

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

RE Moosbrugger, MC Wentzel*, RE Loewenthal, GA Ekama and GvR Marais
Department of Civil Engineering, University of Cape Town, Rondebosch 7700, South Africa

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 digester 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^* alkalinity, 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 $\text{CaCO}_3 > 2$ 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:

$$\text{H}_2\text{CO}_3^*/\text{HAc alk} = \{[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]\} + \{[\text{Ac}^-]\} + \{[\text{OH}^-] - [\text{H}^+]\} \quad (1)$$

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), $\text{H}_2\text{CO}_3^*/\text{HAc alk}$ can be written as the sum of the subsystem alkalinity of the weak acid/bases and water:

$$\text{H}_2\text{CO}_3^*/\text{HAc alk} = \text{Alk H}_2\text{CO}_3^* + \text{Alk HAc} + \text{Alk H}_2\text{O} \quad (2)$$

where:

$$\text{Alk HA} = [\text{Ac}^-] \quad (3a)$$

$$\text{Alk H}_2\text{CO}_3^* = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] \quad (3b)$$

$$\text{Alk H}_2\text{O} = [\text{OH}^-] - [\text{H}^+] \quad (3c)$$

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

$$\text{MH}_2\text{CO}_3^*/\text{HAc alk} = \text{MAlk H}_2\text{CO}_3^* + \text{MAlk HAc} + \text{MAlk H}_2\text{O} \quad (4)$$

With acid titration from pH₁ to pH₂, from Eq. (4) the molar mass decrease of the solution alkalinity and the subsystem alkalinity are:

$$\Delta \text{MH}_2\text{CO}_3^*/\text{HAc alk}_{1,2} = \Delta \text{MAlk H}_2\text{CO}_3^* + \Delta \text{MAlk HAc} + \Delta \text{MAlk H}_2\text{O} \quad (5)$$

where:

$$\Delta \text{MH}_2\text{CO}_3^*/\text{HAc alk}_{1,2} = \text{MH}_2\text{CO}_3^*/\text{HAc alk}_1 - \text{MH}_2\text{CO}_3^*/\text{HAc alk}_2 \quad (6a)$$

$$\Delta \text{MAlk H}_2\text{CO}_3^* = \text{MAlk H}_2\text{CO}_3^*_1 - \text{MAlk H}_2\text{CO}_3^*_2 \quad (6b)$$

$$\Delta \text{MAlk HAc} = \text{MAlk HAc}_1 - \text{MAlk HAc}_2 \quad (6c)$$

*To whom all correspondence should be addressed.

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