Weak acid/bases and pH control in anaerobic systems — A review

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Abstract

This paper briefly reviews the practical approaches that have been developed to evaluate and control anaerobic fermentation processes. Practical parameters considered are the H_2CO_3* alkalinity, short-chain fatty acid (SCFA) concentrations and pH. Various methods have been developed to determine either (1) the H_2CO_3* alkalinity or SCFA, (2) both the H_2CO_3* alkalinity and SCFA but approximately only, or, (3) an approximate H_2CO_3* alkalinity: SCFA ratio. None of these methods are entirely satisfactory for routine monitoring and control, being either too approximate or too elaborate in their analytical procedures. With the increased understanding of mixed weak acid/base chemistry, there is potential to develop a relatively simple acid titration procedure to give both the H_2CO_3* alkalinity and SCFA concentration reasonably accurately.

Introduction

In anaerobic fermentation a number of different microbial species contribute to the breakdown of soluble organic compounds to carbon dioxide and methane (Mosey and Fernandes, 1989; Sam-Soon et al., 1987). The main groups of bacterial species and the reactions they mediate are:

- acidogens: convert influent COD to acetic (HAc), propionic (HPr) and butyric (HBr) acid;
- acetogens: convert HPr and HBr to HAc;
- hydrogenotrophic methanogens: convert H_2 and CO_2 to CH_4; and
- acetoclastic methanogens: convert HAc to CH_4.

Each of these groups has a specific pH region for optimal growth; for acidogens a pH ≃ 6, for acetogens, hydrogenotrophic and acetoclastic methanogens a pH ≃ 7 (Gujer and Zehnder, 1983). The relative rates of growth of these groups change with pH. Under normal operating conditions in anaerobic digestion (see below), Mosey and Fernandes (1989) report the following average doubling times: acidogens: 30 min; acetogens: 1,4 d; hydrogenotrophic methanogens: 6 h; acetoclastic methanogens: 2,6 d. To ensure optimal breakdown one condition that must be satisfied is to provide optimal pH conditions for the slowest growing organism group. From Mosey's work, the acetoclastic methanogens are the rate limiting group; their growth rate is at its maximum at pH ≃ 7,0 but falls sharply at pH < 6,6. Consequently, it is essential to maintain the pH > 6,6. Thus, information on the pH and on the factors causing/resisting change in pH is essential to ensure pH neutrality for the successful operation and control of the anaerobic system.

In anaerobic treatment systems, decline in pH would be due principally to an increase in short-chain fatty acids (SCFA). Increase in SCFA can be induced by a number of factors:

- Complete or partial phase separation of the acidogenic and methanogenic phases would result in an accumulation of SCFA in the acidogenic phase, and a decline of SCFA in the subsequent methanogenic phase. For example, in a plug flow or semi plug flow reactor like the upflow anaerobic sludge bed (UASB) reactor, along the axis of the reactor there is partial phase separation causing an increase in SCFA from the influent entry point to a maximum at some point in the reactor sludge bed, thereafter a decrease in SCFA to near zero at the top of the sludge bed.
- The hydrogen partial pressure ($\bar{p}H_2$) also has a crucial effect on fermentation. For example, glucose is fermented first to pyruvic acid, via the Embden-Meyerhof pathway, and thereafter the pathways depend on the $\bar{p}H_2$ conditions: Under low $\bar{p}H_2$ conditions pyruvic acid is converted to HAc only, whereas under high $\bar{p}H_2$ conditions HAc and the intermediate HPr are formed. Also with a high $\bar{p}H_2$ in the reactor, the conversion of HPr to HAc by the acetogenic organisms is inhibited; these give rise to an increase in HPr and consequentially to an overall increase in SCFA.
- Toxins or inhibitory substances in the influent may act on the methanogenic phase only, causing an accumulation of SCFA.

The magnitude of the decline in pH induced by increased SCFA may be insubstantial due to the "pH buffering agents" in the reactor which would resist the pH change. However, an increase in SCFA in the effluent is in itself undesirable; it causes the effluent COD to increase, decreases gas production and the methane content of the gas. Accordingly, to manage and control an anaerobic system, information on pH, $\bar{p}H_2$, SCFA (HAc and HPr), effluent COD, gas production rate, gas composition and "buffering agents" is desirable. The parameters pH, effluent COD, gas production rate and gas composition can be measured routinely: pH by means of a pH electrode (for plug flow systems pH profiles should be measured along the axis of the reactor, Sam-Soon et al., 1987), effluent COD by conventional wet chemical methods, gas production by gas flow meters and gas composition by Orsat-type apparatus. Measurement of $\bar{p}H_2$ requires a rather sophisticated technique quite inappropriate for routine monitoring and hence its magnitude is inferred indirectly from the behaviour of the SCFA, HAc and HPr. Separate measurement of HAc and HPr in SCFA requires a gas chromatograph, an instrument, however, not usually available on full-scale anaerobic installations in South Africa. Monitoring and measurement of "buffering agents" are of great importance, but this aspect is complex and warrants more detailed attention.

In this paper the intention is to identify the "buffering agents" present in anaerobic treatment systems and to review the

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practical approaches that have been developed to measure these and the SCFA.

pH buffering in anaerobic digestion

As noted earlier, in anaerobic treatment systems under "unbalanced" or transient process operation SCFA may accumulate and constitute a major cause for pH change. The magnitude of pH change will depend on the magnitude of increase in SCFA concentration and the pH buffering. By pH buffering is meant the "ability" of the solution to resist change in pH on addition of H^+ or OH^- (in any form, i.e. strong acid or base, weak acid/base). All weak acid/bases present in the solution and the water itself contribute in a greater or lesser degree to the pH buffering. Weak acid/bases most commonly found in anaerobic fermentation are the carbonate, ammonium, phosphate, sulphide and SCFA (principally HAc and HPr, Pohland and Martin, 1969). The relative contribution of each of these can be illustrated via species concentration and a parameter called buffer index.

Species concentration

In evaluating the contribution of each weak acid/base and the water to solution buffering, the relationships defining the individual species concentration at any pH are useful.

Weak acid/base

For a monoprotic weak acid/base, HA, the dissociation and equilibrium equations can be formulated as (Loewenthal et al., 1989):

$$HA \rightleftharpoons A^- + H^+ \quad (1)$$

$$\frac{(A^-)\,(H^+)}{(HA)} = K_a \quad (2a)$$

i.e.

$$\frac{[A^-]\,(H^+)}{[HA]} = K_a/f_m = K_a' \quad (2b)$$

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

where:

$[\,]$ = concentration (mol/ℓ)
$(\,)$ = activity (mol/ℓ)
K_a, K_a' = thermodynamic and apparent dissociation constants respectively (mol/ℓ)
f_m = monovalent activity coefficient, i.e. $(\,) = f_m [\,]$
A_t = total species concentration of the weak acid/base (mol/ℓ)

From Eqs. (2) and (3) the individual species concentrations $[A^-]$ and [HA] can be expressed in terms of A_t and (H^+) as follows:

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

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

where:

$(H^+) = 10^{-pH}$

Changes in $[A^-]$ and [HA] with pH can be plotted from Eqs. (4) and (5). Similar equations can be developed for di- and triprotic weak acid/bases.

Water

For the water, the equilibrium expression is given by:

$$(H^+)\,[OH^-] = K_w/f_m = K_w' \quad (6)$$

where:

K_w and K_w' = thermodynamic and apparent ionic product constants respectively for the water; K_w is temperature dependent and equal to 10^{-14} $(mol/ℓ)^2$ at 25 °C.

The species concentrations can be written in terms of pH as follows:

$$[H^+] = 10^{-pH}/f_m \quad (7)$$

Rearranging Eq. (6)

$$[OH^-] = 10^{(pK_w' - pH)} \quad (8)$$

where:

$pK_w' = -\log K_w'$

Changes in $[H^+]$ and $[OH^-]$ with pH can be plotted from Eqs. (7) and (8).

Buffer index

The buffering action of a weak acid/base in solution is demonstrated practically by titrating the solution with a strong acid or a strong base. By plotting the cumulative masses of strong acid (Ca) or base (Cb) added versus pH, a titration curve is obtained. The slope of this curve (dCa/dpH or dCb/dpH), at any pH, defines the buffer index ß (Van Slijke, 1922):

$$ß = -\,dCa/dpH = dCb/dpH \quad (9)$$

where:

Ca, Cb = mass of strong acid or strong base added per litre respectively (mol/ℓ)
ß = buffer index, mol/(ℓ · Δ pH)

Note: since the solution is titrated with a strong acid or base, the total species concentration of the weak acid/base remains constant.

An aqueous solution containing a single weak acid/base can be looked upon as a system that is made up of two subsystems, the weak acid/base and water (Loewenthal et al., 1991). Theoretically ß at any pH for the two subsystems can be formulated as follows:

Weak acid/base subsystem

For a monoprotic weak acid/base subsystem its buffer index, ßa, can be formulated in terms of A_t, (H^+) and K'_a as follows (Loewenthal and Marais, 1976):

$$ß_a = - dCa/dpH = 2{,}303\ [A_t\ K'_a\ (H^+)]/\ [K'_a+(H^+)]^2 \qquad (10)$$

For a diprotic weak acid/base, with dissociation constants pK'_{a1} and pK'_{a2} ($pK'_a = -\log_{10} K'_a$), provided the two dissociation constants differ by 4 pH units or more, the buffer index in the pH region around each pK'_a value can be described sufficiently accurately by Eq. (10) (Loewenthal and Marais, 1976).

Water subsystem

For the water subsystem, the buffer index is given by

$$ß_w = 2{,}303\ \{(H^+) + K'_w/(H^+)\} \qquad (11)$$

System

For an aqueous solution containing one weak acid/base, the buffer index of the system, ß, at any pH is given by the sum of the buffer indices of the weak acid/base and the water subsystems:

$$ß = ß_a + ß_w \qquad (12a)$$

Similarly, for an aqueous solution containing more than one weak acid/base, the buffer index of the system, ß, at any pH is given by the sum of the buffer indices of all the weak acid/base subsystems and the water subsystem:

$$ß = ß_{a1} + ß_{a2} + ß_{a3} + \ldots + ß_w \qquad (12b)$$

where:

$ß_{a1}$, $ß_{a2}$, $ß_{a3}$ refer to the buffer indices for the weak acid/base subsystems 1, 2 and 3 respectively.

Species concentration and buffer index - pH diagrams

For the water and the weak acid/bases usually present in anaerobic digestion, species concentrations vs pH (log[species] - pH diagram) can be plotted from Eqs. (4), (5), (7) and (8) and the associated buffer index curves from Eqs. (10) and (11) using the appropriate constants for each weak acid/base, see Fig. 1(a) to (f). The SCFA are represented by acetic acid because the pKa values of the various SCFA typically present in the digester liquid (acetic, propionic and butyric), differ only slightly.

Referring to Fig. 1, the height of the buffer index curve at a selected pH gives an indication of the "ability" of the weak acid/base to resist a change in pH if strong acid or base is added. Between any two pH points, the area under the buffer index curve gives the mass of H^+ ions to be added or removed to bring about the pH change, termed proton accepting/donating capacity respectively. The buffer index diagrams illustrate the following:

- The buffer index for a weak acid/base subsystem is at a maximum where the pH equals the dissociation constant pK_a, i.e. where the component weak acid/base species are in equal concentration.
- The buffer index decreases rapidly on either side of a pK_a value and becomes negligible within two pH units, giving rise to a bell shaped buffering index curve centered around a pK_a value.
- The magnitude of the buffer index at any pH is proportional to the total species concentration of the weak acid/base subsystem [Eq. (10)]; increasing the total species concentration increases the height of the bell shaped buffer index curve and accordingly increases the "ability" to resist pH change.

From Eq. (12b), the buffer index curve for the solution (system) is given by the sum of the buffer index curves of all the weak acid/base subsystems present and the water subsystem. From Fig. 1, in the pH range of normal digester operation, pH 6,6 to 7,4, the contribution to the solution buffer index (i.e. to buffering against pH change) by the different weak acid/base subsystems is as follows:

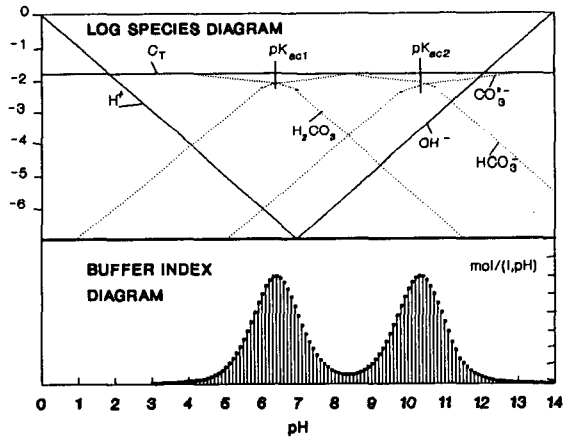

Figure 1a
Log[species] - pH diagram for the carbonate weak acid/base system in aqueous solution and the buffer index diagram for the carbonate subsystem. Note that pH as used in the term [mol/ℓ · pH)] refers to a unit change in pH

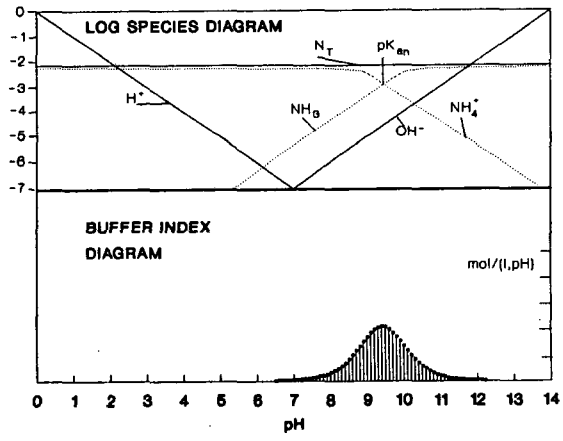

Figure 1b
Log[species] - pH diagram for the ammonium weak acid/base system in aqueous solution and the buffer index diagram for the ammonium subsystem. Note that pH as used in the term [mol/ℓ · pH)] refers to a unit change in pH

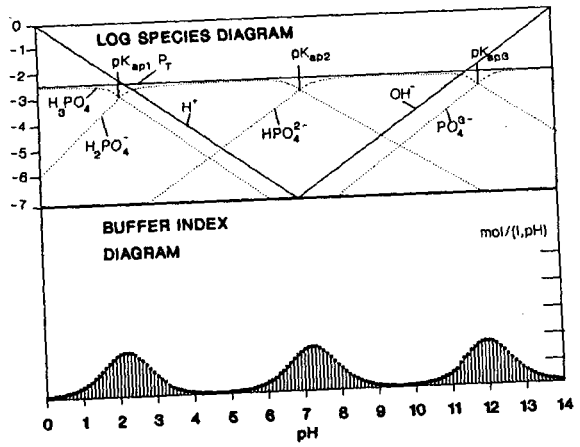

Figure 1c
Log[species] - pH diagram for the phosphate weak aicd/base system in aqueous solution and the buffer index diagram for the phosphate subsystem. Note that pH as used in the term [mol/ℓ · pH)] refers to a unit change in pH

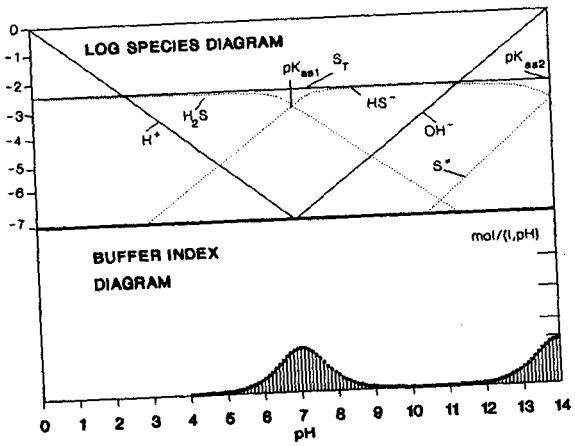

Figure 1d
Log[species] - pH diagram for the sulphide weak acid/base system in aqueous solution and the buffer index diagram for the sulphide subsystem. Note that pH as used in the term [mol/ℓ · pH)] refers to a unit change in pH

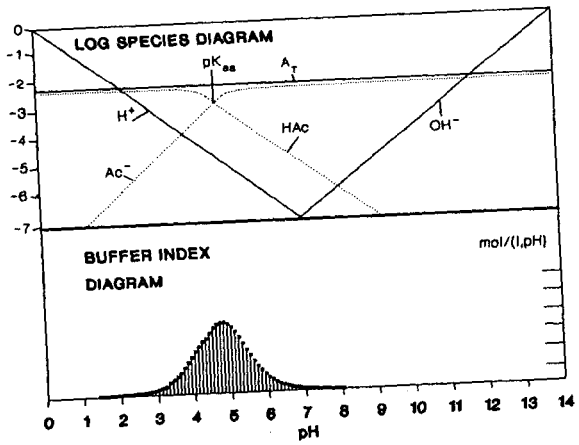

Figure 1e
Log[species] - pH diagram for the acetate weak acid/base system in aqueous solution and the buffer index diagram for the acetate subsystem. Note that pH as used in the term [mol/ℓ · pH)] refers to a unit change in pH

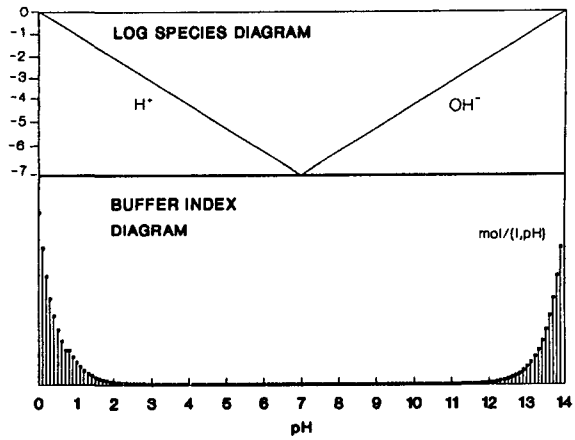

Figure 1f
Log[species] - pH diagram and buffer index diagram for the water subsystem. Note that pH as used in the term [mol/ℓ · pH)] refers to a unit change in pH

- Carbonate, sulphide and phosphate subsystems have pK_a values near to the pH range 6,6 to 7,4 and therefore potentially can contribute significantly to the solution buffer index curve (i.e. can provide significant buffering against pH change). The measure of buffering contributed by each weak acid/base subsystem will depend on its total species concentration [Eq. (10)]. Invariably, the carbonate subsystem is present at significant total species concentrations and hence contributes substantially to buffering. Usually the sulphide subsystem total species concentration is very small compared to the carbonate subsystem so that the buffering contribution of the sulphide subsystem usually is negligible. On occasion the phosphate subsystem may be present at total species concentrations sufficiently high to make a significant contribution to buffering.
- The ammonium subsystem has a pK_a value well outside the pH range 6,6 to 7,4 ($pK_a \simeq 9,4$) and therefore in this pH range affords virtually no buffering against pH change even when present in high concentrations (> 500 mgN/ℓ). If NH_3 is added with the pH remaining in the range 6,6 to 7,4, the NH_3 will change virtually completely [> 99 per cent, Eq. (5)] and immediately to NH_4^+ thereby abstracting H^+, i.e. NH_3 acts as a strong base.
- The SCFA subsystem, as represented by the acetic acid (Fig. 1 e), also has a pK_a value well outside the pH range of 6,6 to 7,4 ($pK_a \simeq 4,75$) and accordingly, like the ammonium subsystem, contributes little to the pH buffering in this pH range. If acetic acid is added with the pH remaining in the range 6,6 to 7,4, it dissociates virtually completely [> 98 per cent, Eq. (4)] to acetate and H^+, i.e. acts as a strong acid.
- The water subsystem (Fig. 1 f) contributes little to pH buffering in the pH range 6,6 to 7,4.

From the above discussion, it is apparent that the carbonate subsystem is the dominant weak acid/base and that the relevant contribution each weak acid/base makes to the buffering of the solution will depend on its total species concentration and its pK_a value. The pK_a values for the weak acid/bases of interest are well established and recorded in the literature. The total species concentrations need to be determined by measurements.

Quantification of weak acid/base subsystem total species concentrations

Methods for quantification of the weak acid/base subsystems present in digester liquid, differ greatly between the weak acid/bases.

Minor weak acid/bases

The phosphate, ammonia and sulphide weak acid/bases fall into this category. Even though these weak acid/bases (under normal circumstances) are of minor importance in pH buffering in the pH range 6,6 to 7,4, they need to be determined for two reasons - to safeguard against nutrient deficiency or inhibition effects (usually from increased concentrations of sulphides and ammonia), and to enhance the accuracy of the determination of the total species concentration of the carbonate subsystem (see later). Measurements of the total species of the phosphate, ammonium and sulphide subsystems can be done by conventional wet chemical methods (*Standard Methods,* 1989) without undue difficulties.

Short-chain fatty acids

The SCFA total species concentration can be measured by straight distillation, steam distillation, chromatographic separation (*Standard Methods,* 1989) or by a colorimetric technique as set out by Montgomery et al. (1962). These methods cannot differentiate individual SCFA but measure this group of weak acid/bases as a whole. If identification and quantification of the individual SCFA are required, these need to be done by gas chromatography. All these methods tend to be time consuming and the last three involve considerable analytical skill and expensive equipment not usually available at full-scale anaerobic installations in South Africa.

Carbonate weak acid/base

Experimentally the carbonate total species concentration (C_T) can be measured by means of an inorganic carbon analyser, an instrument not usually available at full-scale anaerobic plants in South Africa. However, even where this instrument is available,

very likely the measured C_T will be in error: In solution the carbonate weak acid/base consists of four species: (1) CO_2 dissolved; (2) carbonic acid, H_2CO_3; (3) bicarbonate, HCO_3^-; and (4) carbonate CO_3^{2-}. The CO_2 dissolved and H_2CO_3 always exist in a fixed proportion and, accordingly, are dealt with as a combined species, $H_2CO_3^*$ (Stumm and Morgan, 1970) i.e.

$$[H_2CO_3^*] = [CO_2 \text{ dissolved}] + [H_2CO_3] \quad (13)$$

The carbonate subsystem total species concentration, C_T, is given by:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad (14)$$

The ratio CO_2 (dissolved): H_2CO_3 is fixed and equal to 99,76: 0,24 at 25 °C and is independent of pH and ionic strength. The dissolved CO_2 tends to equilibrium with the partial pressure of CO_2 (gas) outside the liquid. This gives rise to CO_2 exchange at the liquid/gas interface, resulting in loss or gain of CO_2 dissolved in the solution. Loss of CO_2 from solution is particularly evident in sampling anaerobic digestion liquid: In the digester the partial pressure of dissolved CO_2 is much higher than that of CO_2 in the atmosphere outside the digester. When a sample is removed from the digester, on exposure to the atmosphere loss of CO_2 takes place, that is, C_T is reduced in the sample. In sample preparation, because of this loss of CO_2, it is not possible to measure C_T of the digester liquid accurately using an inorganic carbon analyser. To avoid the difficulties in determination of C_T due to CO_2 loss, an alternative approach to quantifying the carbonate subsystem total species concentration was developed via pH and the concept of proton accepting capacity or "alkalinity" (Loewenthal et al., 1989), described below.

If either CO_2 (gas), HCO_3^- or CO_3^{2-} species (called reference species) is added to pure water the solution is called an $H_2CO_3^*$, HCO_3^- or CO_3^{2-} equivalent solution respectively. The pH established is called the $H_2CO_3^*$, HCO_3^- or CO_3^{2-} equivalence point respectively; these equivalence points serve as reference pHs for the respective solutions. The $H_2CO_3^*$, HCO_3^- and CO_3^{2-} equivalence points are established by the respective concentrations of reference species $[H_2CO_3^*]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ added to pure water; the respective equivalence points are not fixed but change with the mass of reference species added, temperature and ionic strength. When a strong base is added to the equivalent solutions the pH increases above the respective equivalence points. The mass of strong base added generates a proton (H^+) accepting capacity in the solution relative to the respective equivalence point; this capacity can be measured by titrating back to the equivalence point using a standard strong acid. If a strong acid is added to the equivalent solutions the pH will decrease below the equivalence point giving rise to a proton donating capacity relative to the respective equivalence points and this can be measured by titrating back to the respective equivalence point using a strong base. Note, the proton accepting or donating capacity generated with respect to the equivalence point is equal to the mass of strong base or strong acid originally added to the reference species solution and independent of the mass of reference species present. Conventionally, the proton accepting capacity relative to the equivalence point (generated by addition of strong base) is taken as positive. On this basis, the proton donating capacity relative to the same equivalence point (generated by addition of strong acid) is in effect a negative proton accepting capacity.

Historically the proton accepting capacity between the initial pH point and the equivalence point of the solution has been called alkalinity and the proton donating capacity the acidity. The double nomenclature is unnecessary and creates a measure of confusion because for the same equivalence point, the acidity is equal to the alkalinity but of opposite sign. Because the term alkalinity has acquired an almost universal usage in carbonate weak acid/base chemistry, Loewenthal et al. (1991) suggested that the term alkalinity be retained and continue to define proton accepting capacity when positive; the proton donating capacity is then a negative alkalinity, thereby making the term acidity redundant.

The proton accepting capacity between the initial pH and the $H_2CO_3^*$, HCO_3^- and CO_3^{2-} equivalence points give the $H_2CO_3^*$ alkalinity, HCO_3^- alkalinity, CO_3^{2-} alkalinity respectively. Taking $H_2CO_3^*$ alkalinity as an example, this parameter can be illustrated in the buffer index-pH diagrams (Fig. 1): The $H_2CO_3^*$ alkalinity can be written as the sum of the alkalinity contributions by the carbonate and the water subsystems (Loewenthal et al., 1991), i.e.

$$H_2CO_3^* \text{ alkalinity} = \text{Alk } H_2CO_3^* + \text{Alk } H_2O \quad (15)$$

In terms of the pH - buffer index diagrams, Alk $H_2CO_3^*$ is the area under the carbonate buffer index curve (Fig. 1 a) (identically the carbonate proton accepting capacity contribution) between the initial pH and the $H_2CO_3^*$ equivalence point (pH ≈ 4,0); Alk H_2O is the area under the water buffer index curve (Fig. 1 f) (identically the water proton accepting contribution) between the initial pH and the $H_2CO_3^*$ equivalence point. The $H_2CO_3^*$, HCO_3^- and CO_3^{2-} al-kalinities and C_T are interrelated; if one of these alkalinities can be measured, together with the initial pH of the sample or *in situ* pH, the other alkalinities and C_T can be calculated (Loewenthal et al., 1989).

From a practical point of view, the $H_2CO_3^*$ alkalinity has been found the most useful (Loewenthal and Marais, 1976): The $H_2CO_3^*$ alkalinity is not affected by gain or loss of CO_2 (because CO_2 is the reference species) with the result that it can be measured even if there is loss of CO_2 between sampling and measurement. For this reason the *in situ* $H_2CO_3^*$ alkalinity and sample $H_2CO_3^*$ alkalinity are identical. Consequently, using the relationships linking $H_2CO_3^*$ alkalinity, C_T and pH, C_T in the *in situ* liquid can be calculated from the measured sample $H_2CO_3^*$ alkalinity and the *in situ* pH. Thus CO_2 loss between sampling and testing of the sample does not prevent the determination of *in situ* C_T. However, experimental measurement of $H_2CO_3^*$ alkalinity presents a problem in that the $H_2CO_3^*$ equivalence point depends on C_T which is not known *a priori*. Fortunately, for a solution containing only the carbonate weak/acid base this equivalence point lies in a region of low buffer index so that a slight error in equivalence point estimation (based on rules developed from experience) does not give rise to significant errors in $H_2CO_3^*$ alkalinity except if the $H_2CO_3^*$ alkalinity is low (Loewenthal et al., 1989). Indeed it was because of this feature that the $H_2CO_3^*$ alkalinity concept was developed. For more accurate determination of $H_2CO_3^*$ alkalinity, Gran (1952) developed a titration procedure whereby the $H_2CO_3^*$ alkalinity can be determined without knowledge of the equivalence point, thereby avoiding errors resulting from incorrect equivalence point identification. However, the Gran method is relatively complex and tedious and has not found wide application for general monitoring.

Mixtures of the carbonate and other weak acid/base subsystems

In mixtures of weak acid/base systems, e.g. anaerobic digester liquid, titrating to the $H_2CO_3^*$ equivalence point and equating the mass of H^+ added to the mass of $H_2CO_3^*$ alkalinity virtually always will give an incorrect result. This arises from the presence of other weak acid/base subsystems, i.e. SCFA, phosphate, sulphide and ammonium. Depending on the starting pH of the titration, these weak acid/bases will influence, in a greater or lesser degree, the mass of H^+ required to titrate to the $H_2CO_3^*$ equivalence point. This can be illustrated in the pH - buffer index diagrams (Fig. 1). As noted earlier, the buffer index curve of solution is given by the sum of the buffer index curves for each weak acid/base system present. In titrating from the initial pH to the $H_2CO_3^*$ equivalence point, the mass of H^+ (or OH-) ions that must be added to the solution (i.e. proton accepting capacity) equals the area under the solution buffer index curve between the initial pH and the $H_2CO_3^*$ equivalence point. From Fig. 1 it is evident that the non-carbonate weak acid/bases can make a significant contribution to this area. It is incorrect therefore to equate the mass of H^+ (or OH^-) ions added in the titration to the $H_2CO_3^*$ alkalinity because the $H_2CO_3^*$ alkalinity is defined to include only the areas contributed by the carbonate weak acid/base and the water subsystems (Eq. 15). To address these problems, Loewenthal et al. (1989) extended the concept of alkalinity and the Gran method to mixtures of weak acid/bases that include the carbonate subsystem. Using the extended Gran method, a solution alkalinity measurement can be made relative to a reference solution state for the weak acid/base mixture without titrating to an endpoint. The reference solution state is defined as the pH established on addition of reference species (one for each weak acid/base) to pure water and the solution alkalinity as the mass of H^+ that must be added to titrate from the initial pH to the reference solution state. From this alkalinity measurement C_T is derived. However, the extended Gran method requires that the total species concentrations of all the non-carbonate weak acid/bases (ammonium, phosphate, sulphide and SCFA in anaerobic systems) are known accurately in order to isolate the carbonate subsystem in the mixture. From a practical point of view the extended Gran titration is a relatively complex exercise, so also the independent accurate determination of the SCFA; consequently, in many operational situations this approach will not find ready application.

Practical measurement of control parameters in anaerobic systems

It was noted earlier that in anaerobic digestion, in general, the SCFA as a group are the principal agents inducing a pH decline and the carbonate subsystem the principal agent resisting such a decline. Therefore it is to be expected that practical control of an anaerobic fermentation system would include monitoring a parameter relating to the carbonate subsystem or the SCFA subsystems, or both. In the section above we have noted the difficulties in quantifying parameters relating to the carbonate and SCFA subsystems. These difficulties have prompted the development of practical quantitative or semi-quantitative estimates of these parameters, for control. The following categories of monitoring approaches have been proposed:

- Measurement of $H_2CO_3^*$ alkalinity only
  - DiPinto et al. (1990) without titration
  - Jenkins et al. (1983) using titration
- Measurement of solution proton accepting capacity by titration and separate measurement of SCFA total species, to give the $H_2CO_3^*$ alkalinity
  - McCarty (1974)
- Measurement of ratios of approximate alkalinities of the solution of carbonate and SCFA species
  - Ripley et al. (1986)
- Measurement of total species concentrations of the carbonate and SCFA subsystems by titration
  - Colin (1984)
  - Powell and Archer (1989)

Measurement of $H_2CO_3^*$ alkalinity only

As noted earlier, the $H_2CO_3^*$ alkalinity can be written as the sum of the alkalinity contributions by the carbonate and the water subsystems (Loewenthal et al., 1991), i.e.

$$\begin{aligned} H_2CO_3^* \text{ alkalinity} &= \text{Alk } H_2CO_3^* + \text{Alk } H_2O \\ &= \{[HCO_3^-] + 2[CO_3^{2-}]\} + \{[OH^-] - [H^+]\} \end{aligned} \quad (16)$$

Note: The subsystem alkalinities are written with the alkalinity terms preceding the $H_2CO_3^*$ and H_2O.

In the pH region 7,0 to 8,3, the carbonate subsystem is present virtually totally as HCO_3^- species (see Fig. 1 a) and therefore the HCO_3^- species is virtually the sole contributor to the Alk $H_2CO_3^*$ term (Eq. 16). In this pH range, the contribution of the water subsystem, Alk H_2O, is negligible (see Fig. 1 f and Eq. 16). Hence, in the pH region 7,0 to 8,3 one may closely approximate:

$$H_2CO_3^* \text{ alkalinity} \simeq \text{Alk } H_2CO_3^* \simeq HCO_3^- \text{ concentration} \quad (17)$$

DiPinto et al. (1990) made use of this approximation and proposed determining $H_2CO_3^*$ alkalinity of the digester liquid by measuring the CO_2 over-pressure created when acidifying a sample, as follows: A fixed volume of sample is introduced into a vessel of specified volume; the sample is sparged with CO_2 to achieve CO_2 saturation. The sample is sealed and acidified to convert virtually totally the HCO_3^- to $H_2CO_3^*$. The CO_2 generated causes an over-pressure in the sealed vessel; this-over pressure is related to the mass of $H_2CO_3^*$ generated from HCO_3^- conversion, and accordingly, to $H_2CO_3^*$ alkalinity (Eq. 17). This approach has the merit that it measures $H_2CO_3^*$ alkalinity independently of the presence of other weak acid/bases in the solution.

Another approach to measuring $H_2CO_3^*$ alkalinity was proposed by Jenkins et al. (1983): By titrating from the initial pH of the sample to pH 5,75 about 80 per cent of $H_2CO_3^*$ alkalinity is titrated. However, a considerable proton accepting capacity (PAC) contribution due to the SCFA is also included in such a titration (see Fig. 1 a and e). Because under stable operating conditions the SCFA is low, the influence of SCFA on the titration will be correspondingly low and Jenkins et al. (1983) proposed that it be neglected. Accordingly the $H_2CO_3^*$ alkalinity can be approximated as:

$$H_2CO_3^* \text{ alkalinity} = \text{Soln } PAC_{pHi,5,75}/0{,}8 \quad (18)$$

where Soln $PAC_{pHi,5,75}$ is the solution proton accepting capacity between the initial pH (pH_i) and pH = 5,75 and equals the mass

of H^+ ions added per sample volume to titrate from pH_i to pH = 5,75. (Jenkins et al. (1983) call the $H_2CO_3^*$ alkalinity the TBA or "true bicarbonate"; McCarty (1974) uses the term "bicarbonate alkalinity". Both these terms are based on the assumption that the proton accepting capacity measured by the titration of a digester sample to a selected end point is due to the change of the HCO_3^- species to $H_2CO_3^*$).

Clearly, if the SCFA should be high, for example, where unstable conditions develop, this method would overestimate the $H_2CO_3^*$ alkalinity because the method does not take into account the PAC due to the SCFA in the titration. Further, the titration does not take into account the PAC due to other weak acid/bases in the solution, e.g. phosphate, sulphide etc.

In both approaches above, process deviation from stable steady state conditions is indicated by a change (decline) in $H_2CO_3^*$ alkalinity. The cause for the deviation is not explicitly evident but is inferred, say, to be due to accumulation of SCFA. However, other causes may give rise to changes in $H_2CO_3^*$ alkalinity. For example, in winery wastes, the protein content of the waste can vary appreciably depending on the operation of the distillery plant; a reduced protein content will cause a decline in $H_2CO_3^*$ alkalinity (due to reduced deamination) without an increase in SCFA. Raising the alkalinity by chemical dosing also would upset use of this method. Successful application of the two approaches, therefore, would require the history of the fermentation process and depends to a degree on the experience of the operator.

Measurement of the solution proton accepting capacity with separate SCFA determination to give $H_2CO_3^*$ alkalinity

McCarty (1974) proposed a titration from the initial pH to approximately the $H_2CO_3^*$ equivalence point, pH 4,0, and direct measurement of the SCFA total species concentration. A titration to approximately pH 4 would include virtually 100 per cent of the $H_2CO_3^*$ alkalinity but also a considerable contribution of PAC due to the SCFA subsystem (about 85 per cent of the total PAC of the SCFA subsystem, see Fig. 1 e). Knowing the SCFA total species concentration (as acetic acid) the PAC contribution of the SCFA in the titration to pH 4,0, can be calculated from the SCFA total species concentration as: 0,85· (Total SCFA as acetic acid). Because the $H_2CO_3^*$ alkalinity is expressed as mg/ℓ as $CaCO_3$, the unit of the SCFA has to be adjusted from mg/ℓ as acetic acid to mg/ℓ as $CaCO_3$, accordingly, the factor to calculate the proton accepting contribution of the SCFA changes from 0,85 to 0,71. Hence, the $H_2CO_3^*$ alkalinity can be approximated as:

$$H_2CO_3^* \text{ alk} = \text{Soln } PAC_{pHi;4,0} - 0{,}71 \text{ SCFA} \quad (19)$$

where:

- Soln $PAC_{pHi;4,0}$ = mass of H^+ ions added per volume of sample to titrate from the initial pH, pH_i, to pH = 4,0, and includes the PAC of all weak acid/base subsystems (mg/ℓ as $CaCO_3$)
- SCFA = the sum of the concentrations of all SCFA, i.e. SCFA total species concentration (mg/ℓ as acetic acid)

McCarty's method takes into account the PAC of the SCFA; however, the accuracy of the $H_2CO_3^*$ alkalinity is dependent on a reasonably accurate measurement of the SCFA total species concentration. Furthermore, errors may be introduced by neglecting the PAC contributions due to the minor weak acid/bases.

Measurement of ratios of approximate alkalinities of the carbonate and SCFA subsystems

Ripley et al. (1986) suggested to separate out roughly the SCFA and carbonate subsystems and to base control on a ratio of the two. In their method the sample is titrated to a fixed pH of 5,75 and thereafter to pH 4,3. The mass of H^+ to titrate from the initial pH (pH_i) to pH 5,75 (Soln $PAC_{pHi;5,75}$) is termed the partial alkalinity (PA) indicating that only a part of the solution PAC is covered by titrating to this pH, principally the carbonate subsystem alkalinity. The mass of acid to titrate from pH 5,75 to 4,3 (Soln $PAC_{5,75;4,3}$) is termed the intermediate alkalinity (IA) and is mainly due to the PAC of the SCFA subsystem. Ripley et al. (1986) argue that for stable digester operation adequate buffering due to the carbonate subsystem is necessary and excessive SCFA must be avoided. Consequently, they introduce a ratio made up of a parameter mainly representing the PAC contribution due to the SCFA subsystem (IA) and a parameter mainly representing the PAC contribution due to the carbonate subsystem (PA), i.e.:

$$r = IA/PA \quad (20)$$

Ripley et al. (1986) monitored an anaerobic digester fed with poultry manure and found that the ratio served as a good indicator of stress conditions in the process, when $r > 0{,}3$.

The method requires a simple analytical procedure. The parameters IA and PA are fuzzy in that both include the SCFA and carbonate subsystem PACs, the first dominating in IA and the second in PA. Very likely the critical r values would differ between wastes so that application as a control measure on a plant will require a build-up of experience. Ripley et al.'s method identifies deviant behaviour but would not supply information from which to calculate, say, corrective chemical dosing.

Measurement of the total species concentrations of the carbonate and SCFA subsystems by titration

In the approaches of McCarty (1974) and Jenkins et al. (1983) the basic parameter selected to characterise the carbonate subsystem is $H_2CO_3^*$ alkalinity (in an approximate form). One may obtain $H_2CO_3^*$ alkalinity in two ways: directly by titrating a sample to some pH, usually approximately the $H_2CO_3^*$ equivalence point and relating the mass of H^+ added to $H_2CO_3^*$ alkalinity, or indirectly by determining C_T and measuring the initial pH of the sample which allows calculation of $H_2CO_3^*$ alkalinity. McCarty (1974) and Jenkins et al. (1983) both used direct titration to obtain approximate estimates of $H_2CO_3^*$ alkalinity. We shall now review indirect approaches that estimate C_T in a solution also containing the SCFA subsystem, by titration. Having estimated C_T together with the initial pH of the sample $H_2CO_3^*$ alkalinity is derived.

DiLallo and Albertson (1961) proposed that supernatant of a centrifuged digester sample be titrated from the initial pH to pH 4,0; this titration includes the PAC of the carbonate, SCFA and minor weak acid/bases. The sample is then titrated to pH 3,3 to ensure complete conversion of HCO_3^- species to (H_2CO_3 + dissolved CO_2) species; these carbonate species are now removed from the sample by boiling lightly for 3 min. The sample is back titrated with strong base and the amount of base added between pH 4,0 and 7,0 forms an estimate of the "volatile acid alkalinity"

which is the PAC between these two pH points exerted by the SCFA and minor weak acid/bases, because the carbonate species have been removed from the sample (see Fig. 1 c,d,e). From the "volatile acid alkalinity" the SCFA concentration is then calculated using conversion factors specified by DiLallo and Albertson (1961).

Powell and Archer (1989) modified and extended DiLallo and Albertson's approach and developed it into an automated procedure to estimate C_T and SCFA. The sample pH is raised to pH > 11 using a strong base. A "carbonate" alkalinity is then measured by titrating from pH 11 to pH 9,4 which is the PAC of the solution from pH 11 to 9,4 (Soln $PAC_{11;9,4}$). Inserting pH = 11 and 9,4 in Eq. (4) yields two equations relating the concentration of CO_3^{2-} species at each pH to C_T; to calculate C_T they assume that the molar mass difference in CO_3^{2-} species at the two pHs equals the mass of H^+ added in the titration (Soln $PAC_{11;9,4}$) and subtract the two equations. The sample pH is then lowered to 6,9 and titrated from pH 6,9 to 4,0. Between these two pHs the titration gives Soln $PAC_{6,9;4,0}$ which they assume is principally due to the carbonate and SCFA weak acid/bases. After this the sample pH is lowered to pH 2,2 and the sample is sparged with air, expelling virtually all carbonate system species in the form of CO_2. Then the sample is back titrated between pH 4,0 and 6,9; this titration provides Soln $PAC_{4,0;6,9}$, due principally to the SCFA subsystem (the carbonate system having been removed). Via Eq. (4), analogous to the determination of C_T in the pH range 11 to 9,4, the total species concentration of the SCFA system is derived. Having the data from the titration from pH 6,9 to 4,0 (Soln $PAC_{6,9;4,0}$) which is principally due to the carbonate + SCFA subsystems, and from the titration from pH 4,0 to 6,9 (Soln $PAC_{4,0;6,9}$) which is principally due to the SCFA subsystem, they subtract Soln $PAC_{4,0;6,9}$ from Soln $PAC_{6,9;4,0}$. This gives the PAC of the carbonate system between the two pH values 6,9 and 4,0 which closely equals the change in HCO_3^- species concentration. Via Eq. (4) two equations relating the HCO_3^- species concentration to C_T at pH 6,9 and 4,0 can be established, and a second C_T value estimated by subtracting the two equations, noting that the change in HCO_3^- concentrations between the two pHs equals the known (measured) PAC of the carbonate subsystem. Thus two C_T values become available and the mean of these two values is accepted as the best estimate of C_T. The method was tested by Powell and Archer (1989) on solutions of pure carbonate, pure acetate and mixtures of these. The results give estimates within about 1 mmol of the true values (at 95% confidence) for concentration ranges from 5 mmols to 50 mmols. No data were supplied on the performance of this procedure on anaerobic digester liquids. The following comments are pertinent:

Raising the pH to > 11 may cause carbonate species precipitation, thereby leading to an underestimate of the proton accepting capacity of the carbonate system in the subsequent titration between pH 11 to 9,4. Additionally in this pH range the water and ammonium systems have significant PACs (see Figs. 1 f and 1 b), both if not accounted for, giving rise to an overestimate of C_T. In the back titration from pH 4,0 to 6,9 the phosphate and sulphide systems may have significant PACs thereby causing an overestimate of the SCFA. However, if the ammonium, phosphate and sulphide systems are measured by conventional methods then their PACs can be evaluated via Eq. (4) and the titrations duly corrected to give closer estimates of the carbonate and SCFA systems. Another difficulty foreseen would be the problem with pH calibration over the pH range of 4 to 11.

Colin (1984) also proposed an automated method using acid and base titrations to different pH end points and, inserting the titration results in appropriate equilibrium equations, defined the ammonium, SCFA and carbonate subsystems. Colin's method differs from those of Powell and Archer (1989) and DiLallo and Albertson (1961) in that there is no need to remove the carbonate subsystem (by aerating or boiling the sample at a low pH). Insufficient detail on the experimental requirements and calculation procedures is supplied to make an assessment of the method.

Discussion

From this review it is clear that estimation of the SCFA and carbonate subsystems is of major importance in monitoring the performance of anaerobic fermentation systems. It is clear also that no simple practical method is available to determine these subsystems with reasonable accuracy. From the basic theory on the behaviour of mixtures of weak acid/bases (Loewenthal et al., 1989) and the work of Powell and Archer (1989), it would seem that it should be possible to evaluate some of the weak acid/bases in a mixture via a simple titration procedure: Proton accepting capacity, in general, arises from titration between any two pH points and is the mass of H^+ (or OH^-) ions that must be added to titrate from one pH to another. Diagrammatically it is given by the sum of the areas under the buffer index curves between the two pH points (see Fig. 1). For a particular weak acid/base, theoretically the proton accepting capacity between any two pH points allows the total species concentration to be determined, but the relationship is quite complex - practical application requires the assistance of a personal computer or programmable calculator. This approach to determining total species concentration has received little attention in the past. In a series of papers, the approach will be examined and a relatively simple acid titration procedure will be developed that provides reliable estimation of both the carbonate and SCFA subsystems. Detailing this development, the series will deal with estimation of:

- $C_T/H_2CO_3^*$ alkalinity in an aqueous solution containing only the carbonate subsystem
- $C_T/H_2CO_3^*$ alkalinity in an aqueous solution also containing other weak acid/bases (ammonia and phosphate) of known concentrations
- $C_T/H_2CO_3^*$ alkalinity and SCFA total species concentration in an aqueous solution also containing other weak acid/bases (ammonia and phosphate) of known concentrations.

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References

COLIN, F (1984) *Anaerobic Digestion and Carbohydrate Hydrolysis of Waste.* Elsevier Applied Science Publishers.

DILALLO, R and ALBERTSON, O (1961) Volatile acids by direct titration. *JWPCF* **33**(4) 356-365.

DiPINTO, AC, LIMONI, N, PASSINO, R, ROZZI, A and TOMEI, MC (1990) Anaerobic process control by automated bicarbonate monitoring. *Adv. in Water Pollut. Control* 51- 58.

GUJER, W and ZEHNDER, AJB (1983) Conversion processes in anaerobic digestion. *Water Sci. Technol.* **15** 127-167.

GRAN, G (1952) Determination of the equivalence point in

potentiometric titrations. *The Analyst* **77** 661.
JENKINS, SR, MORGAN, JM and SAWYER, CL (1983) Measuring anaerobic sludge digestion and growth by a simple alkalimetric titration. *JWPCF* **55** 448-453.
LOEWENTHAL, RE and MARAIS, GvR (1976) *Carbonate Chemistry of Aquatic Systems - Theory and Application*. Ann Arbor Science Publishers Inc. Michigan.
LOEWENTHAL, RE, EKAMA, GA and MARAIS, GvR (1989) Mixed weak acid/base systems. Part I: Mixture characterisation. *Water SA* **15**(I) 3-24.
LOEWENTHAL, RE, WENTZEL, MC, EKAMA, GA and MARAIS, GvR (l99l) Mixed weak acid/base systems. Part II: Dosing estimation, aqueous phase. *Water SA* **17**(2) 107-122.
McCARTY, PL (1974) *Anaerobic Processes*. International Association of Water Pollution Research, Birmingham, England. September 18, 1974.
MONTGOMERY, HAC, DYMOCK, JF and THOM, NS (1962) The rapid colorimetric determination of organic acids and their salts in sewage sludge liquor. *The Analyst* **87** 947.
MOSEY, FE and FERNANDES, XA (1989) Patterns of hydrogen in biogas from the anaerobic digestion of milk-sugars. *Water Sci. Technol.* **21** 187-196, Brighton.
POHLAND, FG and MARTIN, JC (1969) Discussion on paper by Andrews, JF "Dynamic model of the anaerobic digestion process". *Proc. of Am. Soc. of City Eng.*, Sanitary Engineering Division.
POWELL, GE and ARCHER, DB (1989) On-line titration method for monitoring buffer capacity and total volatile fatty acid levels in anaerobic digesters. *Biotechnol. and Bioeng.* **33** 570-577.
RIPLEY, LE, BOYLE, JC and CONVERSE, JC (1986) Improved alkalimetric monitoring for anaerobic digestion of high-strength wastes. *JWPCF* **58** 406-411.
SAM-SOON, PALNS, LOEWENTHAL R E, DOLD P L and MARAIS G v R (1987) Hypothesis for pelletisation in the upflow anaerobic sludge bed reactor. *Water SA* **13**(2) 69-80.
STANDARD METHODS (1989) *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, American Water Works Association and Water Pollution Control Federation, Washington DC.
STUMM, W and MORGAN, JT (1970) *Aquatic Chemistry*. Wiley - Interscience, New
VAN SLIJKE, DD (1922) On measurement of buffer values. *J. Biol. Chem.* **52** 525-590.