem. From the measured titration data in 5 pH point titration, in addition to the pH pairs above, we form an unsymmetrical pH pair around pK'_{ac1} (pH_1;pH_4) and retain the symmetrical pH pair around pK'_{aa} (pH_3;pH_4). With these two pH pairs a further set of two equations is formed from Eqs. (11) and (12):

Second set: (pH_1, pH_4) and (pH_3, pH_4), giving MC_{T2} and MA_{T2}

$$(Ca\ V_{x1,4} - \Delta MAlk_{1,4}H_2O) = MC_{T2}\ X_{1,4} + MA_{T2}\ Y_{1,4} \qquad (18)$$

$$(Ca\ V_{x3,4} - \Delta MAlk_{3,4}H_2O) = MC_{T2}\ X_{3,4} + MA_{T2}\ Y_{3,4} \qquad (19)$$

where:

$V_{x1,4}$ = volume of titrant added between pH_1 and pH_4 (ℓ).

The solution of Eqs. (18) and (19) provides a second value for MC_T, MC_{T2} and MA_T, MA_{T2}. Focusing on MC_T, if ΔpH is present, MC_{T2} will be lower than MC_{T1} provided the carbonate dominates over the SCFA weak acid/base, i.e. $MC_T \geq 2\ MA_T$. If MC_T dominates, by trial, the observed pH values can be adjusted incrementally, and MC_{T1} and MC_{T2} (also MA_{T1} and MA_{T2}) recalculated using the adjusted pH values; when the adjusted pH values give $MC_{T1} = MC_{T2}$, the adjusted pH values theoretically equal the error free pH values and the adjustment (ΔpH) gives the associated systematic error in pH. From the error free MC_{T1} and MA_{T1}, C_T and A_T can be calculated and are free from the influence of the systematic pH error. Experience with this method is that if $C_T < 2\ A_T$ no reliable estimate of ΔpH can be made. The reason for this is not yet clear, but possibly it is due to the solution procedure combined with the formulation of the 4 equations - in fact there are only three independent equations. This matter requires further investigation.

Algorithm for 5 pH point titration procedure

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

* Titrate the sample from its initial pH (pH_0) to four appropriately selected pH points, pH_1, pH_2, pH_3 and pH_4 (see section below).
* From the titration data for the symmetrical pH pairs (pH_1;pH_2) and (pH_3;pH_4), via Eqs. (16) and (17) calculate MC_{T1} and MA_{T1}.
* From the titration data for the unsymmetrical and the symmetrical pH pairs (pH_1;pH_4) and (pH_3;pH_4) respectively, via Eqs. (18) and (19) calculate MC_{T2} and MA_{T2}.
* Compare MC_{T1} and MC_{T2}. If different, pH_1, pH_2, pH_3 and pH_4 are all adjusted by ΔpH, and the MC_{T1} and MA_{T1} and MC_{T2} and MA_{T2} values recalculated. This step is repeated by progressively changing ΔpH until MC_{T1} equals MC_{T2}. When MC_{T1} equals MC_{T2} the adjusted pH values should closely equal their true pH values. The difference between the true and observed pH gives ΔpH, Eq. (13).
* From MC_{T1} and MA_{T1}, calculate C_T and A_T using Eqs. (9b) and (10b) respectively.
* With pH_0 corrected for ΔpH, calculate the sample $H_2CO_3^*$ alkalinity from C_T [Part 1, 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 [Part 1, Eq. (20)].

The above procedure applies only if $MC_T > 2MA_T$; if not, no reliable estimate of ΔpH can be made and C_T and A_T will contain errors due to ΔpH.

Optimal selection of pH points

In the selection of pH points for the 5 pH point titration, the following require consideration:

* For optimal pH probe calibration the titration range should be bracketed by the pHs of the buffer solutions, and kept as narrow as possible.
* The titration must span a pH range in which the proton accepting capacities of the carbonate and SCFA weak acid/bases are both appreciable.
* The first pH pair (pH_1;pH_2) must be formed approximately symmetrically around pK'_{ac1}. (pH_1;pH_2) must not be selected too far from pK'_{ac1}, because pH_1 might be greater than the initial pH (pH_0) in which event pH_0 must first be raised to pH_1 by strong base addition. Also, the pH pair must not be selected too close to pK'_{ac1} otherwise random errors in the pH and titration measurements become significant. From experience, the effect of random errors is contained if the pH pair is selected not less than 0,4 pH units from pK'_{ac1}, giving the smallest first symmetrical pH pair around pK'_{ac1} of approximately (pH_1;pH_2 = 6,7;5,9).
* The second pH pair (pH_3, pH_4) must be formed approximately symmetrical around pK'_{aa} = 4,75, also spaced more than 0,4 pH units away to give the smallest second symmetrical pH pair of (pH_3;pH_4 = 5,2;4;3).

From the criteria above, the optimal pH points are: pH_1 = 6,7; pH_2= 5,9; pH_3= 5,2; pH_4=4,3.

Determination of C_T and A_T in aqueous solutions containing known concentration of other weak acid bases

In **Part 2** (Moosbrugger et al., 1993b) a method was proposed to determine C_T in a solution containing carbonate and other weak acid bases of known concentration. This method can be extended directly to the 5 pH point method to determine C_T and A_T in a solution containing carbonate and acetate (unknown concentrations) and known concentrations of other weak acid bases. As an example, consider the weak acid/bases, ammonium and phosphate. Ammonium is a monoprotic weak acid/base; phosphate is polyprotic, but from **Part 2**, in the pH range 7,5 to 4 the phosphate subsystem can be considered monoprotic with a single dissociation constant $pK_{ap2} \approx 7,2$ and dissociation species $H_2PO_4^-$ and HPO_4^{2-}. Accepting the most protonated species for each weak acid/base as the reference species, one may write the solution alkalinity in terms of the subsystem alkalinities of the weak acid/bases in the solution:

$$H_2CO_3^*/HAc/NH_4^+/H_2PO_4^-alkalinity$$
$$= AlkH_2CO_3^* + AlkHAc + AlkNH_4^+ + AlkH_2PO_4^- + AlkH_2O \qquad (20)$$

From **Part 2**, in an acid titration between pH_1 and pH_2, the mass changes in solution and subsystem alkalinities can be expressed as:

$$\Delta MH_2CO_3^*/HAc/NH_4^+/H_2PO_4^-\ alkalinity_{1,2}$$
$$= \Delta MAlk_{1,2}H_2CO_3^* + \Delta MAlk_{1,2}HAc + \Delta MAlk_{1,2}NH_4^+$$
$$+ \Delta MAlk_{1,2}H_2PO_4^- + \Delta MAlk_{1,2}H_2O \qquad (21)$$

In the titration, the mass of H^+ added equals the mass decrease in solution alkalinity. Substituting into Eq. (21) for solution alkalinity and for $\Delta MAlk_{1,2}H_2CO_3^*$ and $\Delta MAlk_{1,2}HAc$ [from Eqs. (9a) and (10a) respectively] and rearranging in the form of Eq. (16) gives:

HAc MEASURED (mg/l)

4 pH POINT TITRATION

AQUEOUS SOLUTIONS OF NaHCO3 plus HAc

NaHCO3: 5,04 g/l
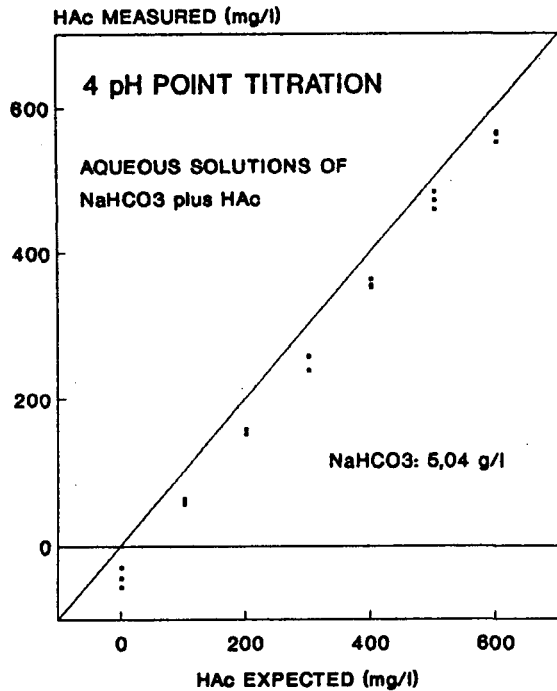
HAc EXPECTED (mg/l)

Figure 3
Made-up aqueous solutions of mixtures of HAc and NaHCO₃:
varying concentrations of HAc in base solution of
2 985mg NaHCO₃/ℓ as CaCO₃; measured HAc values were
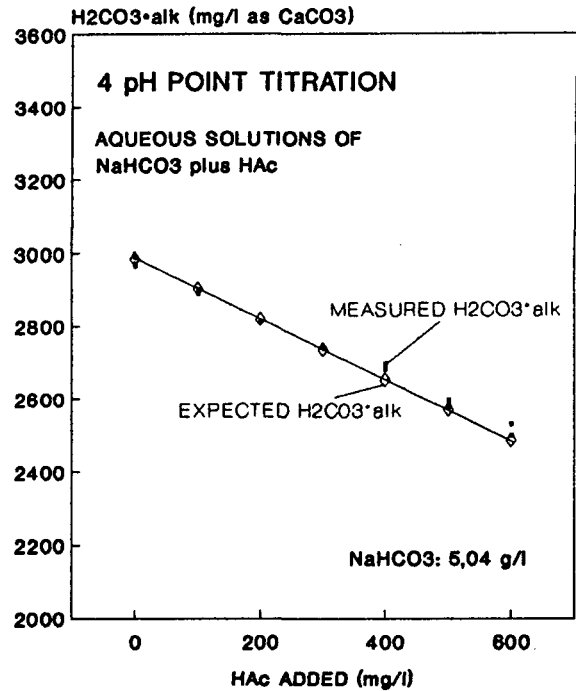*determined using 4 pH point titration method*

H2CO3·alk (mg/l as CaCO3)

4 pH POINT TITRATION

AQUEOUS SOLUTIONS OF NaHCO3 plus HAc

MEASURED H2CO3·alk

EXPECTED H2CO3·alk

NaHCO3: 5,04 g/l

HAc ADDED (mg/l)

Figure 4
Made-up aqueous solutions of mixtures of HAc and NaHCO₃:
varying concentrations of HAc in base solution of
2 985mg NaHCO₃/ℓ as CaCO₃; measured H₂CO₃* values were
determined using 4 pH point titration method

$$(Ca\ V_{x1,2} - \Delta MAlk_{1,2}NH_4^+ - \Delta MAlk_{1,2}H_2PO_4^- - \Delta MAlk_{1,2}\ H_2O)$$
$$= MC_{Ti}X_{1,2} + MA_{Ti}\ Y_{1,2} \qquad (22)$$

From **Part 2**, if the total species concentration of a weak acid/base is known, then the mass change in subsystem alkalinity for such a weak/acid base when titrating from pH_1 to pH_2 can be calculated and inserted into Eq. (22) [see **Part 2** Eqs. (16) and (19) for ammonium and phosphate respectively]. Similarly, the equations developed for the other pH pairs in the 5 pH point titration [Eqs. (17), (18) and (19)] can be appropriately modified, and due account taken of the additional weak acid/bases of known concentration in the procedure for determining C_T, A_T and ΔpH.

Experimental

All experiments were conducted at 20° C.

Solution containing only carbonate and SCFA weak acid/bases

4 pH point titration method

Solutions were made up (at different times) with an input C_T = H_2CO_3* alkalinity = 2 985 mg/ℓ as $CaCO_3$, using $NaHCO_3$, together with additions of glacial acetic acid (HAc) to give A_T = 100, 200, 300, 400 and 500 mg/ℓ as HAc. The solutions were titrated with standardised HCl from the initial pH (pH_0) to pH_1 ≈ 7,4, pH_2 ≈ 5,4 and pH_3 ≈ 4,1; pH_2 lies approximately mid-way between pK'_{ac1} and pK'_{aa}, pH_1 and pH_2 are approximately

symmetrical around pK'_{ac1} and pH_2 and pH_3 approximately symmetrical around pK'_{aa}. From these pH points two pH pairs were selected, (pH_1; pH_2), and (pH_2; pH_3). The algorithm employed to derive C_T and A_T using these two pH pairs has been set out earlier [Eqs. (11) and (12)].

Knowing C_T and the initial pH of the made up solution (pH_0), the H_2CO_3* alkalinity was calculated. H_2CO_3* alkalinity plays a key role in the practical evaluation of the buffering behaviour of an anaerobic digestion liquor; in contrast C_T is of limited interest. Accordingly, the focus was on the H_2CO_3* alkalinity - C_T is of importance only in so far it influences the accurate determination of H_2CO_3* alkalinity. The expected H_2CO_3* alkalinity, after each addition of HAc, was determined as follows: After addition of HAc, pH_0 ranged from about 8 (with 100 mg/ℓ HAc) to about 7 (with 600 mg/ℓ HAc). In this pH range the dissociation of HAc to Ac⁻ is virtually 100 per cent complete. (This can be checked from Eq. (4) in **Part 2**). Accordingly the input H_2CO_3* alkalinity (2 985 mg/ℓ as $CaCO_3$) was decreased by the alkalinity equivalent of HAc added - 1 mol HAc removes 1 mol H_2CO_3* alkalinity, or equivalently, 1 mgHAc removes 50/63 = 0,794 mg alkalinity as $CaCO_3$.

In Fig. 3 the measured A_T concentrations, and in Fig. 4 the expected and measured H_2CO_3* alkalinities are plotted versus the input A_T concentrations of the made-up solutions. Figure 3 shows an appreciable underestimation of A_T of approximately 45 mg/ℓ as HAc; Fig. 4 indicates a slight overestimate in the measured H_2CO_3* alkalinity, of approximately 20 mg/ℓ. These consistent errors may be attributed to the fact that the terms $Y_{1,2}$ in Eq. (11) and $X_{2,3}$ in Eq. (12) include an error resulting from ΔpH.
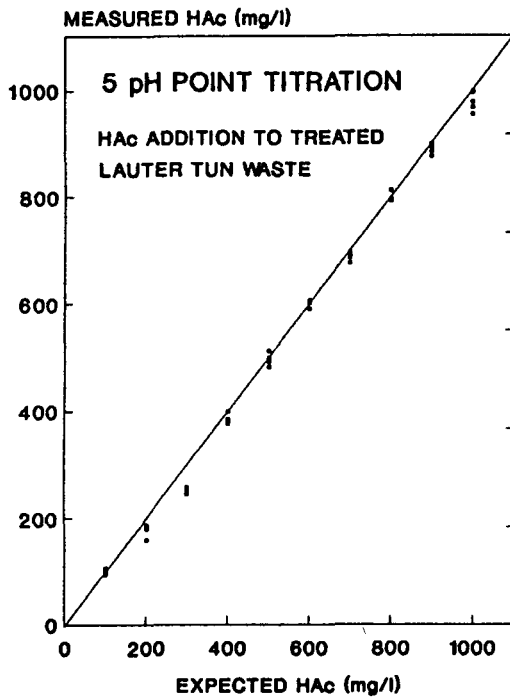
Figure 5
Made-up aqueous solutions of mixtures of HAc and NaHCO₃:
varying concentrations of HAc in base solution of 1 990 and
2 488 mg NaHCO₃/ℓ as CaCO₃; measured HAc values were
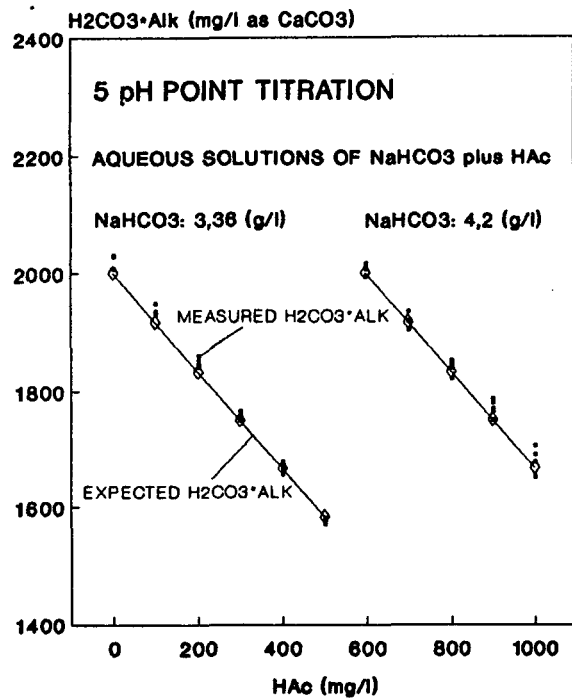*determined using 4 pH point titration method*

Figure 6
Made-up aqueous solutions of mixtures of HAc and NaHCO₃:
varying concentrations of HAc in base solution of 1 990 and
2 488 mg NaHCO₃/ℓ as CaCO₃; measured H₂CO₃* values were
determined using 5 pH point titration method

5 pH point titration method

Two sets of solutions were made up from $NaHCO_3$ and HAc. The first set had an input $C_T = H_2CO_3$* alkalinity = 1 990 mg/ℓ as $CaCO_3$ together with additions of HAc to give $A_T = 0$, 100, 200, 300, 400 and 500 mg/ℓ as HAc. The second set had an input $C_T = H_2CO_3$* alkalinity = 2 488 mg/ℓ as $CaCO_3$ together with additions of HAc to give $A_T = 600$, 700, 800, 900 and 1 000 mg/ℓ as HAc. The H_2CO_3* alkalinity in the second set was increased to ensure an initial pH greater than 6,7 at the higher A_T concentrations. The solutions were titrated with standardised HCl. For each A_T concentration, five replica titrations were performed, from its initial pH_0 to $pH_1 \simeq 6,7$ to $pH_2 \simeq 5,9$ to $pH_3 \simeq 5,2$ and to $pH_4 \simeq 4,3$. With these titration data, C_T, A_T and pH were determined, using the pH pairs (pH_1; pH_2 and pH_3; pH_4) and (pH_1; pH_4 and pH_3; pH_4) in the solution algorithm described earlier. From the adjusted pH_0 and C_T values, the H_2CO_3* alkalinity was calculated. For the first set of solutions with input H_2CO_3* alkalinity of 1 990 mg/ℓ, the expected H_2CO_3* alkalinity after each addition of HAc, was determined by subtracting the alkalinity equivalent of the HAc as described for the 4 pH point tests above. For the H_2CO_3* alkalinity input of 2 488 mg/ℓ, with the high A_T input ranging from 600 to 1 000 mg HAc/ℓ, the pH_0 declined below 7; the mass fraction of Ac⁻ formed was calculated from Eq. (4) **Part 2** and subtracted from the input H_2CO_3* alkalinity to give the expected alkalinity.

In Fig. 5 the measured A_T are plotted versus the respective expected values. This plot shows a high correlation; clearly the consistent error in A_T obtained with the 4 pH point method (Fig. 3) was eliminated. Figure 6 shows a plot of the measured and

expected H_2CO_3* alkalinity values versus A_T. This plot indicates little difference between the measured and expected H_2CO_3* alkalinity values, except in the range of high A_T additions ($A_T > 700$ mg/ℓ) where the measured H_2CO_3* alkalinities exceed their expected values. However, these deviations do not exceed 1,5 per cent.

Detection and estimation of ΔpH

The procedure in the 5 pH point titration method provides for the existence of a systematic pH measurement error, ΔpH. This error is estimated and taken into account in the calculation of the A_T C_T and H_2CO_3* alkalinity. It was now of interest to enquire whether the method would detect a deliberately faulty pH calibration.

A solution was made up with an input $C_T = H_2CO_3$* alkalinity = 1 990 mg/ℓ as $CaCO_3$ together with $A_T = 300$ mg/ℓ as HAc. Five replica titrations (5 pH point titrations) using standardised HCl were performed under each of the following conditions:

* *Stage 1*: Calibrate the pH probe with NBS buffer solutions (Radiometer, Copenhagen), pH = 7,02 and 4,00 (at 20° C).
* *Stage 2*: Using the same buffer solutions as in Stage 1, set the calibration points on the pH meter deliberately higher by 0,1 units to give 7,12 (at pH = 7,02 NBS buffer) and 4,1 (at pH = 4,00 NBS buffer).
* *Stage 3*: Again using the same buffer solution as in Stage 1, set the calibration points on the pH meter deliberately lower by 0,1 units, to give 6,92 (at pH = 7,02 NBS buffer) and 3,90 (at pH = 4,00 NBS buffer).

Using the 5 pH point titration methodology the values of A_T, $H_2CO_3^*$ alkalinity and ΔpH were calculated. Taking the averaged results for ΔpH for each stage, ΔpH (Stage 1) = - 0,07, ΔpH (Stage 2) = -0,18 and ΔpH (Stage 3) = + 0,05. The true pH is given by $pH_{true} = pH_{observed} + \Delta pH$. To determine whether the deliberately introduced pH calibration error was reflected in the calculated ΔpH, the ΔpH values from Stage 1 were compared to the values obtained from Stages 2 and 3; ΔpH values calculated at Stage 1 and 2 gave a difference of $[-0,07 - (-0,18)] = + 0,11$ pH units; the ΔpH values calculated at Stage 1 and 3 gave a difference of $[0,07 - (+ 0,05)] = -0,12$ pH units. In both instances the calculated differences in ΔpH (relative to Stage 1) correlate closely with the deliberately induced differences of +0,1 and −0,1 respectively. This indicates that the ΔpH calculated by the 5 pH point titration method indeed reflects systematic ΔpH measurement errors reasonably accurately.

The averaged A_T values for Stages 2 and 3 differed from the averaged results of Stage 1 by only +2 and −2 per cent respectively. The averaged $H_2CO_3^*$ alkalinity values for Stages 2 and 3 differed from the averaged results of Stage 1 by less than +0,5 percent in both instances. From this it may be concluded that by using the 5 pH point titration method the errors in the derived values of A_T and $H_2CO_3^*$ alkalinity due to systematic pH measurement errors are effectively eliminated.

Solutions containing other weak acid/bases of known concentrations in addition to the carbonate and SCFA weak acid/bases

In **Part 2** (Moosbrugger et al., 1993b) it was shown that if the ammonium and phosphate weak acid/bases are included in the algorithm of the 4 pH point titration method for the determination of C_T only, their effects on C_T can be eliminated. In this paper, the effects of these weak acid/bases have been incorporated also in the algorithm for the 5 pH point titration method to determine C_T and A_T; accordingly these latter two parameters can be obtained free from the influence of the ammonium and phosphate weak acid/bases. To account for the ammonium or phosphate their respective total species concentrations need to be known. It was now of interest to enquire what consequences the neglect or inaccurate determination of these two weak acid/bases would have on the estimates of A_T and C_T when using the 5 pH point titration method. In this enquiry the parameter C_T was preferred to $H_2CO_3^*$ alkalinity because C_T is independent of the initial pH of the sample and does not change with the addition of species of other weak acid/bases, e.g. NH_4^+. The effects of each of the two weak acid/bases were investigated separately.

Influence of the ammonium weak acid/base

From an investigation into the effect of the ammonium weak acid/base on the determination of C_T in aqueous solutions containing the carbonate and ammonium weak acid/bases, in **Part 2** it was concluded that the influence of an error in the total species concentration of the ammonium subsystem (N_T) can be reduced greatly by choosing the symmetrical pH pair (7,4; 5,4) instead of pH pair (8,3; 4,8), i.e. the first pH of the symmetrical pH pair located closer to pK'_{acl} and further away from pK'_{an} gave rise to smaller errors in C_T resulting from the presence of N_T. In the 5 pH point titration the first pH of the symmetrical pH pair around pK'_{acl} (6,7;5,9) is located even further away from pK'_{an}, and consequently the presence of N_T should have an even smaller

effect on C_T and A_T.

To assess experimentally the influence of an error in N_T on the 5 pH point titration, a solution was made up with NaHCO$_3$ giving an input $C_T = H_2CO_3^*$ alkalinity = 1 990 mg/ℓ as CaCO$_3$ with zero addition of A_T. On this solution a 5 pH point titration was performed. From the titration data, to assess the theoretical influence of an error in N_T the calculation for ΔpH, C_T and A_T was done with zero N_T and, assuming there was 500 mg/ℓ as N present. To account for the (in this case hypothetical) ammonium, the algorithm to calculate C_T and A_T was applied including this weak acid/base (see earlier). From this algorithm, C_T and A_T are obtained with N_T equal to zero, and equal to 500 mg/ℓ as N. Calculating C_T and A_T for the case of zero N_T addition gave C_T = 2 029 mg/ℓ as CaCO$_3$ and A_T = — 2 mg/ℓ as HAc. Calculating C_T and A_T for the case of the assumed N_T addition of 500 mg/ℓ as N gave C_T = 2 019 mg/ℓ as CaCO$_3$ and A_T = — 6 mg/ℓ as HAc. From these results it becomes clear that even with large errors of 500 mg/ℓ as N the influence of the error on the determination of C_T (and hence $H_2CO_3^*$ alkalinity) and A_T when using the 5 pH point titration method, is very small. Hence, errors in N_T are of little consequence in the determination of C_T and A_T.

Influence of the phosphate weak acid/base

In **Part 2** it was shown that for the 4 pH point titration in aqueous solutions containing the carbonate and phosphate weak acid/bases, neglecting the total species concentration of the phosphate weak acid/base (P_T) had a significant influence on the value of C_T irrespective of the choice of the symmetrical pH pairs. It may be expected accordingly that an error in P_T also would influence the value of C_T, and possibly A_T, when using the pH pairs of the 5 pH point titration method. To assess this effect on C_T and A_T, the following tests were carried out:

Solutions were made up with an input $C_T = H_2CO_3^*$ alkalinity = 1 990 mg/ℓ as CaCO$_3$ together with additions of K$_2$HPO$_4$ to give $P_T \approx 0$, 33, 65 and 98 mg/ℓ as P and zero HAc. Using standardised HCl, three replica titrations where performed from the initial pH to 6,7 to 5,9 to 5,2 and 4,3, giving a 5 pH point titration.

From the measured titration data, two sets of values for A_T and C_T were calculated: (1) taking into account the presence of the phosphate weak acid/base to give A_{T1} and C_{T1}; and (2) neglecting the presence of the phosphate weak acid/base (i.e. P_T = 0) to give A_{T2} and C_{T2}. To estimate the errors induced in A_T and C_T by not correcting for the presence of the phosphate weak acid/base, the values of A_T and C_T in the tests in which zero phosphate had been added were averaged and accepted as the best estimates for A_T and C_T in the set of tests. These values were subtracted from their respective A_{T1} and C_{T1} values to give ΔA_{T1} and ΔC_{T1} and, from their respective A_{T2} and C_{T2} values to give ΔA_{T2} and ΔC_{T2}. In Fig. 7 ΔA_{T1} and ΔA_{T2} are plotted versus the phosphate concentrations, and in Fig. 8 ΔC_{T1} and ΔC_{T2} are plotted versus the phosphate concentrations. From these plots it is evident that phosphate has very little effect on the determination of the SCFA via the 5 pH point titration method; that is, in the determination of A_T, knowledge of the phosphate concentration is not necessary. However, the effect of phosphate is significant in the determination of the carbonate weak acid/base: 100 mg/ℓ (as P) causes an error in C_T of 90 mg/ℓ (as CaCO$_3$). Hence, if accurate determination of C_T or $H_2CO_3^*$ alkalinity is required the concentration of P_T needs to be known accurately.
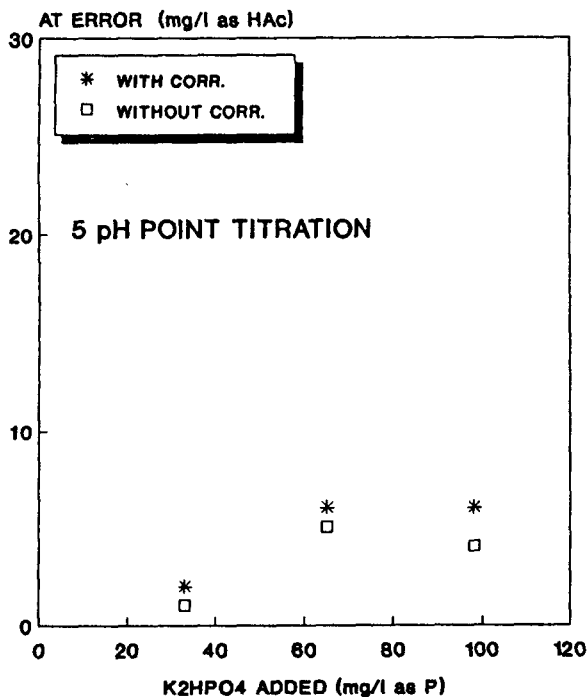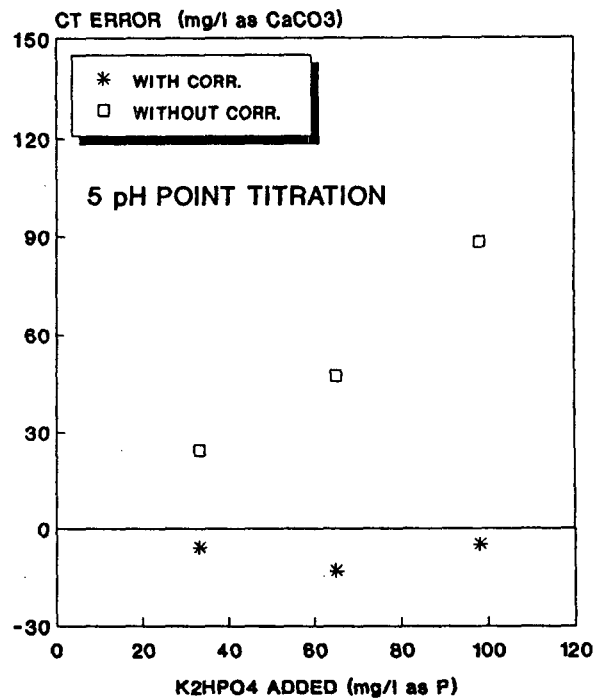
Figure 7

Effect of error in total species concentration of phosphate subsystem on determination of A_T by the 5 pH point titration; varying concentrations of K_2HPO_4 in base solution of 1 990 mg $NaHCO_3/\ell$ as $CaCO_3$. Two values were determined for A_T: (1) taking into account the phosphate subsystem giving a corrected A_T; and (2) not taking into account the phosphate subsystem giving an uncorrected A_T. Both A_T values were subtracted from a separately determined expected A_T value to give the respective errors

Figure 8

Effect of error in total species concentration of phosphate subsystem on determination of A_T by the 5 pH point titration; varying concentrations of K_2HPO_4 in base solution of 1 990 mg $NaHCO_3/\ell$ as $CaCO_3$. Two values were determined for C_T: (1) taking into account the phosphate subsystem giving a corrected C_T; and (2) not taking into account the phosphate subsystem giving an uncorrected C_T. Both C_T values were subtracted from a separately determined expected C_T value to give the respective errors

Industrial wastes augmented with different concentrations of HAc

Having analysed the potential errors of the 5 pH point titration method on made-up solutions, the method was now applied to real life aqueous wastes. The difficulty here was that the weak acid/bases in the samples were unknown and needed to be determined. To evaluate the reliability of the 5 pH point titration method for these solutions, one approach would be to augment the solution with a known mass of, say, HAc and check if the derived estimates reflect the increase in HAc. In this fashion the effluents from laboratory-scale UASB reactors treating brewery (lauter tun) and wine distillery wastes were tested. In both instances the 5 pH point titration method and a colorimetric test for SCFA (Montgomery et al., 1962) indicated that the effluent contained low concentrations of SCFA.

The test procedure was as follows: On a filtered sample (filter paper, Schleicher und Schuell 505) taken from the reactor effluent, the ammonium and phosphate concentrations of the sample were determined according to Standard Methods (1989). The ionic strength of the sample was approximated through measurement of the specific conductivity (Loewenthal et al., 1989). A 5 pH point titration was carried out and, using the algorithm including the ammonium and phosphate effects, the SCFA (as A_T) H_2CO_3* alkalinity and ΔpH were determined. Following this, a further five samples from the same effluent

batch were prepared identically to the first sample and augmented with a selected concentration of HAc, say A_T = 100 mg/ℓ as HAc. On each augmented sample a 5 pH point titration was performed to determine A_T, H_2CO_3* alkalinity and ΔpH. This procedure was repeated daily on new batches of effluent, but with each new batch the samples were augmented with an increased concentration of HAc in the following steps, $A_T \approx$ 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1 000 mg/ℓ as HAc. In this manner, over a period of ten days, ten sets of data were obtained for the brewery waste; likewise over ten days, ten sets of data were obtained for the wine distillery waste.

To evaluate the accuracy of the measured results of A_T the HAc added was measured by subtracting the SCFA concentration (given as HAc) of the sample not augmented with HAc from the respective sample augmented with HAc. To evaluate the accuracy of the measured results of H_2CO_3* alkalinity, the expected values had to be determined, as follows: On addition of HAc the pH of the solution declines causing both the carbonate and phosphate subsystem alkalinities to decrease. The decrease in the solution alkalinity [carbonate + phosphate + water subsystem alkalinities, see Eq. (20)] is equal to the alkalinity equivalent of the HAc added. The change in phosphate subsystem alkalinity (ΔAlk $H_2PO_4^-$) can be calculated using Eq. (19) Part 2 from the pH before and after HAc addition. The H_2CO_3* alkalinity (Δ carbonate + Δ water subsystem alkalinities by definition) is then given by the alkalinity equivalent of HAc
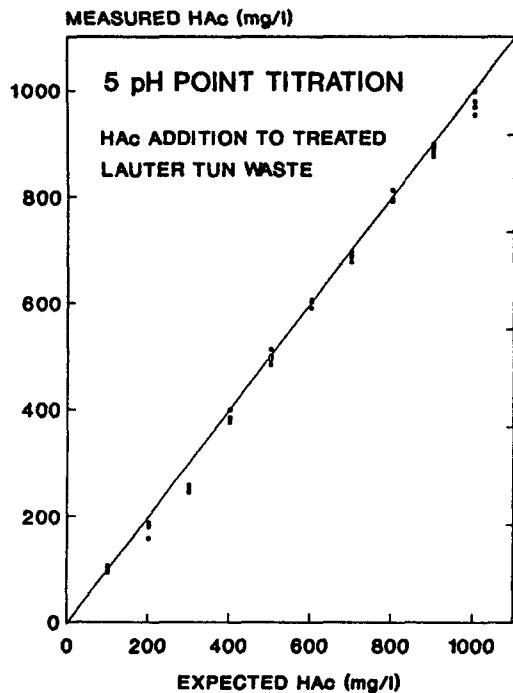
Figure 9

Addition HAc to treated (in laboratory UASB reactor) lauter tun waste and measurement of added (expected) HAc concentrations by the 5 pH point titration method
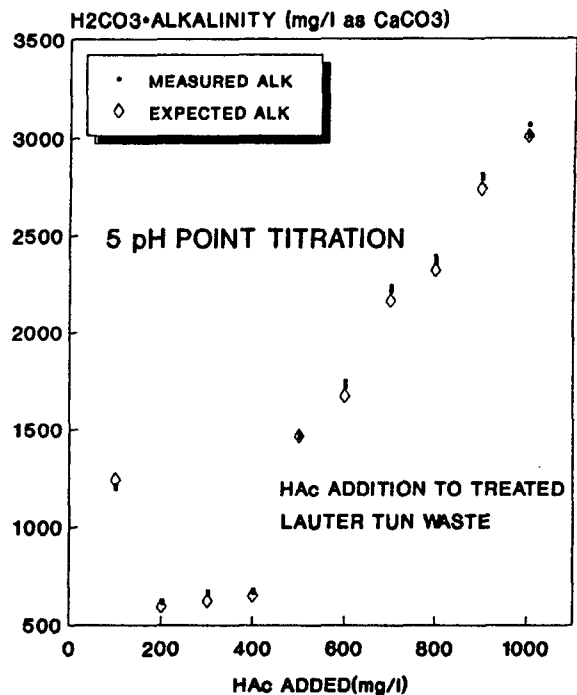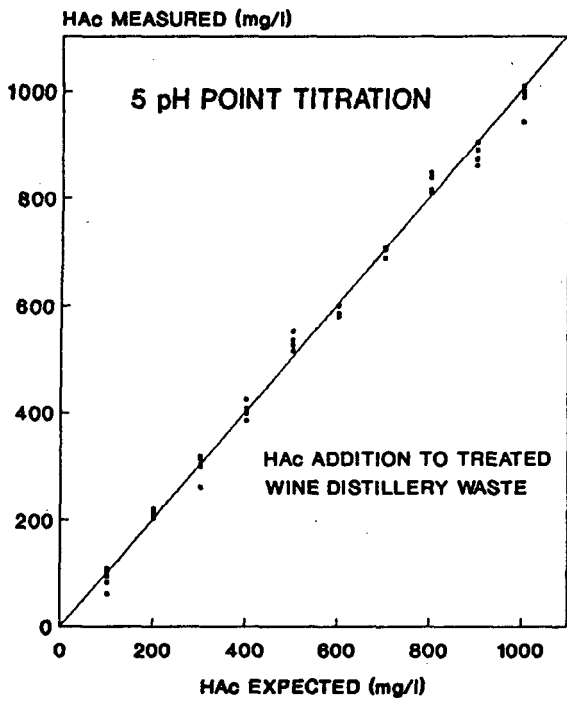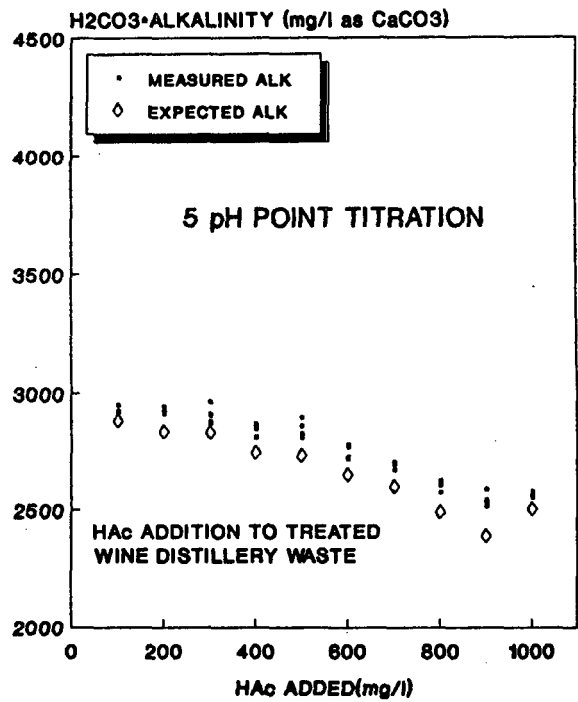

Figure 10

Addition of HAc to treated (in laboratory UASB reactor) lauter tun waste and measurement of $H_2CO_3^*$ alkalinity after addition of HAc. These results were obtained over a period of time under different operating conditions, i.e. different $H_2CO_3^*$ alkalinities in the UASB reactor effluent

added less ΔAlk $H_2PO_4^-$. Hence, the expected $H_2CO_3^*$ alkalinity after HAc addition is ($H_2CO_3^*$ alkalinity before HAc addition – $\Delta H_2CO_3^*$ alkalinity).

In Figs. 9 and 11 the measured A_T added for the brewery and wine distillery wastes respectively are plotted versus the known added A_T. In Figs. 10 and 12 the expected and measured $H_2CO_3^*$ alkalinities of the brewery and wine distillery wastes are plotted versus the added A_T. The plots in Figs. 9 and 11 show close correlation between the measured and added A_T values indicating that the 5 pH point titration is capable of detecting, quite accurately, accumulation of A_T in the UASB reactor effluent treating the two types of wastes. The plots in Figs. 10 and 12 show that in general the measured $H_2CO_3^*$ alkalinity was consistently higher than the expected; the deviations averaged about 3 per cent, with a maximum deviation of 5 per cent. A possible reason for this deviation may be that weak acid/bases other than the carbonate, ammonium and phosphate were present in the sample thereby also buffering against pH change on addition of HAc. This would lead to a higher initial pH of the sample and, consequently, to an increase in measured $H_2CO_3^*$ alkalinity.

Conventional chemical versus 5 pH point titration method

In the experiments above, the 5 pH point titration method had been tested for HAc in solutions containing various concentrations of $H_2CO_3^*$ alkalinity and in some cases, the phosphate and ammonium subsystems. However, in anaerobic digester liquids, besides acetic acid other SCFA, e.g. propionic

and butyric acid, are also present. Because the pK_a values of the different SCFA are located closely together, the SCFA subsystem is treated as equivalent acetic acid when determined via the 5 pH point titration method. To enquire if this approach to determining the SCFA is valid, the 5 pH point titration was compared to the conventional chemical method for SCFA developed by Montgomery et al. (1962) on samples taken daily from the effluent of laboratory-scale UASB systems treating brewery and wine distillery wastes.

Samples were filtered (Schleicher und Schuell, 505 filter paper), subsequently divided and tested for A_T using the 5 pH point titration method, and using the method of Montgomery et al. (1962). Montgomery's method involves spectrophotometry, and experience with the tests on the samples showed that this method is very susceptible to residual colour present in the sample. Through comparison with gas chromatography it was found that colour removal prior to testing was necessary to obtain reliable results. Accordingly, in subsequent tests the samples were flocculated using aluminium sulphate (8 mℓ of saturated aluminium sulphate per 100 mℓ of sample) to remove the colour. Flocculant addition influenced the alkalinity of the sample but this did not present a problem as the objective was to evaluate the equivalence of the two methods for determining the SCFA. In Montgomery's method the samples were diluted into the appropriate range of optimal accuracy, SCFA below 600 mg/ℓ. Samples were tested over a period of about 40 d. The results were subdivided into the results obtained from brewery and wine distillery waste.

In Fig. 13 the results for A_T from 5 pH point titration method are plotted versus those from Montgomery's method for the

HAc MEASURED (mg/l)

Figure 11
Addition of HAc to treated (in laboratory UASB reactor) wine
distillery waste and measurement of added (expected) HAc
concentrations by the 5 pH point titration method

H2CO3·ALKALINITY (mg/l as CaCO3)

Figure 12
Addition of HAc to treated (in laboratory UASB reactor) wine
distillery waste and measurement of H_2CO_3* alkalinity after
addition of HAc. These results were obtained over a period of
time under different operating conditions, i.e. different H_2CO_3*
alkalinities in the UASB reactor effluent

SCFA CHEM (mg/l as HAc)
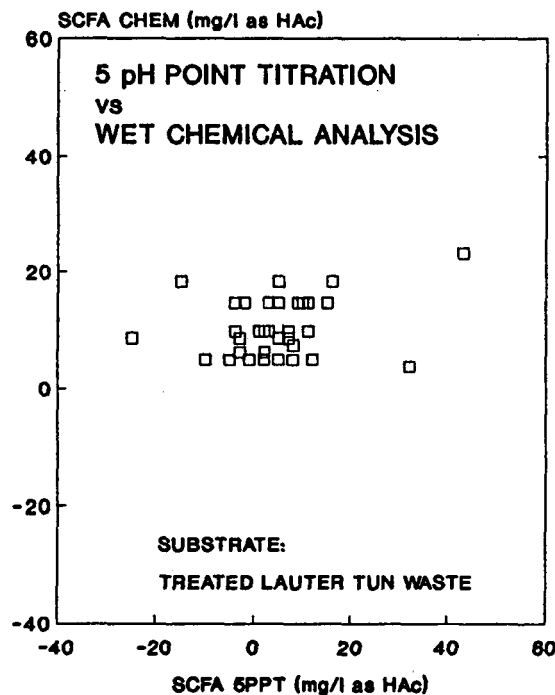
Figure 13
Comparison of results for SCFA obtained through wet chemical
analysis (Montgomery's method) and 5 pH point titration:
Samples taken from laboratory-scale UASB reactor treating
lauter tun waste under low COD loading conditions
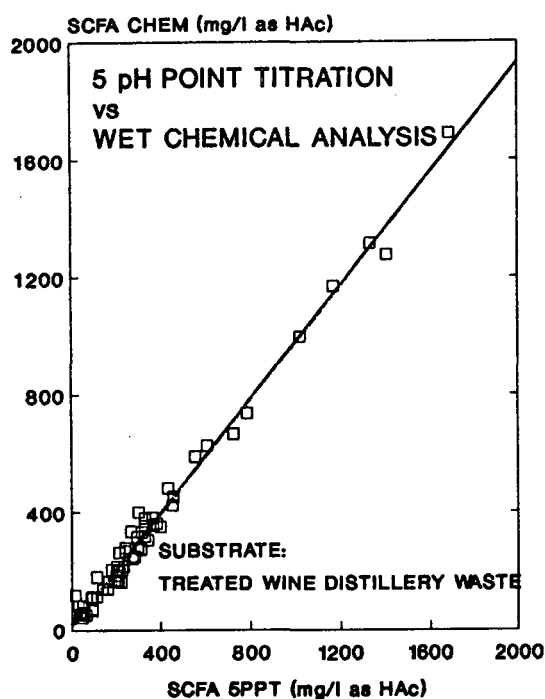
Figure 14
Comparison of results for SCFA obtained through wet chemical analysis (Montgomery's method) and 5 pH point titration: Samples taken from laboratory-scale UASB reactor treating wine distillery waste under low and high COD loading conditions. Correlation coefficient = 0,98

system treating brewery waste. This system was operated at a low COD loading rate and thus produced very low SCFA (represented by A_T). Nevertheless, the plot shows that at very low concentrations of SCFA the two methods are in reasonable agreement.

In Fig. 14 the results from the 5 pH point titration method are plotted versus those from Montgomery's method for the UASB system treating wine distillery waste. During the period these tests were done, the UASB system loading rate changed from lightly loaded to an overloaded condition giving rise to SCFA that ranged from zero to 1 800 mg/ℓ. The two methods are in close correlation; the errors appear to be random and may be due to measurement errors in both methods.

Discussion and conclusions

In this paper it has been shown that the 5 pH point titration method has great potential as a testing procedure for the $C_T/H_2CO_3^*$ alkalinity and SCFA for the purpose of monitoring anaerobic digesters. Compared to other similar titration procedures reported in the literature, the method is an improvement with regard to attainable accuracy; testing time required; and simplicity of testing procedure.

The method can be applied to aqueous solutions containing mixtures of the carbonate and SCFA weak acid/bases, both of unknown concentrations and other weak acid/bases (e.g. phosphate, ammonium and sulphide) of known total species concentrations. Knowing the species concentrations of these

weak acid/bases, provision is made to eliminate their influence on the determination of C_T (and $H_2CO_3^*$ alkalinity) and SCFA. Examples of two weak acid/bases prominent in anaerobic digestion are ammonium and phosphate. Their influences are as follows: With the ammonium weak acid/base, if neglected in the calculation, the errors induced in the determination of C_T (and $H_2CO_3^*$ alkalinity) and SCFA are very small and negligible in most cases. With phosphate, its neglect, or even an incorrect concentration, will give rise to a minor error in the estimation of SCFA, but a substantive error in the estimation of $H_2CO_3^*$ alkalinity. Whether the error in $H_2CO_3^*$ alkalinity is considered significant will depend on the accuracy demanded.

The method can be readily automated if the initial pH of the sample is > 6,7; in this event only a strong acid titration is required to the four lower pH points. If the initial sample pH is < 6,7 the pH needs to be raised to $\sim$ 6,7 by addition of strong base. The requirement here is only to raise the pH; it is not necessary to standardise the strong base, but the volume of the strong base added must be noted in addition to the volumes of acid to titrate from pH_1 (6,7 ± 0,1) to the lower pH values, similar to the situation where pH_0 > 6,7.

The method allows a check on the pH probe and provides an estimate of the systematic pH error where this may be present due to poor calibration or due to the residual liquid junction and other effects. If C_T < $2A_T$ the calculation of the pH error (ΔpH) becomes uncertain. In this event the calculated values of A_T and $H_2CO_3^*$ alkalinity also will become less accurate. However, in anaerobic digestion this situation will arise only when the system is failing and then accurate values for A_T and $H_2CO_3^*$ alkalinity are not crucial for control.

Closure

The theory of the 5 pH point titration method is elaborate and calculation of the results by hand is not practical. However, the experimental procedure for the 5 pH point titration requires little experimental effort and skill, and the calculation procedures can be readily coded into a computer program (Source code (Turbo Pascal) and executable versions of such a computer program are available from the Water Research Commission, PO Box 824, Pretoria 0001, South Africa).

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