Rapid communication

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

O Lahav and RE Loewenthal*

Department of Civil Engineering, University of Cape Town, Rondebosch 7700, Cape Town, South Africa

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),

* To whom all correspondence should be addressed.
☎(021) 650-3499; fax (021) 689-7471; e-mail: dick@eng.uct.ac.za
Received 20 June 2000.