Rapid communication

Measurement of VFA in anaerobic digestion: The five-point titration method revisited

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Abstract

The 5-point titration method proposed by Moosbrugger et al. (1993) provides a cheap and rapid means for measuring *inter alia* short-chain volatile fatty acids. However, output from the analysis requires invoking a 'systematic pH error'. The authors ascribed this to either residual liquid junction potential effects or pH calibration errors. However, from a scientific standpoint this detracts from confidence in the method. In this paper, it is shown that Moosbrugger et al's 'systematic pH error' is an artefact of the numerical techniques employed in their analysis. An alternative numerical approach is presented which also gives excellent results, without invoking the pH error affect.

Introduction

In anaerobic digestion the control of the process is usually effected by measurements of short-chain fatty acids (VFA), pH, alkalinity and gas (CH_4, CO_2) production. Generally, change in VFA concentration is the most sensitive parameter, the reason being that the primary cause of digester failure hinges around imbalance between acidogenic, acetogenic and methanogenic organisms. However, in industry very few laboratories are equipped to measure VFA directly. Therefore, normally pH, alkalinity and gas production constitute the control strategy, sometimes with disastrous results.

Moosbrugger et al. (1992; 1993) addressed the problem of VFA measurement and devised a rapid simple titration technique for VFA and alkalinity measurements. Where applied, their method has proved to be successful. However, there are some factors associated with the method, which tend to undermine the confidence of the user. The principal problem that arises from the Moosbrugger method is that the analysis requires imposing a systematic error on all pH observations. This is ascribed by the authors to result from either a residual liquid junction potential error in pH measurements (the residual liquid junction error arises from differences in dissolved salts between the pH buffer used to standardize the probe and the test solution) or from poor pH meter calibration (Moosbrugger et al., 1993).

Moosbrugger et al.'s (1992; 1993) pH observations were effected on the NBS scale and the total dissolved salts concentration in their samples varied between 500 and 1 000 mg/ℓ (after dilution). It is impossible to ascribe their "systematic pH error" to liquid junction affects because, firstly, from a practical standpoint the residual liquid junction potential error in sea water (TDS around 32 000 mg/ℓ) was estimated as approximately 0.075 pH units (Loewenthal and Marais, 1983; Bates and Macaskill, 1975). Secondly, from a theoretical semi-empirical approach, the Henderson equation gives residual liquid junction values of less than 0.003 pH units for the TDS range of the solutions reported by Moosbrugger (Loewenthal and Marais, 1983). Thirdly, when applied to a particular water the Moosbrugger method gave pH error between tests that varied between 0.02 to 0.08 pH units. For these reasons, from a purist point of view, this does not lead to confidence in the method.

In this paper it is shown that the Moosbrugger approach does indeed give excellent prediction of VFA (as the authors showed), but that the so called "pH error" is an artefact of the numerical methods which they used. An alternative numerical approach to the solution is presented that gives as good, if not better, estimates of VFA, but that does not introduce the "systematic error" to correct pH observations.

Basic theory

The basic theory of the 5-point method was presented in detail by Moosbrugger et al (1993). In this paper these basics are dealt with briefly in order to highlight the divergence with the approach developed here.

The 5-point method approach involves equating a mass balance relationship for alkalinity in terms of volume of titrant added (Eq. (1)) to a mass balance of alkalinity in terms of species concentration (Eq.(2)).

$$M\ total\ alk_x = Ve \cdot Ca - Vx \cdot Ca \qquad (1)$$

where:

$M\ total\ alk_x$ = total mass of alkalinity after the addition of V_x mℓ of standard strong acid (mol),

V_e = the unknown volume of standard strong acid to be added to the alkalimetric end point (ℓ),

V_x = the volume of standard strong acid added to a point x with pH equal to pH_x (ℓ), and

C_a = concentration of standard strong acid (mol/ℓ).

$$M\ total\ alk_x = \{[HCO_3^-]_x + 2[CO_3^{2-}]_x + [A^-]_x + [OH^-]_x - [H^+]_x\} \cdot (V_x + V_s) \qquad (2)$$

where:

$[y]_x$ indicates concentration of species y after addition of x mℓ of standard acid (mol/ℓ),

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$[A^-]$ = dissociated short chain VFA species concentration (mol/ℓ) and

V_s = volume of sample (ℓ).

Eq. (2) can be reformulated in terms of total weak acid species concentrations using equilibrium equations for the weak acid systems and mass balance equations for each of the weak acid systems as represented in Eqs. (3) to (7) below. For the carbonate subsystem:

$$\frac{(H^+)_x \cdot [HCO_3^-]_x}{[H_2CO_3^*]_x} = K'_{C1} \quad (3)$$

$$\frac{(H^+)_x \cdot [CO_3^{2-}]_x}{[HCO_3^-]_x} = K'_{C2} \quad (4)$$

$$C_T = [H_2CO_3^*]_x + [HCO_3^-]_x + [CO_3^{2-}]_x \quad (5)$$

where:

( ) denotes activity,

[ ] molarity and

K' equals apparent equilibrium constant after adjustment for Debye-Huckel effects.

For the VFA subsystem:

$$\frac{(H^+)_x [A^-]_x}{[HA]_x} = K'_a \quad (6)$$

$$A_T = [HA]_x + [A^-]_x \quad (7)$$

All the short-chain VFAs are lumped together to form a single weak acid system with equilibrium constant because they all have pK values very close to each other.

Solving for C_T from Eqs. (3), (4) and (5) and for A_T from Eqs. (6) and (7) respectively gives the desired equations:

$$[HCO_3^-]_x = \frac{C_T}{1 + \frac{K'_{C2}}{(H^+)_x} + \frac{(H^+)_x}{K'_{C1}}} \quad (8)$$

$$[CO_3^{2-}]_x = \frac{K'_{C2} \cdot C_T}{(H^+)_x + K'_{C2} + (H^+)_x / K'_{C1}} \quad (9)$$

$$[A^-]_x = \frac{A_T \cdot K'_a}{(H^+)_x + K'_a} \quad (10)$$

Substituting Eqs. (8), (9) and (10) into Eq. (2) gives an equation for total mass of alkalinity in terms of A_T, C_T and pH:

$$M\ total\ alk_x = \left\{ C_T \cdot \frac{V_s}{V_s + V_x} \cdot fn_1(pH)_x + A_T \cdot \frac{V_s}{V_s + V_x} \cdot fn_2(pH)_x - \frac{10^{-pH_x}}{f_m} \right\} \cdot (V_s + V_x) \quad (11)$$

where:

f_m = monovalent activity coefficient, and

fn_1 and fn_2 are functions of pH_x and equilibrium constants for the carbonate and acetate subsystems as given in Eqs. (8) to (10).

Equating Eqs. (1) and (11) gives the desired equation linking mass of alkalinity based on acid added and mass of alkalinity based on species concentrations:

$$(V_e \cdot Ca) - (V_x C_a) = \left\{ C_T \cdot \frac{V_s}{V_s + V_x} \cdot fn_1(pH)_x + A_T \cdot \frac{V_s}{V_s + V_x} \cdot fn_2(pH)_x - \frac{10^{-pH_x}}{f_m} \right\} \cdot (V_s + V_x) \quad (12)$$

Equation (12) includes 3 unknowns: V_e, A_T and C_T (provided temperature and TDS are known so that the various equilibrium constants can be determined from reported data). Substituting an observed V_x and corresponding pH_x into Eq. (12) gives an independent equation. Thus, to solve for V_e, A_T and C_T only 3 data pairs (i.e. 3 values for corresponding V_x and pH_x pairs) need to be known. This, however, leads to poor prediction. Moosbrugger et al. (1993) showed that the best results are obtained from 5 points: the initial pH value (where $V_x = 0$) and two pairs of points, each pair symmetrical about the pK'_{C1} and pK'_a values. They showed that such symmetry gives the best first estimate of A_T, C_T and total alkalinity. The extra information (i.e. the initial pH and V_x value) was used as follows: for the first estimate of A_T, C_T and total alkalinity the value of the initial pH is calculated and compared with the measured initial pH. If these don't agree, all pH values are then adjusted by the same amount (readjusting A_T, C_T and total alkalinity) to get the best final fit between calculated and observed initial pH values. In essence, Moosbrugger et al. (1993) infer there is a constant error arising in observed pH values. This they ascribed to either residual liquid junction potential effects and/or calibration errors. This explanation, however, is unacceptable for reasons set out in the introduction to this paper.

A modified approach to the 5-point titration method

The apparent inconsistency arising from the so-called 'systematic pH error' using the Moosbrugger et al. approach can be by-passed as follows: We again accept that the two symmetrical pairs of pH_x and V_x observations around the relevant pK values give the best **initial** estimate of A_T, C_T and total alkalinity. However, we accept that they also give the best **final** estimate of the sum of A_T and C_T. These statements can be depicted graphically (see Fig. 1).

In Fig. 1, the buffer intensity curves for the acetate and bicarbonate subsystems together with total buffer intensity curve are shown. One notes that the strong acid added between points is represented by the area under the total buffer intensity (equal to the sum of the two subsystem buffering intensities) curve between the two points. One notes that the two subsystem buffer intensity areas overlap. As a result of the overlap, the subsystem with the higher concentration and hence larger area will have a greater influence on the total area than the subsystem with the lower total species concentration (compare the area below the curve connecting Points 4' and 5' with the actual area (obtained from the titration) underneath the graph connecting Points 4 and 5). In contrast to the individual species concentration affect, the sum of C_T and A_T is unbiased. This observation is used in computation as follows: for each pH_x and V_x and the initial best estimate of A_T and C_T one can determine the total alkalinity using equation 11. The total alkalinity determined from point 1 (see figure 1) incorporates the combined affect of the A_T and C_T estimate (because at point 1 V_x=0) and is termed therefore 'total alkalinity worst'. On the other hand, the estimate of total alkalinity from point 5 incorporates the minimum effect of A_T and C_T and maximum effect of the accurately measured V_x, therefore termed 'total alkalinity best'. These two alkalinities are now compared. If the difference exceeds a preselected value, C_T and A_T are increased and decreased respectively keeping $A_T + C_T$ constant and the procedure is repeated.

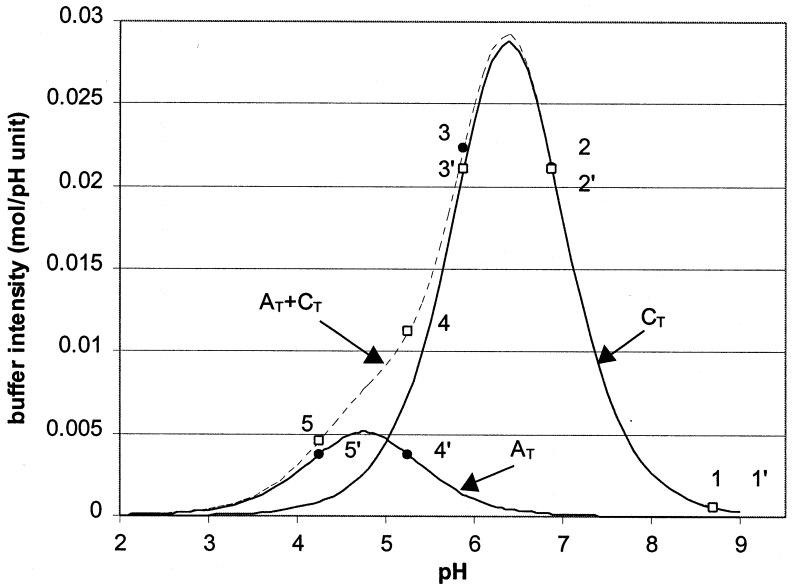

Figure 1
*The sum and individual buffer intensity curves for the carbonate ($H_2CO_3^*/HCO_3^-$) and acetate systems (A_T=1*10^{-2} M, C_T=5*10^{-2} M). Point 1 represents the initial state, Points 2 and 3 are symmetrical about pK_{C1}', Points 4 and 5 are symmetrical about pK_a'*

Results and discussion

In Table 1 below are presented results from 5-point titration measurements on a number of solutions (Moosbrugger et al., 1991) using the Moosbrugger approach and that presented here. Referring to this table, both approaches give excellent prediction. However, the Moosbrugger approach invokes a systematic error in pH. Furthermore, for a particular test solution the systematic error in pH varies between samples. Though this does not affect their excellent results, it does detract from their method.

In conclusion, the objective of this paper is not to undermine utilisation of the Moosbrugger approach, but rather to diminish the fears of skeptics who may be detracted by an unacceptable "systematic pH error".

TABLE 1
5-POINT TITRATION METHOD - COMPARISON OF RESULTS BETWEEN MOOSBRUGGER AND THIS PAPER

Original sample		Moosbrugger approach*			This paper		
VFA mg/ℓ HA	Alkalinity mg/ℓ $CaCO_3$	VFA mg/ℓ HA	Alkalinity mg/ℓ $CaCO_3$	ΔpH (-)	VFA mg/ℓ HA	Alkalinity mg/ℓ $CaCO_3$	ΔpH (-)
100	1 907	97	1 948	-0.03	93	1 942	0
		102	1 930	-0.03	93	1 942	0
		82	1 937	-0.01	82	1 946	0
		112	1 929	-0.05	103	1 871	0
		95	1 935	-0.01	96	1 944	0
200	1 823	199	1 844	-0.03	193	1 856	0
		212	1 841	-0.05	197	1 853	0
		198	1 860	-0.03	194	1 853	0
		217	1 852	-0.04	203	1 846	0
		208	1 844	-0.03	205	1 840	0
400	1 657	397	1 663	-0.02	393	1 691	0
		401	1 678	-0.03	396	1 686	0
		397	1 656	-0.02	393	1 690	0
		387	1 671	-0.01	388	1 699	0
		398	1 662	-0.02	394	1 694	0
600	1 988	609	1 994	-0.04	593	2 037	0
		595	2 007	-0.05	582	2 056	0
		606	1 994	-0.04	591	2 039	0
		601	2 015	-0.03	597	2 026	0
		601	2 006	-0.04	585	2 049	0

*Data from: Moosbrugger et al. (1991)

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