

Alkalinity measurement: Part 1 - A 4 pH point titration method to determine the carbonate weak acid/base in an aqueous carbonate solution

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Abstract

Theory of a 4 pH point acid titration method is presented to measure the H_2CO_3 alkalinity and the total carbonate species (C_T) in aqueous solutions containing only the carbonate weak acid/base. The influence of a systematic pH measurement error (due to faulty calibration, residual liquid junction effect, temperature) on the calculation of C_T and H_2CO_3 alkalinity is examined, and methods presented to minimise the influence of the error. The influence of CO_2 loss during titration on C_T and H_2CO_3^* alkalinity estimates is shown to be negligible provided the titration is completed within 10 min with gentle stirring. Comparative tests using the 4 pH point titration and First Gran Function methods, on aqueous NaHCO_3 solutions ranging from 10 to 50 mg/l as CaCO_3 gave closely equal results with $r = 0,99$. For NaHCO_3 solutions ranging from 100 to 1 750 mg/l as CaCO_3 , the 4 pH point titration method has high accuracy, and a standard deviation of < 2 per cent.

Introduction

Reviewing weak acid/bases and pH control in anaerobic systems, Moosbrugger et al. (1993) identified the importance of measuring one parameter relating to the carbonate and one to the short-chain fatty acid (SCFA) weak acid/bases. Parameters identified for measurement were total species concentration (C_T) or H_2CO_3^* alkalinity for the carbonate weak acid/base, and total species concentration for the SCFA weak acid/bases (A_T). An evaluation of techniques available to measure these parameters indicated that:

- For determination of C_T , inorganic carbon analysers are available. However, with this instrument C_T is very likely to be in error due to CO_2 loss on sampling anaerobic digester liquid.
- The H_2CO_3^* alkalinity has the merit that its reference specie is H_2CO_3^* and hence CO_2 loss does not affect its value. For determination of H_2CO_3^* alkalinity in solutions containing only the carbonate weak acid/base or mixtures of weak acid/bases, the Gran and Extended Gran methods respectively (Loewenthal et al., 1989) are available. Both Gran methods are relatively complex and tedious and for the Extended Gran method the required independent accurate determination of A_T is not a simple task. For routine monitoring, the Gran and the Extended Gran methods would not find ready application.
- For determination of A_T distillation/titration, colorimetric and chromatographic methods are available. These methods are time-consuming and involve considerable analytical skill and/or expensive equipment.
- For determination of $C_T/\text{H}_2\text{CO}_3^*$ alkalinity or A_T , or $C_T/\text{H}_2\text{CO}_3^*$ alkalinity and A_T , simplified titration methods are available. These methods are either too cumbersome, or provide only approximations of the parameters of interest.

With the increased understanding of mixed weak acid/base chemistry (Loewenthal et al., 1989; 1991), a study of the basic theory indicated that, by using an alternative approach, it should

be possible to evaluate one or more weak acid/bases by a simple titration procedure. The development of this approach and the titration procedure is detailed in this series of papers, dealing with estimation of: Part 1 (this paper) - $C_T/\text{H}_2\text{CO}_3^*$ alkalinity in an aqueous solution containing only the carbonate weak acid base; Part 2 - $C_T/\text{H}_2\text{CO}_3^*$ alkalinity in an aqueous solution also containing other weak acid/bases of known concentration; and Part 3 - $C_T/\text{H}_2\text{CO}_3^*$ alkalinity and SCFA in an aqueous solution also containing other weak acid/bases of known concentration.

Theory

To completely characterise a weak acid/base in solution, the total species concentration and pH are required (Loewenthal and Marais, 1976). With the carbonate weak acid/base in solution, the practical difficulties in measuring total species concentration (C_T) have led to the development of a substitute parameter, "alkalinity" (Loewenthal and Marais, 1976; Loewenthal et al., 1989). Alkalinity is defined as the proton accepting capacity of the solution relative to a reference state; quantitatively the alkalinity equals the mass of H^+ (or OH^-) that must be added to titrate from the solution pH to the reference state pH (called the equivalence point), where the reference state pH is the pH established on addition of a reference species to pure water. For example, CO_2 reference species (equivalently H_2CO_3^*) addition to pure water gives the H_2CO_3^* equivalence point, and titration to this pH gives the H_2CO_3^* alkalinity. However, measurement of alkalinity itself is not a simple task due to the problem of identifying the equivalence point in the titration. Techniques are available to overcome this problem (Gran and Extended Gran titrations, Loewenthal et al., 1989), but as noted earlier, these are complex and tedious.

In general, a proton accepting capacity exists between any two pH points and quantitatively equals the mass of H^+ (or OH^-) ions that must be added to titrate from the one pH to the other. For a particular weak acid/base in solution, theoretically measurement of the proton accepting capacity between any two pH points allows the total species concentration to be determined. This approach has received little attention in the past. The theory for this approach now will be developed to determine C_T in an aqueous solution containing only the carbonate weak acid/base.

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