

# Alkalinity measurement: Part 2 - A 4 pH point titration method to determine the carbonate weak acid/base in aqueous solutions containing other weak acid/bases of known concentrations

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## Abstract

In this paper the 4 pH point titration method (see **Part 1**) is extended to determine the carbonate total species concentration ( $C_T$ ) and  $H_2CO_3^*$  alkalinity in aqueous solutions containing other weak acid/bases of known concentrations. Two typical other weak acid/bases are selected, ammonium with a  $pK_a$  far from, and inorganic phosphate with a  $pK_a$  near to, the 4 pH point titration range of 7,2 to 4,8. The influence of the phosphate and ammonium on the 4 pH point titration is examined theoretically and experimentally. Knowing the total species concentrations of the ammonium and phosphate, their respective effects on the 4 pH point titration are assessed and corrected for, to isolate  $C_T$  and  $H_2CO_3^*$  alkalinity. With regard to the effect of ammonium, this is negligible for most practical applications of the 4 pH point titration and normally requires no correction. However, the effect of phosphate can be significant and should be corrected for by the proposed method.

## Introduction

In a previous paper (**Part 1**) Moosbrugger et al. (1993b) proposed a 4 pH point titration method to determine the carbonate total species concentration ( $C_T$ ) and  $H_2CO_3^*$  alkalinity in aqueous solutions, provided the carbonate weak acid/base is the only one present. In practice this method can be applied only where the carbonate weak acid/base is dominant, to such a degree that other non-carbonate weak acid/bases can be neglected. However, in many practical situations in addition to the carbonate, other weak acid/bases may be present in such concentrations that they contribute significantly to the proton accepting capacity in the pH range covered by the 4 pH point titration method (see **Part 1**). This will lead to an error in the determination of  $C_T$  and  $H_2CO_3^*$  alkalinity from the titration data. For example, in anaerobic systems the phosphate, sulphide, ammonium and short-chain fatty acids (SCFA) weak acid/bases may be present in appreciable concentrations. Consequently, in these systems the effect of the non-carbonate weak acid/bases no longer can be neglected.

In this paper, the 4 pH point method is extended to determine  $C_T$  and  $H_2CO_3^*$  alkalinity in aqueous solutions that include known-total species concentrations of non-carbonate weak acid/bases.

## Theory

In the 4 pH point titration proposed by Moosbrugger et al. (1993b), the sample is titrated from its initial pH ( $pH_0$ ) to pH, to  $pH_2$  [ $pH_1$  and  $pH_2$  situated approximately equidistant around the first apparent dissociation constant of the carbonate weak acid/base ( $pI_{Q(1)}$ )], and to a lower pH point ( $pH_3$ ). Two equations for sample mass of  $C_T$  ( $MC_T$ ) are formed, for the approximately symmetrical ( $pH_1;pH_2$ ) and unsymmetrical ( $pH_1;pH_3$ ) pH pairs respectively. By successive approximation, all the pH values are

adjusted until  $MC_T$  for both equations is the same; this constitutes the best estimate for  $MC_T$  and accordingly  $C_T$ , and the magnitude of the pH adjustment ( $\Delta pH$ ) gives an estimate of the systematic error in pH, i.e.  $pH_{observed} + \Delta pH = pH_{true}$ . Knowing  $\Delta pH$ , the initial pH of the sample is adjusted which allows a more accurate calculation of the sample  $H_2CO_3^*$  alkalinity, from the corrected  $C_T$  and corrected initial pH.

Moosbrugger et al. (1993b) concluded that if the carbonate weak acid/base is the only one present, the pH data points in the 4 pH point method would range from pH,  $\sim 7,2$ ,  $pH_2 \sim 5,4$  and  $pH_3 \sim 4,8$  to pH,  $\sim 6,7$ ,  $pH_2 \sim 5,9$  and  $pH_3 \sim 5,3$ , i.e. the maximum titration range is from pH  $\sim 7,2$  to  $\sim 4,8$ . In a mixture of weak acid/bases, if the  $pK_a$  values of the non-carbonate weak acid/bases are near or within this pH range, the proton accepting capacity (PAC) contributions of these weak acid/bases to the titration must be isolated and removed in order to determine the correct value for  $C_T$ . If the total species concentrations of the non-carbonate weak acid/bases are known it is possible to calculate the PAC for each of these in the pH region covered by the 4 pH point titration and take account of these in the determination of  $C_T$  and  $H_2CO_3^*$  alkalinity. An approach to achieve this will now be presented for a mixture of the carbonate and a general monoprotic weak acid/base.

## Determination of $C_T$ in a mixture of the carbonate and a monoprotic weak acid/base

The basic equations defining the carbonate weak acid/base have been presented in **Part 1**. The basic equations defining a monoprotic weak acid/base are:

$$\frac{(H^+) [A^-]}{[HA]} = K_a/f_m = Ka \quad (1)$$

$$A = [HA] + [A^-] \quad (2)$$

where:

$$(H^+) = \text{hydrogen ion activity (mol/l)}$$

$$pH = -\log(H^+)$$

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