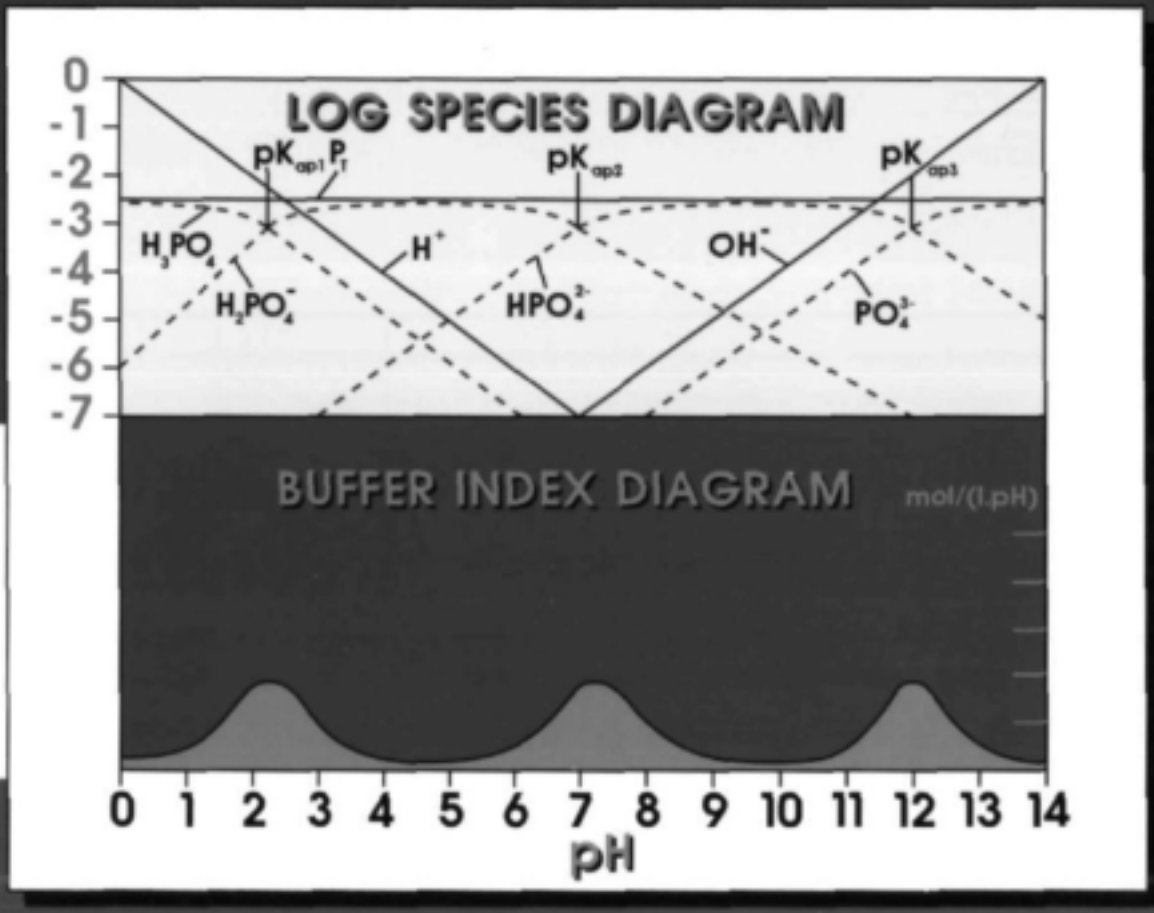
Simple titration procedures to determine $H_2CO_3^*$ alkalinity and short-chain fatty acids in aqueous solutions containing known concentrations of ammonium, phosphate and sulphide weak acid/bases



RE Moosbrugger • MC Wentzel • GA Ekama • GvR Marais

SIMPLE TITRATION PROCEDURES TO DETERMINE H_2CO_3*ALKALINITY AND SHORT-CHAIN FATTY ACIDS IN AQUEOUS SOLUTIONS CONTAINING KNOWN CONCENTRATIONS OF AMMONIUM, PHOSPHATE AND SULPHIDE WEAK ACID/BASES

by

R E Moosbrugger, M C Wentzel, G A Ekama and GvR Marais

Water Research Group
Department of Civil Engineering
University of Cape Town
Rondebosch 7700, Republic of South Africa

Prepared for the

WATER RESEARCH COMMISSION
P O Box 824, Pretoria 0001
Republic of South Africa

WRC Report No. TT 57/92
UCT Research Report W 74
December 1992

Obtainable from:

Water Research Commission
P O Box 824
Pretoria
0001
Republic of South Africa

ISBN 1 874858 54 3

This publication arises from a research project entitled:

"Pelletization in upflow anaerobic sludge bed (UASB) systems"

(WRC Project No. K5/249)

NOTICES

- The views expressed in this manual are those of the authors and do not necessarily constitute endorsement or recommendation by the Water Research Commission.
- The contents of this manual are subject to change without notice.
- All efforts have been made to ensure the accuracy of the programs and the contents of this manual. Should users find any errors the Water Research Commission will greatly appreciate being informed.
- The above notwithstanding, the Water Research Commission and the authors can assume no responsibility for any errors in the programs or the consequences of such errors.

DISCLAIMER

While it is believed that the programs are based on the best available knowledge and that considerable effort has been expended in eliminating errors, users are strongly warned that in the application of the programs the results obtained are the sole responsibility of the user.

FOREWORD

Anaerobic digestion technology is finding increasing application world–wide. In 1988 the Water Research Commission set up a contract with the University of Cape Town to conduct research on one aspect of anaerobic digestion, namely upflow anaerobic sludge bed (UASB) systems. One of the objectives set for this contract was development of strategies for control and operation of UASB systems. From an extensive experimental investigation, control of the minimum pH in the sludge bed emerged as of crucial importance. For pH control, monitoring of alkalinity and short–chain fatty acid concentrations is essential. However, the numerous difficulties with existing methods for measurement of these parameters precluded their widespread incorporation in control and operation strategies, in particular the lack of (expensive) sophisticated equipment at most full–scale installations in South Africa. Considerable research effort by the University of Cape Town was directed towards resolving this problem.

With this manual, simple elegant titration methods are presented to determine $H_2CO_3^*$alkalinity and short–chain fatty acids. These titration methods have decided advantages over existing methods in (1) attainable accuracy; (2) testing time required; and (3) simplicity of testing procedure. The methods should find wide application for routine monitoring of anaerobic digestion systems.

P E Odendaal

Executive Director

Water Research Commission

EXECUTIVE SUMMARY

Successful operation of anaerobic systems depends on, amongst others, maintenance of a near neutral pH in the reactor liquid. The pH established in an anaerobic system is a result of the interaction between the weak acid/bases present. In the desired operating pH range ($6,6 < pH < 7,4$), the main weak acid/base buffering against pH change is the carbonate [characterized by H_2CO_3*alkalinity and pH, or, total species concentration (C_T) and pH] and the main weak acid/bases causing pH decline are the short–chain fatty acids [characterized by total species concentration (A_T) and pH]. For pH control in anaerobic systems, monitoring these weak acid/bases is essential. However, the numerous difficulties with existing methods for measurement of these weak acid/bases preclude their widespread use: For direct measurement of total species concentrations (C_T and A_T), there is a lack of the necessary expensive sophisticated equipment at most full–scale installations in South Africa; for the existing indirect titration techniques, the methods are cumbersome and provide only approximations of the parameters of interest.

To overcome these problems, with this manual two simple titration procedures are presented: A 4 pH point titration for determining the carbonate weak acid/base and a 5 pH point titration for determining both the carbonate and short–chain fatty acid (SCFA) weak acid/bases in aqueous solutions. Besides the carbonate and SCFA weak acid/bases, the most common additional weak acid/bases in anaerobic digestion are phosphate, ammonium and sulphide. These can be accounted for in the titration procedures if their total species concentrations are known. Where these are not available, guidance is given on their influence on the accuracy of the results.

The titration methods require only an acid titration over the middle range of pH (initial pH to pH 6,7; 5,9; 5,2 for 4 pH point titration and to additional pH 4,3 for 5 pH point titration). If the initial pH is below 6,7, strong base addition is required to reach pH 6,7 before the strong acid titration can be commenced; however, the requirement is only to increase the pH to 6,7, i.e. there is no need to standardize the strong base. These features of the titration methods provide decided advantages over existing methods in testing time required and simplicity of testing procedure, and overcome criticisms levelled at previous titration methods, of difficulties in adequate pH probe calibration due to large pH ranges and precipitation.

Algorithms for calculating the carbonate C_T and H_2CO_3*alkalinity from the 4 pH point titration data, or the carbonate H_2CO_3*alkalinity and short–chain fatty acid A_T from the 5 pH point titration data, have been encoded into two computer programs, **TITRA4** and **TITRA5** respectively, which are included with the manual. Besides quantifying the carbonate or carbonate plus SCFA, the computer programs allow a check on the pH probe by providing an estimate of a systematic pH error where this may be present, due to poor calibration, residual liquid junction effect or any other influences on the glass electrode. The systematic pH error is taken into account automatically by the computer programs in the calculations. This increases the accuracy of data derived from the titration procedures.

The titration procedures presented with this manual should find wide use for routine monitoring of anaerobic digestion systems, and for a range of other applications.

ACKNOWLEDGEMENTS

The writers wish to express their gratitude to the following persons for their contribution to the research reported here:

- Assoc. Prof. Richard Loewenthal, for advice and comment on the procedures.
- Mr Taliep Lakay – Technical Assistant, for his invaluable help in running the experimental units and the laboratory.
- Mrs Heather Bain – Clerical Assistant, for so cheerfully typing and retyping papers and reports.

Thanks also are due to the members of the Steering Committee who guided the research work during the contract period:

- Dr J E McGlashan – Water Research Commission (Acting Chairman, 1988)
- Dr W H J Hattingh – Water Research Commission (Chairman, 1989)
- Dr H M Saayman – Water Research Commission (Chairman, 1990; Member 1991)
- Dr S A Mitchell – Water Research Commission (Chairman, 1991)
- Mr G Offringa – Water Research Commission (Member, 1989–1991)
- Mr H A Nicholls – Johannesburg City Health Department (Member, 1988)
- Mr A R Pitman – Johannesburg City Engineer's Department (Member, 1989–1991)
- Dr L H Lötter – Johannesburg City Health Department (Member, 1990–1991)
- Dr W R Ross – DWT,CSIR (1988); Ross CC (1989–1991) (Member, 1988–1991)
- Mr H A de Villiers – DWT,CSIR (Member, 1989–1991)
- Ms H Louw – Water Research Commission (Acting Committee Secretary, 1988)
- Mr P W Weideman – Water Research Commission (Committee Secretary, 1988–1991)

The writers also would like to thank the Water Research Commission and the Foundation for Research Development for financial support of the research.

TABLE OF CONTENTS

LIST OF SYMBOLS

A_T	Total short–chain fatty acid (represented by acetic acid) species concentration (mg/ℓ as HAc) $= [HAc] + [Ac^-]$
C_T	Total carbonate species concentration (mg/ℓ as $CaCO_3$) $= [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$
Ca	Normality of strong acid (mol/ℓ)
Cb	Normality of strong base (mol/ℓ)
DOS	*Disk operating system*
F_{1x}	First Gran function value $= 10^{-pH_x} (V_s + V_x)$
HAc	Acetic acid
M	Molarity (mol/ℓ)
m	Initial $H_2CO_3^*$alkalinity concentration of sample (mol/ℓ)
N	Normality; concentration of H^+ or OH^- (mol/ℓ)
N_T	Inorganic nitrogen total species concentration (mgN/ℓ) $= [NH_4^+] + [NH_3]$
P_T	Inorganic phosphorus total species concentration (mgP/ℓ) $= [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$
PC	Personal computer
pH_x	pH reading for First Gran Function, in range 3,9 to 3,4.
pH_0	Initial pH of sample
$pH_1 ... pH_4$	pH readings in titration procedures
SC	Specific conductivity (mS/m)
SCFA	Short–chain fatty acids (also called volatile fatty acids, VFA)
S_T	Sulphide total species concentration (mgS/ℓ) $= [H_2S] + [HS^-]$ ($[S^{2-}]$ negligible at pH < 12)
s	Seconds
TDS	Total dissolved solids (mg/ℓ)

TITRA4	Computer program for the 4 pH point titration
TITRA5	Computer program for the 5 pH point titration
V_s	Initial sample volume (mℓ)
V_x	Volume of strong acid (or strong acid + base) required to titrate to pH_x (mℓ)
$V_{x1}...V_{x4}$	Volume of strong acid (or strong acid + base) required to titrate to $pH_1...pH_4$ (mℓ)
V_{xe}	Volume of strong acid required to titrate to $H_2CO_3^*$ reference species equivalence point pH (mℓ)
β	Buffer index [mol/($\ell \cdot \Delta$pH)]
β_{ax}	Buffer index of weak acid/base X [mol/($\ell \cdot \Delta$pH)]
β_c	Buffer index of carbonate weak acid/base [mol/($\ell \cdot \Delta$pH)]
β_w	Buffer index of water [mol/($\ell \cdot \Delta$pH)]

CHAPTER 1

INTRODUCTION

In anaerobic fermentation a number of different microbial species contribute to the breakdown of soluble organic compounds to carbon dioxide and methane (Mosey and Fernandes, 1989; Sam-Soon *et al.*, 1987). The main groups of bacterial species and the reactions they mediate are:

- acidogens: convert influent COD to acetic (HAc), propionic (HPr) and butyric (HBr) acids and to CO_2 and H_2;
- acetogens: convert HPr and HBr to HAc, CO_2 and H_2;
- hydrogenotrophic methanogens: convert H_2 and CO_2 to CH_4; and
- acetoclastic methanogens: convert HAc to CH_4 and CO_2.

Each of these groups has a specific pH region for optimal growth; for acidogens a pH $\simeq$ 6, for acetogens, hydrogenotrophic and acetoclastic methanogens a pH $\simeq$ 7 (Gujer and Zehnder, 1983). The relative rates of growth of these groups change with pH. Under normal operating conditions in anaerobic digestion (see below), Mosey and Fernandes (1989) report the following average doubling times: acidogens – 30 min; acetogens – 1,4 d; hydrogenotrophic methanogens – 6 h; and acetoclastic methanogens – 2,6 d. To ensure optimal breakdown one condition that must be satisfied is to provide optimal pH conditions for the slowest growing organism group. From Mosey and Fernandes' work, the acetoclastic methanogens are the rate-limiting group; their growth rate is at its maximum at pH $\simeq$ 7,0 but falls sharply at pH $<$ 6,6. Consequently, it is essential to maintain the pH $>$ 6,6.

In anaerobic treatment systems, decline in pH would be due principally to an increase in short-chain fatty acids (SCFA). Increase in SCFA can be induced by a number of factors:

- Complete or partial phase separation of the acidogenic and methanogenic phases would result in an accumulation of SCFA in the acidogenic phase, and a decline of SCFA in the subsequent methanogenic phase: For example, in a plug flow or semi plug flow reactor, such as the upflow anaerobic sludge bed (UASB) reactor, along the axis of the reactor there is partial phase separation; this gives rise to

an increase in SCFA from the influent entry point to a maximum at some point up the reactor sludge bed, thereafter a decrease in SCFA to near zero at the top of the sludge bed (Sam-Soon *et al.*, 1987;1989).

- The hydrogen partial pressure ($\bar{p}H_2$) also has a crucial effect on fermentation. For example, glucose is fermented first to pyruvic acid, via the Embden-Meyerhof pathway, and thereafter the pathways depend on the $\bar{p}H_2$ conditions: Under low $\bar{p}H_2$ conditions pyruvic acid is converted to HAc only, whereas under high $\bar{p}H_2$ conditions HAc and the intermediate HPr are formed. Also with a high $\bar{p}H_2$ in the reactor, the conversion of HPr to HAc by the acetogenic organisms is inhibited. These give rise to an increase in HPr and consequently to an overall increase in SCFA (Sam-Soon *et al.*, 1989;1990).

- Toxins or inhibitory substances in the influent may act on the methanogenic phase only, causing an accumulation of SCFA.

Thus, in anaerobic treatment systems under "unbalanced" or transient process operation, SCFA may accumulate and constitute a major cause for pH change. The magnitude of pH change will depend on the magnitude of increase in SCFA concentration and the pH buffering.

By pH buffering is meant the "ability" of the solution to resist change in pH on addition of H^+ or OH^- (in any form, i.e. strong acid or base, weak acid/base). All weak acid/bases present in the solution and the water itself contribute in a greater or lesser degree to pH buffering. To quantify the weak acid/bases in solution and their contribution to pH buffering, the total species concentration of each weak acid/base and pH are required (Loewenthal and Marais, 1976). Weak acid/bases most commonly found in anaerobic fermentation are the carbonate, ammonium, phosphate, sulphide and SCFA (principally HAc and HPr, Pohland and Martin, 1969). Of these, the total species concentration of the ammonium, phosphate and sulphide weak acid/bases can be measured by conventional wet chemical techniques without undue difficulty (*Standard Methods*, 1989). With regard to the carbonate and SCFA weak acid/bases:

- For determination of carbonate total species concentration (C_T), inorganic carbon analyzers 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.

- For determination of SCFA total species concentration (A_T), distillation/titration, colorimetric and chromatographic methods are available. These methods are time consuming and involve considerable analytical skill and/or expensive equipment not usually available on full-scale anaerobic installations in South Africa.

The practical difficulties in measuring C_T have led to the development of a substitute parameter, H_2CO_3*alkalinity; if measurements of H_2CO_3*alkalinity and pH are available, C_T can be determined (Loewenthal and Marais, 1976; Loewenthal *et al.*, 1989, Chapter 2):

- The H_2CO_3*alkalinity has the merit that CO_2 loss does not affect its value (provided that carbonate precipitation does not take place). 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 the Extended Gran method requires independent accurate determination of A_T, not a simple task. For routine monitoring, the Gran and the Extended Gran methods will not find ready application.

- For determination of H_2CO_3*alkalinity/C_T or A_T, or H_2CO_3*alkalinity/C_T and A_T, simplified titration methods are available. However, these methods are either too cumbersome, or provide only approximations of the parameters of interest.

From the above, a need exists for a simple method to measure H_2CO_3*alkalinity/C_T and A_T for routine monitoring and control of anaerobic systems.

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 these parameters by a simple titration procedure. The development of this approach and the titration procedures have been detailed by Moosbrugger *et al.* (1991;1992;1993a;b;c;d). In this manual, methods for the titration procedures are set out, to determine:

- H_2CO_3*alkalinity/C_T in an aqueous solution that may contain ammonium,

phosphate and sulphide weak acid/bases of known concentration – the 4 pH point titration method.

- H_2CO_3*alkalinity/C_T and A_T in an aqueous solution that may contain ammonium, phosphate and sulphide weak acid/bases of known concentrations – the 5 pH point titration method.

The calculation of the above parameters from the data obtained in the titrations is a laborious and tedious task. To facilitate this calculation, algorithms of the calculation procedures for the 4 and 5 pH point titration methods have been developed and are encoded in computer programs which may be found on the 5¼" floppy disk that accompanies this manual. The floppy disk contains listed (Turbo Pascal Version 4.0) and compiled versions of IBM PC compatible computer programs for the 4 and 5 pH point titration methods:

Listed	Compiled
Titra4.pas	Titra4.exe
Titra5.pas	Titra5.exe

The data from the titrations are inserted in the appropriate computer program, and the results for H_2CO_3*alkalinity and A_T are computed. Details on running the computer programs are supplied in the manual.

CHAPTER 2

ALKALINITY CONCEPTS AND DEFINITIONS

INTRODUCTION

In Chapter 1 it was stated that to quantify a weak acid/base in solution, the total species concentration and pH are required. For the carbonate weak acid/base, experimentally the carbonate total species concentration (C_T) can be measured by means of an inorganic carbon analyzer, an instrument not usually available at full-scale anaerobic plants in South Africa. However, even where this instrument is available, very likely the measured C_T will be in error: In solution the carbonate weak acid/base consists of four species viz. CO_2 dissolved; carbonic acid, H_2CO_3; bicarbonate, HCO_3^-; and carbonate CO_3^{2-}. The CO_2 dissolved and H_2CO_3 always exist in a fixed proportion and, accordingly, are dealt with as a combined species, $H_2CO_3^*$ (Stumm and Morgan, 1970), i.e.

$$[H_2CO_3^*] = [CO_2 \text{ dissolved}] + [H_2CO_3] \qquad (2.1)$$

The ratio CO_2 (dissolved) : H_2CO_3 is fixed and equal to 99,76 : 0,24 at 25° C and is independent of pH and ionic strength. The dissolved CO_2 tends to equilibrium with the partial pressure of CO_2 (gas) outside the liquid. This gives rise to CO_2 exchange at the liquid/gas interface, resulting in loss or gain of CO_2 dissolved in the solution. Loss of CO_2 from solution is particularly evident in sampling anaerobic digester liquid: In the digester the partial pressure of dissolved CO_2 is much higher than that of CO_2 in the atmosphere outside the digester. When a sample is removed from the digester, on exposure to the atmosphere loss of CO_2 takes place, that is, C_T is reduced in the sample. Due to this loss of CO_2 in sample preparation, it is not possible to measure the C_T of the digester liquid accurately using an inorganic carbon analyzer. To avoid the difficulties in determination of C_T due to lack of equipment and CO_2 loss, an alternative approach to quantifying the carbonate subsystem total species concentration was developed via pH and the concept of proton accepting capacity or "alkalinity" (see Loewenthal *et al.*, 1986;1989 for a more detailed discussion).

In application, a number of different interpretations have been placed on the concept of alkalinity, for example, "Phenolphthalein alkalinity" and "Total

alkalinity" (*Standard Methods*, 1989); "bicarbonate alkalinity" (McCarty, 1974); "true bicarbonate" (Jenkins *et al.*, 1983), etc. This has led to considerable confusion and misapplication of the alkalinity concept.

In this Chapter, the intention is to define unambiguously the interpretation of alkalinity used by the authors, in particular what is meant by the $H_2CO_3^*$alkalinity which is determined using the titration procedures. This will enable the reader to relate the authors' use of alkalinity to the concepts with which the reader may be familiar.

To define the authors' interpretation of alkalinity, the situation where the carbonate weak acid/base only in solution is considered first, and then the concepts are extended to mixtures of weak acid/bases.

CARBONATE WEAK ACID/BASE ONLY IN SOLUTION

Alkalinity definition

If any one of the carbonate weak acid/base species, $H_2CO_3^*$, HCO_3^- or CO_3^{2-} species (called reference species) is added to pure water the solution is called an $H_2CO_3^*$, HCO_3^- or CO_3^{2-} equivalent solution respectively. The respective pHs established are called the $H_2CO_3^*$, HCO_3^- or CO_3^{2-} equivalence points; these equivalence points serve as reference pHs for the respective solutions. The $H_2CO_3^*$, HCO_3^- and CO_3^{2-} equivalence points are established by the respective concentrations of reference species $[H_2CO_3^*]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ added to pure water. The respective equivalence points are not fixed but change with the mass of reference species added, temperature and ionic strength. When a strong base is added to one of the equivalent solutions, the pH increases above the respective equivalence point. The mass of strong base added generates a proton (H^+) accepting capacity in the solution relative to the respective equivalence point. This capacity can be measured in a titration as the molar mass of H^+ that needs to be added to titrate back to the equivalence point using a standard strong acid. If a strong acid is added to one of the equivalent solutions, the pH will decrease below the respective equivalence point giving rise to a proton donating capacity relative to the respective equivalence point and this can be measured in a titration as the molar mass of OH^- that needs to be added to titrate back to the respective equivalence point using a strong base. Note, the proton accepting or donating capacity generated with respect to the equivalence point is equal to the mass of strong base or strong acid *originally added to the*

reference species solution and *is independent of the mass of reference species present.* Conventionally, the proton accepting capacity relative to the equivalence point (generated by addition of strong base) is taken as positive. On this basis, the proton *donating* capacity relative to the same equivalence point (generated by addition of strong acid) is in effect a negative proton *accepting* capacity.

> Historically the proton accepting capacity between the solution pH and the reference species equivalence point has been called *alkalinity* and the proton donating capacity the *acidity*. The double nomenclature is unnecessary and creates a measure of confusion because for the same equivalence point, the acidity is equal to the alkalinity but of opposite sign. Because the term alkalinity has acquired an almost universal usage in carbonate weak acid/base chemistry, Loewenthal *et al.* (1991) suggested that the term alkalinity be retained and continue to define proton accepting capacity when positive; proton donating capacity is then a negative alkalinity, thereby making the term acidity redundant.

The proton accepting capacity between the solution pH and the $H_2CO_3^*$, HCO_3^- and CO_3^{2-} equivalence points give the $H_2CO_3^*$alkalinity, HCO_3^- alkalinity, and CO_3^{2-} alkalinity respectively. From a practical point of view, the $H_2CO_3^*$alkalinity has been found the most useful (Loewenthal and Marais, 1976): The $H_2CO_3^*$alkalinity is not affected by gain or loss of CO_2 (because CO_2 is the reference species) with the result that it can be measured even if there is loss of CO_2 between sampling and measurement. For this reason the *in situ* $H_2CO_3^*$alkalinity and sample $H_2CO_3^*$alkalinity are identical. Accordingly, $H_2CO_3^*$alkalinity has been selected as the parameter for use in the titration procedures presented with this manual.

<u>System and subsystem alkalinities</u>

Following Loewenthal *et al.* (1989;1991) an aqueous solution containing only the carbonate weak acid/base constitutes the carbonate system. The carbonate system is made up of two subsystems, the carbonate subsystem and the water subsystem. The carbonate system and subsystem alkalinities for the $H_2CO_3^*$ reference species are related as follows:

$$H_2CO_3^*\text{alkalinity} = \left\{[HCO_3^-] + 2[CO_3^{2-}]\right\} + \left\{[OH^-] - [H^+]\right\} \quad (2.2)$$

$$= \text{Alk } H_2CO_3^* + \text{Alk } H_2O \quad (2.3)$$

where:

$H_2CO_3^*$alkalinity = carbonate system alkalinity with $H_2CO_3^*$ as reference species

$\text{Alk } H_2CO_3^*$ = carbonate subsystem alkalinity = $[HCO_3^-] + 2[CO_3^{2-}]$ (2.4)

$\text{Alk } H_2O$ = water subsystem alkalinity = $[OH^-] - [H^+]$ (2.5)

This formulation for $H_2CO_3^*$alkalinity applies irrespective of the presence of other weak acid/bases in the solution.

Buffer index

The carbonate system and subsystem alkalinities can be illustrated via the concept of buffer index. Consider addition of $H_2CO_3^*$ reference species to pure water, to give the $H_2CO_3^*$ equivalent solution with associated pH called the $H_2CO_3^*$ equivalence point. Incremental addition of strong base to this equivalent solution increases the pH above the $H_2CO_3^*$ equivalence point, and the molar mass of strong base added equals the $H_2CO_3^*$alkalinity. Plotting the cumulative masses of strong base (Cb) added versus pH, a titration curve is obtained; the slope of this curve (dCb/dpH) at any pH defines the buffer index (Van Slijke, 1922):

$$\beta = \mathrm{dCb/dpH} \tag{2.6a}$$

where:

Cb = mass of strong base added per litre respectively (mol/ℓ)

β = buffer index [mol/($\ell \cdot \Delta$pH)]

Note: since the solution is titrated with a strong base, the total species concentration of the weak acid/base remains constant.

Addition of strong acid to the $H_2CO_3^*$ equivalence solution has the reverse effect on pH to addition of strong base. β can be written also in terms of the mass of strong acid added (Ca):

$$\beta = -\mathrm{dCa/dpH} \tag{2.6b}$$

Thus, the buffer index is a measure of the mass of strong acid or base that must be added to effect a change in pH, or in other words, the ability of the solution at any pH to resist change in pH on addition of acid or base.

From Loewenthal and Marais (1976), β at any pH for the carbonate system and subsystems can be formulated as follows:

Carbonate subsystem:

For the carbonate weak acid/base subsystem its buffer index, β_c, can be formulated

in terms of C_T, (H^+) and K_a' as follows (Loewenthal and Marais, 1976):

$$\beta_c = -\,dCa/dpH = 2{,}303\,[C_T\,K_a'\,(H^+)]\,/\,[K_a'+(H^+)]^2 \qquad (2.7)$$

where:

C_T = carbonate total species concentration

(H^+) = proton activity at the pH of the sample

$= 10^{-pH}$

K_a' = apparent dissociation constant (see Loewenthal *et al.*, 1989).

For the diprotic carbonate weak acid/base with dissociation constants pK_{a1}' and pK_{a2}' ($pK_a' = -\log_{10} K_a'$), since the two dissociation constants differ by 4 pH units or more, the buffer index in the pH region around each pK_a' value can be described sufficiently accurately by Eq (2.7), (Loewenthal and Marais, 1976).

Water subsystem:

For the water subsystem, the buffer index is given by

$$\beta_w = 2{,}303\,\{(H^+) + K_w'/(H^+)\} \qquad (2.8)$$

where

K_w' = apparent ion product constant for water subsystem (see Loewenthal *et al.*, 1989;1991)

System:

For an aqueous solution containing the carbonate weak acid/base only, the buffer index of the system, β, at any pH is given by the sum of the buffer indices of the carbonate and the water weak acid/base subsystems:

$$\beta = \beta_c + \beta_w \qquad (2.9)$$

Alkalinity and the buffer index diagram

Since the slope of the titration curve at any pH defines the buffer index β, the area under a plot of buffer index versus pH (the buffer index diagram) between two pHs defines the mass of strong acid (or base) that must be added to the solution to move from the one pH to the other, i.e. equals the alkalinity between the two pHs. If one of the pHs is, for example, the $H_2CO_3^*$ equivalence point, then the area under the

buffer index diagram between any pH and the $H_2CO_3^*$ equivalence point quantifies the $H_2CO_3^*$alkalinity at that pH.

The buffer index diagrams for the carbonate and water subsystems have been constructed using Eqs (2.7) and (2.8) and are given in Figs 2.1a and 2.1b respectively. For $H_2CO_3^*$alkalinity as an example, this parameter can be illustrated in the buffer index–pH diagrams: As noted earlier, the $H_2CO_3^*$alkalinity can be written as the sum of the alkalinity contributions by the carbonate and the water *subsystems* (Loewenthal *et al.*, 1991), i.e.

$$H_2CO_3^*\text{alkalinity} = \text{Alk } H_2CO_3^* + \text{Alk } H_2O \qquad (2.10)$$

In terms of the pH – buffer index diagrams, Alk $H_2CO_3^*$ is the area under the carbonate buffer index curve (Fig 2.1a) (identically the carbonate proton accepting capacity contribution) between the solution pH and the $H_2CO_3^*$equivalence point (pH ≈ 4,0); Alk H_2O is the area under the water buffer index curve (Fig 2.1b) (identically the water proton accepting contribution) between the solution pH and the $H_2CO_3^*$ equivalence point; and $H_2CO_3^*$alkalinity is the sum of the two areas.

In a strong acid titration to measure $H_2CO_3^*$alkalinity, on addition of H^+ the original solution pH will decrease to say pH_x and the molar mass of H^+ added equals the area under the carbonate + water buffer index curves between the original solution pH and pH_x; the $H_2CO_3^*$alkalinity also decreases by this area and is now equal to the area under the carbonate + water buffer index curves between pH_x and the $H_2CO_3^*$ equivalence point. As more strong acid is added, so the pH will decrease further and at the point where the pH equals the $H_2CO_3^*$ equivalence point, the $H_2CO_3^*$alkalinity will equal zero – the molar mass of H^+ added now equals the area under the carbonate + water buffer index curves between the original solution pH and the $H_2CO_3^*$ equivalence point, i.e. the $H_2CO_3^*$alkalinity of the original solution. Thus, by titrating from the original solution pH to the $H_2CO_3^*$ equivalence point we can equate the molar mass of H^+ (or similarly OH^-) added to the $H_2CO_3^*$alkalinity. However, the problem in such a titration is that the $H_2CO_3^*$ equivalence point must be identified. Practically this is possible only approximately because C_T is not known before commencing the test; the equivalence point (end point in the titration) is selected empirically and the determination has validity only because the $H_2CO_3^*$ equivalence point (pH ≈ 4,0) lies in a region of low buffer index (see Figs 2.1a and 2.1b). To overcome the

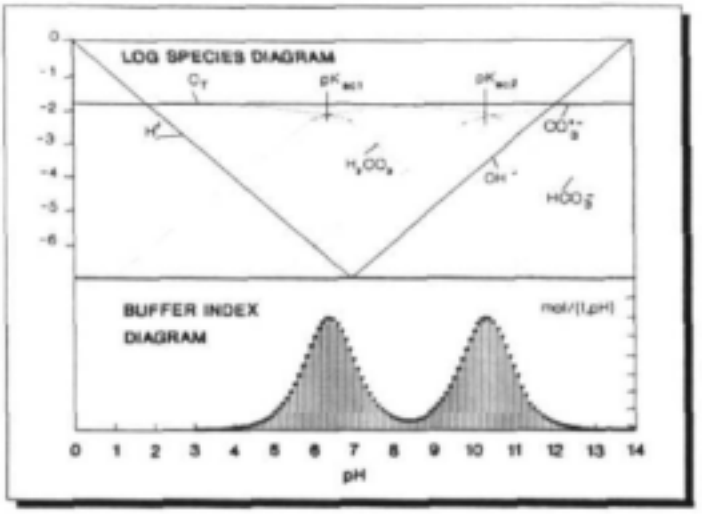


Fig 2.1a: Log [species]–pH diagram for the carbonate weak acid/base system in aqueous solution and the buffer index diagram for the carbonate subsystem. Note that pH as used in the term [mol/ℓ.pH)] refers to unit change in pH.

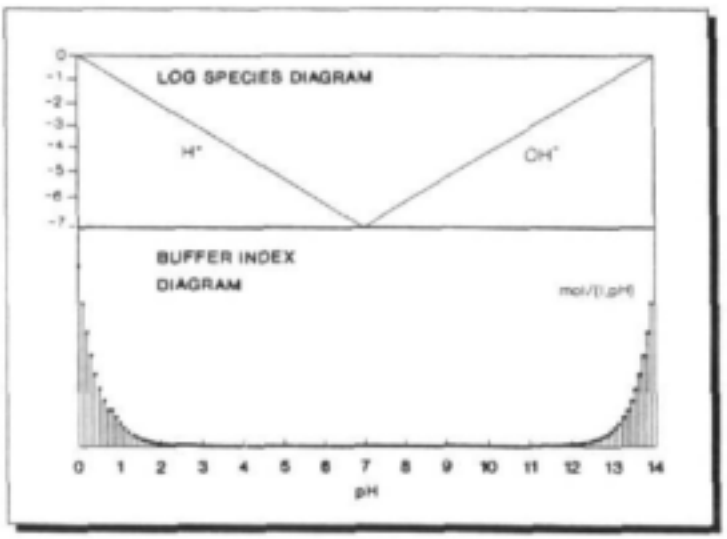


Fig 2.1b: Log [species]–pH and buffer index diagrams for the water subsystem. Note that pH as used in the term [mol/ℓ.pH)] refers to a unit change in pH.

problem of $H_2CO_3^*$ equivalence point identification and provide a more accurate estimate for $H_2CO_3^*$alkalinity, Gran (1952) developed a titration procedure whereby the $H_2CO_3^*$alkalinity can be determined without knowledge of the $H_2CO_3^*$ equivalence point. However, the Gran method is relatively complex and tedious and is unlikely to find ready application for routine monitoring. In this manual an alternative to the Gran method is presented which also allows the $H_2CO_3^*$alkalinity to be determined without titrating to the $H_2CO_3^*$ equivalence point: Referring to the buffer index curves for the carbonate (Fig 2.1a) and water (Fig 2.1b) subsystems, addition of a molar mass of H^+ (or OH^-) to the solution causes the $H_2CO_3^*$alkalinity to decrease (increase) by an equivalent amount and also the pH to decrease (increase). The magnitude of the decreases (increases) in $H_2CO_3^*$alkalinity (equal to the area under the carbonate and water buffer index curves between the two pHs) and in pH can be used to quantify the $H_2CO_3^*$alkalinity. That is, by measuring the change in $H_2CO_3^*$alkalinity between the two pH values (equivalent to the molar mass of H^+ added to move from the one pH to the other), the $H_2CO_3^*$alkalinity of the sample can be determined. The theory is quite complex but in application the calculations can be readily incorporated in a computer program. Knowing the initial pH and the change in $H_2CO_3^*$alkalinity between any two pH values (measured in the titration as the molar mass of H^+ added from one pH to the other), the $H_2CO_3^*$alkalinity can be calculated immediately. These concepts have been used to develop the titration procedures presented here (see Moosbrugger *et al.*, 1991;1993a;b;c;d).

MIXTURES OF THE CARBONATE AND OTHER WEAK ACID/BASES

In mixtures of weak acid/base systems, e.g. anaerobic digester liquid, titrating to the $H_2CO_3^*$ equivalence point and equating the mass of H^+ added to the mass of $H_2CO_3^*$alkalinity virtually always will give an incorrect result. This arises from the presence of other weak acid/base subsystems, i.e. SCFA, phosphate, sulphide and ammonium. Depending on the starting pH of the titration, these weak acid/bases will influence, in a greater or lesser degree, the mass of H^+ required to titrate to the $H_2CO_3^*$ equivalence point. This necessitates that the concept of alkalinity be extended to mixed weak acid/base systems.

Alkalinity definition

Loewenthal *et al.* (1989) extended the concept of alkalinity to mixtures of weak acid/bases that include the carbonate subsystem. They defined an alkalinity for the

solution (system) as follows: One reference species is selected for each of the weak acid/bases in solution. Addition of these reference species to pure water gives a solution reference state with associated solution reference state pH (an equivalence point for the mixture). Addition of strong base (or acid) to the solution reference state causes the pH to increase above (decrease below) the solution reference state pH and imparts an alkalinity (negative alkalinity) to the solution. The alkalinity for the solution is the proton accepting capacity between the solution and the solution reference state and can be measured in a titration as the mass of H^+ (or OH^-) that now must be added to move from the solution pH to the solution reference state pH. As an example, for a mixture of the carbonate, phosphate and ammonium weak acid/bases, the species $H_2CO_3^*$, H_3PO_4 and NH_4^+ respectively can be selected as reference species and addition of these species to pure water defines the solution reference state for this mixture by some pH, i.e. the equivalent point for the solution. Addition of strong base to the solution reference state causes the pH to increase and imparts an alkalinity (proton accepting capacity) to the solution called the $H_2CO_3^*/H_3PO_4/NH_4^+$ alkalinity (Loewenthal *et al.*, 1989;1991). It can be measured in a titration as the mass of H^+ that must be added to return to the solution reference state (solution equivalence point pH). The problem is that in attempting to determine the solution alkalinity it is necessary to know the solution equivalence point. With mixtures of weak acid/bases of unknown concentration the equivalence point invariably is not known. To resolve this problem, the relationships between the system and subsystem alkalinities need to be set out.

<u>System and subsystem alkalinities</u>

Analogous to the carbonate weak acid/base only in water, system and subsystem alkalinities for mixtures of weak acid/bases can be defined (Loewenthal *et al.*, 1991) as follows:

$$\text{System alkalinity} = \sum_{j=1}^{n} \text{Alk}_j + \text{Alk } H_2O \qquad (2.11)$$

where:

Alk_j = subsystem alkalinity for the j^{th} weak acid/base relative to its selected reference species in a mixture of n weak acid/bases.

Taking the carbonate, phosphate and ammonium weak acid/base mixture as an example:

$$\begin{aligned} H_2CO_3^*/H_3PO_4/NH_4^+ \text{ alkalinity} &= \text{Alk } H_2CO_3^* + \text{Alk } H_3PO_4 + \text{Alk } NH_4^+ \\ &\quad + \text{Alk } H_2O \\ &= \left\{2[CO_3^{2-}] + [HCO_3^-]\right\} + \left\{3[PO_4^{3-}]\right. \\ &\quad \left. + 2[HPO_4^{2-}] + [H_2PO_4^-]\right\} + \left\{[NH_3]\right\} \\ &\quad + \left\{[OH^-] - [H^+]\right\} \end{aligned} \tag{2.12}$$

Now, in Eq (2.3) we have defined $H_2CO_3^*$alkalinity = Alk $H_2CO_3^*$ + Alk H_2O; accordingly:

$$H_2CO_3^*\text{alkalinity} = H_2CO_3^*/H_3PO_4/NH_4^+ \text{ alkalinity} - \text{Alk } H_3PO_4 - \text{Alk } NH_4^+ \tag{2.13}$$

Thus, by subtracting the alkalinity contributions due to (in this example) the phosphate and ammonium weak acid/base subsystems from the solution alkalinity, the $H_2CO_3^*$alkalinity can be isolated. The alkalinity contributions for each of the non–carbonate weak acid/bases can be determined if their total species concentrations are known (Moosbrugger *et al.*, 1993b). However, the problem remains of quantifying the solution alkalinity via titration, a difficult task since the reference solution state pH cannot be identified.

Buffer index

Analogous to the carbonate weak acid/base only in solution, buffer index curves can be constructed for any weak acid/base; for examples see Figs 2.1a to 2.1f.

For an aqueous solution containing more than one weak acid/base the buffer index of the system, β, at any pH is given by the sum of the buffer indices of all the weak acid/base subsystems and the water subsystem:

$$\beta = \beta_{a1} + \beta_{a2} + \beta_{a3} + ... + \beta_w \tag{2.13}$$

where β_{a1}, β_{a2}, β_{a3} refer to the buffer indices for the weak acid/base subsystems 1, 2 and 3 respectively.

This is illustrated in the pH – buffer index diagrams (Fig 2.1); the buffer index of the solution at any pH is given by the sum of the buffer indices for each weak acid/base system present in the solution.

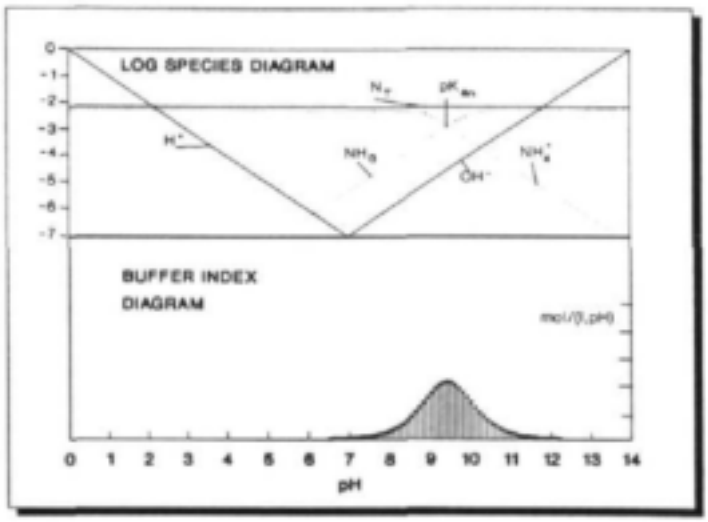


Fig 2.1c: Log [species]–pH diagram for the ammonium weak acid/base system in aqueous solution and the buffer index diagram for the ammonium subsystem. Note that pH as used in the term [mol/ℓpH)] refers to unit change in pH.

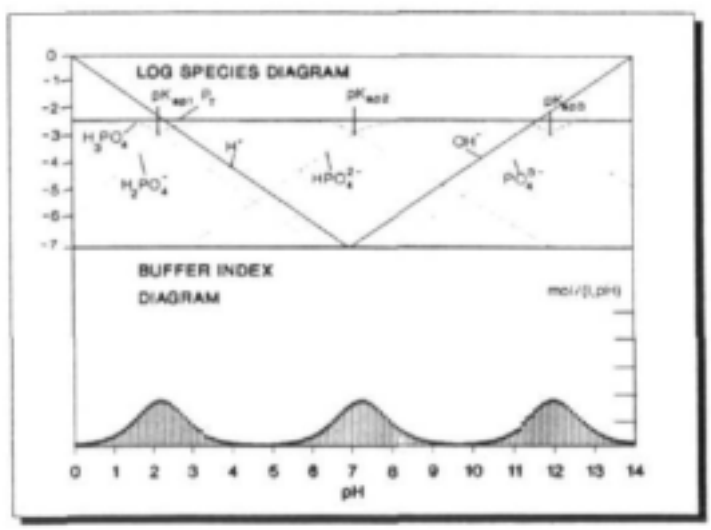


Fig 2.1d: Log [species]–pH diagram for the phosphate weak acid/base system in aqueous solution and the buffer index diagram for the phosphate subsystem. Note that pH as used in the term [mol/ℓpH)] refers to unit change in pH.

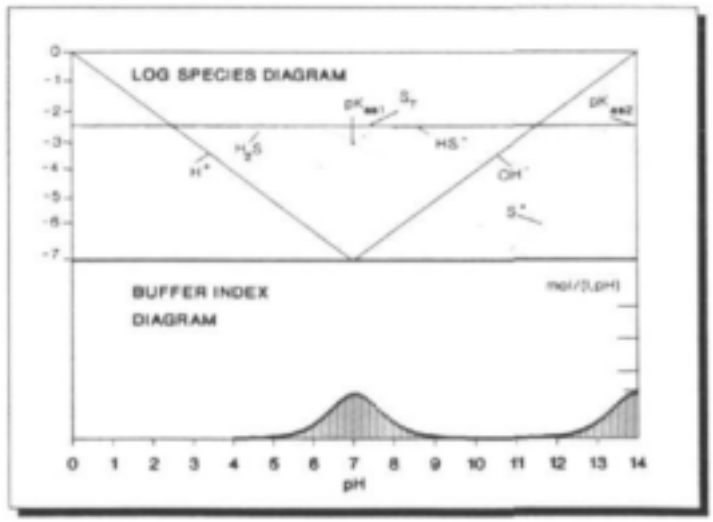


Fig 2.1e: Log [species]–pH diagram for the sulphide weak acid/base system in aqueous solution and the buffer index diagram for the sulphide subsystem. Note that pH as used in the term [mol/ℓ.pH)] refers to unit change in pH.

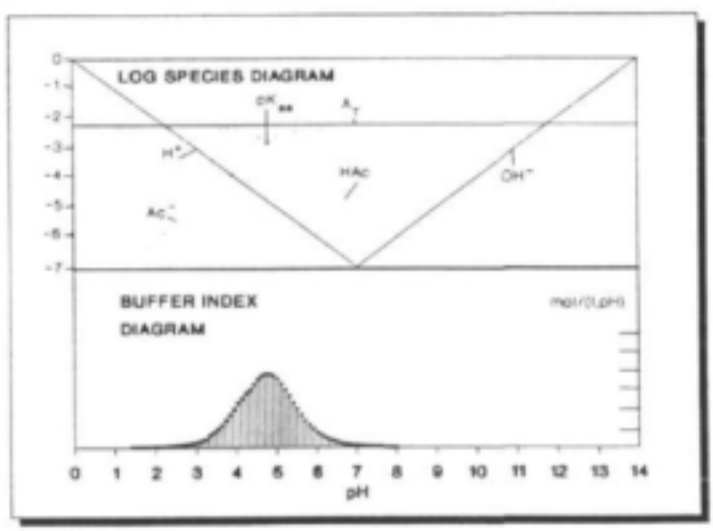


Fig 2.1f: Log [species]–pH diagram for the acetate weak acid/base system in aqueous solution and the buffer index diagram for the acetate subsystem. Note that pH as used in the term [mol/ℓ.pH)] refers to unit change in pH.

Alkalinity and the buffer index diagram for weak acid/base mixtures

With the carbonate weak acid/base only in solution, it was stated that in a titration between two pH points the molar mass of H^+ (or OH^-) added equals the *change* in $H_2CO_3^*$alkalinity and that this change and the two pH values can be used to calculate the $H_2CO_3^*$alkalinity. With mixtures of weak acid/bases in solution, in titrating from the first pH to the second pH, the mass of H^+ (or OH^-) ions that must be added to the solution equals the area under the *solution* buffer index curve (sum of areas under all weak acid/base buffer index curves) between the two pHs. From Fig 2.1 it is evident that the non-carbonate weak acid/bases can make a significant contribution to this area. It is incorrect therefore to equate the mass of H^+ (or OH^-) ions added in the titration to the change in $H_2CO_3^*$alkalinity because the $H_2CO_3^*$alkalinity is defined to include only the areas contributed by the carbonate weak acid/base and the water subsystems (Eq 2.3). Rather, addition of a molar mass of strong acid causes the *solution alkalinity* (e.g. $H_2CO_3^*/H_3PO_4/NH_4^+$ alkalinity for a mixture of the carbonate, phosphate and ammonium weak acid/bases) to decrease by an equivalent amount (equal to the sum of the areas under the buffer index curves between the two pHs for all the weak acid/bases in the solution). If the total species concentrations of each of the non-carbonate weak acid/bases are known, then the contribution of these weak acid/bases to the solution alkalinity decrease can be subtracted, and the decrease in $H_2CO_3^*$alkalinity determined [similar to Eq (2.13)]; this decrease in $H_2CO_3^*$alkalinity can be used again to quantify the $H_2CO_3^*$alkalinity. This approach forms the basis for the titration procedures presented here for determination of $H_2CO_3^*$alkalinity in a mixture of weak acid/bases provided the total species concentration of all the non-carbonate weak acid/bases are known – the 4 pH point titration (for details see Moosbrugger *et al.*, 1993b;1993c). Using a similar approach, titration procedures have been developed to determine $H_2CO_3^*$alkalinity *and* SCFA total species concentration in a mixture that includes ammonium, phosphate and sulphide weak acid/bases of known concentrations – the 5 pH point titration (for details see Moosbrugger *et al.*, 1993b).

CHAPTER 3

4 pH POINT TITRATION PROCEDURE

OBJECTIVE

The testing procedure for the 4 pH point titration method is set out for determination of the $H_2CO_3^*$alkalinity and the total carbonate species concentration, C_T, in aqueous solutions containing zero or known concentrations of free and saline ammonia, inorganic phosphate and sulphides. The method also provides an estimate of any systematic pH error due to inadequate calibration, residual liquid junction effect, or other causes giving rise to a consistent pH error.

BACKGROUND

The theory for this method is set out in detail by Moosbrugger *et al.* (1991;1993b;1993c).

PRINCIPLE

The sample is titrated from its initial pH to 3 further pH points. Knowing the concentrations of inorganic phosphate, free and saline ammonia and sulphides, the concentrations of $H_2CO_3^*$alkalinity and C_T are derived from the theory on which the method is based. The measured data are entered in a PC program (see attached disk and Chapters 5 and 6) to facilitate the necessary calculations.

METHOD

Apparatus

The following apparatus is required:

- titration burette (10 mℓ) allowing dosing increments of 0,02 mℓ of titrant
- pH meter allowing readings to the second decimal place
- pH probe, preferably of the combined glass electrode type
- a magnetic stirrer and stirrer bar (length $\simeq$ 25 mm)
- thermometer accurate to $\pm$ 0,5 °C

- filter stand and ordinary filter paper, e.g. Schleicher und Schuell 505
- measuring pipettes (A grade) from 5 to 50 mℓ
- 100 mℓ Erlenmeyer flask
- specific conductivity meter and probe (if available)
- mass scale accurate to ± 1 mg
- stop watch.

Chemicals

The following chemicals are required:

- hydrochloric acid
- sodium hydroxide
- distilled water
- anhydrous sodium carbonate
- pH buffer solutions (pH = 4,00 and pH = 7,00).

The hydrochloric acid requires accurate standardization, see **Appendix A Standardization of strong acid**. With the sample volumes (for anaerobic digester samples) suggested in the testing procedure below, standardization of the strong acid solution of hydrochloric acid to about 0,08 N is recommended, using high purity sodium carbonate. The strong base solution of sodium hydroxide (if required), should be made up to approximately the same normality as the hydrochloric acid, e.g. 0,08 to 0,1 N; standardization of the strong base is not necessary.

The pH probe needs to be calibrated using two pH buffer solutions bracketing the *pH titration range of the 4 pH point titration (excluding the initial pH)*. It is recommended to use the following two National Bureau of Standards (NBS) buffer solutions: (1) 0,05 M KH phthalate buffer (pH = 4,00 at 25 °C); and (2) 0,0275 M disodium hydrogen phosphate and 0,025 M potassium dihydrogen phosphate (pH 7,00 at 25 °C).

Ancillary measurements

All ancillary measurements are made on the filtered *undiluted* samples.

Ammonium/ammonia total species concentration

To enhance the accuracy of the $H_2CO_3^*$alkalinity and C_T estimates the influence of the ammonium weak acid/base subsystem on the 4 pH point titration can be

minimized by taking into account its total species concentration (N_T) in the algorithm employed to calculate the $H_2CO_3^*$alkalinity and C_T. The N_T can be measured according to *Standard Methods* (1989) and is measured on the *undiluted* sample. If no measurement is available an approximate estimate of N_T, or N_T = zero, is entered into the computer program. An assessment of error in measurement or neglect of this subsystem on the estimates of $H_2CO_3^*$alkalinity and C_T is presented by Moosbrugger *et al.* (1991;1993c); neglect of N_T does not have a significant influence on the estimates of $H_2CO_3^*$alkalinity and C_T. If no ammonium/ammonia is present in the sample, N_T = zero is entered into the computer program.

Phosphate total species concentration

Analogous to the ammonium weak acid/base subsystem the accuracy of the $H_2CO_3^*$alkalinity and C_T estimates can be enhanced by taking into account the total species concentration of the phosphate weak acid/base subsystem (P_T). The P_T can be measured according to *Standard Methods* (1989), and is measured on the *undiluted* sample. If no measurement is available an approximate estimate of P_T, or, P_T = zero is entered into the computer program. An assessment of error in measurement or neglect of this subsystem on the estimates of $H_2CO_3^*$alkalinity and C_T is presented by Moosbrugger *et al.* (1991;1993c); neglect of P_T has a significant influence on the estimates of $H_2CO_3^*$alkalinity and C_T. If no phosphate is present in the sample, P_T = zero is entered into the computer program.

Sulphide total species concentration

Analogous to the ammonium and phosphate weak acid/base subsystems, the accuracy of the $H_2CO_3^*$alkalinity and C_T estimates can be enhanced by taking into account the total species concentration of the sulphide weak acid/base subsystem (S_T). The S_T can be measured according to *Standard Methods* (1989) and is measured on the *undiluted* sample. If no measurement is available, an approximate estimate of S_T or S_T = zero is entered in the computer program. In most situations, the concentrations of sulphides will be minor compared to the carbonate subsystem (Moosbrugger *et al.*, 1991;1993c) and its neglect in estimation of $H_2CO_3^*$alkalinity and C_T will give rise to negligible error. If no sulphides are present in the sample, S_T = zero is entered into the computer program.

Total dissolved solids (TDS) or specific conductivity (SC) of undiluted sample

To calculate the apparent dissociation constants of the different weak acid/bases (carbonate, free and saline ammonia, inorganic phosphate and sulphide) in the computer program the total dissolved solids (TDS), or alternatively the specific conductivity (SC), of the *undiluted* sample must be entered and hence needs to be measured. Accurate measurement of one of these parameters requires additional experimental effort which may not be justified – the algorithm developed to determine C_T and H_2CO_3*alkalinity acts in a compensative fashion to make the estimates of C_T and H_2CO_3*alkalinity relatively insensitive to TDS or SC. Hence approximation of TDS or SC is adequate in most cases. Whether measurement of TDS or SC for each test is necessary will depend on the accuracy desired for the determination of C_T and H_2CO_3*alkalinity.

Sample preparation

The undiluted sample must be representative of the liquid to be tested. Usually a sufficiently large liquid volume is available for testing purpose. Filter the sample prior to the titration to separate the solid from the liquid phase and expel CO_2 from the sample (this has the important effect of raising the pH of the undiluted sample, a matter of particular importance in the event that the pH of the undiluted sample is below 6,7). *The ancillary measurements are done on the filtered undiluted sample.* From the filtered undiluted sample a volume needs to be selected for titration; a choice has to be made with regard to:

- Sample size (mℓ) undiluted.
- Sample size (mℓ) diluted.

Sample size (undiluted)

The choice of undiluted sample volume is determined by the dilution required and the diluted sample volume [see section ***Sample size (diluted)*** below]. Dilution of the sample is necessary for two reasons: (1) to achieve a total carbonate species concentration, C_T, below about 500 mg/ℓ as $CaCO_3$ to avoid undue CO_2 loss during titration; and (2) to reduce the temperature of the diluted sample to about 20 to 25 °C. Dilutions to meet these requirements are recommended for optimal accuracy. Experience has shown that for TDS up to 15 000 mg/ℓ, TDS usually is not a criterion in dilution (for analysis see Chapter 4). The dilution ratio is kept as low as possible to avoid multiplication effects of titration errors: H_2CO_3*alkalinity/C_T determined by titration are for the *diluted* sample; the

respective values for the undiluted sample are obtained by multiplying the values of the diluted sample with the dilution ratio. Hence, any titration error in the diluted sample will be multiplied by the dilution ratio leading to loss of accuracy and precision.

Sample size (diluted)

The diluted sample size depends on the physical properties of the pH probe and the titration vessel. In developing the 4 pH point titration method, the pHs were measured using a combined glass electrode (Radiometer Copenhagen GK2401C). The basic physical requirement to be satisfied is that the tip and porous pin (liquid junction) are immersed in the sample below the liquid surface. With the 100 mℓ Erlenmeyer flask as titration vessel, for the Radiometer probe the tip and porous pin are well immersed using a diluted sample volume of 50 mℓ. With titration vessels greater than 100 mℓ, greater diluted sample volumes are required. Using Erlenmeyer flasks as titration vessels, in general, it should be noted that the surface (open to atmosphere) to volume ratio of the diluted sample should be small to minimize CO_2 loss; stirring time should be short and the stirring rate gentle in order to minimize CO_2 loss, yet adequate to achieve homogeneous mixing conditions. From practical experience these conditions appear to be satisfied with 50 mℓ of diluted sample in a 100 mℓ Erlenmeyer flask using a magnetic stirrer bar of 25 mm length rotating at approximately 60 rpm. Dilution of the sample is effected by pipetting a volume of undiluted sample, say 10 mℓ, into the flask and making up the volume to 50 mℓ by adding distilled water, in this case 40 mℓ.

Titration procedure

The 4 pH point titration involves the following step by step procedure:

(1) Draw sample and filter using ordinary filter paper, e.g. Schleicher and Schuell 505. On the filtered sample, measure TDS (or SC), P_T, N_T and S_T.

(2) Pipette 50 mℓ of filtered sample into a 100 mℓ Erlenmeyer flask. If dilution is required pipette a smaller amount of filtered sample, say 10 mℓ, into the flask and make up the volume to 50 mℓ by adding distilled water, in this case 40 mℓ. The requirement for dilution is that C_T is below about 500 mg/ℓ as $CaCO_3$.

(3) Insert thermometer and pH probe, stir gently (± 60 rpm with magnetic stirrer bar of 25 mm) for 15 seconds (s), take temperature reading, remove thermometer and stop stirring.

(4) Wait a further 45 s and record initial pH (pH_0) reading (this gives the probe a total stabilization period of 60 s at pH_0).

(5) Switch on stirrer and titrate sample from pH_0 to pH_1 (6,7 ± 0,1). When pH_1 has been reached, stir for about 30 s, then switch off stirrer, record volume of titrant added from pH_0 to pH_1 and take pH_1 reading about 30 s after termination of stirring. The volume of titrant added to titrate from pH_0 to pH_1 is designated V_{x1}.

(6) Repeat step (5) to titrate from pH_1 to pH_2 (5,9 ± 0,1), from pH_2 to pH_3 (5,2 ± 0,1). The volumes of titrant recorded at each pH point (V_{x2}, V_{x3}) are the *cumulative volumes, i.e. the volume added from the initial pH point* (pH_0) to reach the respective lower pH points.

Note: If the initial pH (pH_0) of the diluted sample is below 6,7, then pH_0 is recorded; strong base is added to raise pH_0 to $pH_1 = 6,7 \pm 0,1$. The volume of strong base added is V_{x1} when entered into the computer program. Acid titration commences from pH_1. The cumulative volumes for the strong acid titration, V_{x2} and V_{x3}, are the *sum* of strong base and acid volumes added to reach pH_2 and pH_3 from the initial pH point, pH_0.

If pH_0 of the diluted sample is 6,7 ± 0,1 then pH_0 equals pH_1 and $V_{x1} = 0$ (V_{x1} is set to zero when entered into the computer program). The cumulative volumes for the strong acid titration V_{x2} and V_{x3} are the strong acid volumes added to reach pH_2 and pH_3 from the starting pH point, $pH_0 = pH_1$.

Depending on the initial pH of the diluted sample, two different types of titration data tables will be obtained which can be summarized as follows:

(1) Data table for titration with strong acid only (if initial diluted sample pH $\geq$ 6,7):

V_x	:	pH_x
0	:	initial diluted sample pH (pH_0) $\geq$ 6,7
V_{x1}	:	pH_1 (6,70 $\pm$ 0,1) ($V_{x1} = 0$ if $pH_0 = 6,7$)
V_{x2}	:	pH_2 (5,90 $\pm$ 0,1)
V_{x3}	:	pH_3 (5,20 $\pm$ 0,1)

Note that V_{x2} and V_{x3} are the cumulative volumes of strong acid added.

(2) Data table for titration with strong acid after addition of a strong base to raise the initial pH to pH_1 (if initial diluted sample pH < 6,7 $\pm$ 0,1):

V_x	:	pH_x
0	:	initial diluted sample pH (pH_0) < 6,7
V_{x1}	:	pH_1 (6,7 $\pm$ 0,1 after adding V_{x1} mℓ of strong base)
V_{x2}	:	pH_2 (5,90 $\pm$ 0,1)
V_{x3}	:	pH_3 (5,20 $\pm$ 0,1)

Note that V_{x2} and V_{x3} are the sum of the volume of strong base and the cumulative volume of strong acid added.

Ideally, the pH values should be located within a $\pm$ 0,1 limit of the values given above (easily attainable even with little experience). In some cases the pH values pH_1, pH_2 and pH_3 might be outside the above mentioned limit of $\pm$ 0,1 pH units, say due to "over enthusiastic" addition of titrant. However, from experience if the sample is being "over titrated" accidentally it is not necessary to repeat the titration provided the pH value is located within 0,2 pH units from the appropriate value. If the sample is being "under titrated", step (5) of the step by step procedure may be repeated to obtain pH_1, pH_2 or pH_3 within the acceptable limit of $\pm$ 0,1 pH units from the appropriate pH value.

CALCULATION OF RESULTS

Input data for computer program

H_2CO_3*alkalinity and C_T are calculated using the personal computer program **TITRA4** (see floppy disk and Chapter 5). The input data required from the titration for the computer program are as follows:

pH_0 – initial pH of diluted sample
pH_1 – pH after addition of V_{x1}
pH_2 – pH after addition of V_{x2}
pH_3 – pH after addition of V_{x3}
V_{x1} (mℓ) – Volume of strong acid or base added from pH_0 to pH_1
V_{x2} (mℓ) – Cumulative volume of strong acid (and strong base, if any) added from pH_0 to pH_2
V_{x3} (mℓ) – Cumulative volume of strong acid (and strong base, if any) added from pH_0 to pH_3
Normality of strong acid titrant (mol/ℓ)
Sample size (undiluted) (mℓ)
Sample size (diluted) (mℓ)
Temperature (°C)
TDS (mg/ℓ) – Total dissolved solids, or,
SC (mS/m) – Specific conductivity
N_T (mg/ℓ as N) – Total species conc. of free and saline ammonia
P_T (mg/ℓ as P) – Total species conc. of inorganic phosphate
S_T (mg/ℓ as S) – Total species conc. of sulphides

Note that either TDS or SC need to be entered in the program; if TDS is entered SC is calculated internally, and, similarly, TDS is calculated if SC is entered. The parameters TDS (or SC), N_T, P_T and S_T are measurements on the *undiluted* sample.

<u>Output data from computer program</u>
The computer program supplies the following data:

- H_2CO_3*alkalinity of undiluted sample (mg/ℓ as $CaCO_3$)
- Total carbonate species concentration (C_T) of undiluted sample (mg/ℓ as $CaCO_3$)
- Estimate of systematic pH error

<u>Note</u>:
(1) The systematic pH error may be due to poor pH probe calibration, residual liquid junction or any other effects on the pH electrode. The systematic pH error is taken into account automatically by the program in calculating H_2CO_3*alkalinity and C_T.

(2) The correction for systematic pH error is subject to the condition that the carbonate weak acid/base dominates [i.e. $C_T > 2 \cdot (N_T + P_T + S_T)$] in the sample.

(3) The maximum correction for systematic pH errors made by the program is set to ± 0,2 pH units. From practical experience an average systematic pH error of about – 0,05 pH units will be encountered with the diluted sample. It would appear therefore that with systematic pH errors of > ± 0,2 indicated by the computer program, the pH probe needs to be recalibrated and the test repeated.

(4) The $H_2CO_3^*$alkalinity and C_T are the concentrations present in the *undiluted* sample. The $H_2CO_3^*$alkalinity of the undiluted sample is identical to that of the *in situ* solution. However, C_T of the undiluted sample and *in situ* solution may differ due to CO_2 loss between sampling and testing. If C_T of the *in situ* solution is required, this is found from the *in situ* pH, *in situ* temperature, *in situ* TDS and the undiluted sample $H_2CO_3^*$alkalinity measured with the 4 pH point titration method, see Loewenthal *et al.* (1989). Usually *in situ* C_T is of no practical importance and therefore this calculation is not included in the computer programs.

CHAPTER 4

5 pH POINT TITRATION PROCEDURE

OBJECTIVE

The testing procedure for the 5 pH point titration method is set out for determination of the H_2CO_3*alkalinity (via the total carbonate species concentration, C_T, and initial sample pH) *and* SCFA in aqueous solutions also containing zero or known concentrations of the ammonium, phosphate and sulphide weak acid/bases, e.g. anaerobic digester liquid. The method also provides an estimate of any systematic pH error due to inadequate calibration, residual liquid junction effect, or other causes giving rise to a consistent pH error. It was developed for application in monitoring anaerobic fermentation systems.

BACKGROUND

The theory of the method is set out in detail by Moosbrugger *et al.* (1991;1993d).

PRINCIPLE

The sample is titrated from its initial pH to 4 further pH points. Knowing the concentrations of inorganic nitrogen, phosphate and sulphides, the concentrations of SCFA and H_2CO_3*alkalinity can be derived from the theory on which the method is based. The measured data are entered in a PC program to facilitate the necessary calculations (see attached disk and Chapters 5 and 6).

METHOD

Apparatus

The following apparatus is required:

- titration burette (10 mℓ) allowing dosing increments of 0,02 mℓ of titrant
- pH meter allowing readings to the second decimal place
- pH probe, preferably of the combined glass electrode type
- a magnetic stirrer and stirrer bar (length $\simeq$ 25 mm)
- thermometer accurate to $\pm$ 0,5 °C

- filter stand and ordinary filter paper, e.g. Schleicher und Schuell 505
- measuring pipettes (A grade) from 5 to 50 mℓ
- 100 mℓ Erlenmeyer flask
- specific conductivity meter and probe (if available)
- mass scale accurate to * 1 mg
- stop watch.

Chemicals

The following chemicals are required:

- hydrochloric acid
- sodium hydroxide
- distilled water
- anhydrous sodium carbonate
- pH buffer solutions (pH = 4,00 and pH = 7,00).

The hydrochloric acid requires accurate standardization, see **Appendix A Standardization of strong acid**. With the sample volumes (for anaerobic digester samples) suggested in the testing procedure below, standardization of the strong acid solution of hydrochloric acid to about 0,08 N is recommended, using high purity sodium carbonate. The strong base solution of sodium hydroxide (if required), should be made up to approximately the same normality as the hydrochloric acid, e.g. 0,08 to 0,1 N; standardization of the strong base is not necessary.

The pH probe needs to be calibrated using two pH buffer solutions bracketing the pH titration range of the 5 pH point titration (excluding the initial pH). It is recommended to use the following two National Bureau of Standards (NBS) buffer solutions: (1) 0,05 M KH phthalate buffer (pH = 4,00 at 25 °C), and (2) 0,0275 M disodium hydrogen phosphate and 0,025 M potassium dihydrogen phosphate (pH 7,00 at 25 °C).

Ancillary measurements

All ancillary measurements are made on the filtered *undiluted* samples.

Inorganic nitrogen total species concentration

To enhance the accuracy of the H_2CO_3*alkalinity and SCFA estimates, the influence of the ammonium weak acid/base subsystem on the 5 pH point titration can be minimized by taking into account its total species concentration (N_T) in the

algorithm employed to calculate the $H_2CO_3^*$alkalinity and SCFA. The N_T can be measured according to *Standard Methods* (1989), and is measured on the *undiluted* sample. If no measurement is available an approximate estimate of N_T, or N_T = zero, is entered into the computer program. An assessment of error in measurement or neglect of this subsystem on the estimates of $H_2CO_3^*$alkalinity and SCFA, is presented by Moosbrugger *et al.* (1991;1993b); neglect of N_T does not have a significant influence on the estimates of $H_2CO_3^*$alkalinity and SCFA. If the ammonium weak acid/base is not present in the sample, N_T = zero is entered into the computer program.

Inorganic phosphate total species concentration

Analogous to the ammonium weak acid/base subsystem, the accuracy of the $H_2CO_3^*$alkalinity and SCFA estimates can be enhanced by taking into account the total species concentration of the phosphate weak acid/base subsystem (P_T). The P_T can be measured according to *Standard Methods* (1989), and is measured on the *undiluted* sample. If no measurement is available an approximate estimate of P_T, or, P_T = zero is entered into the computer program. An assessment of error in measurement or neglect of this subsystem on the estimates of $H_2CO_3^*$alkalinity and SCFA, is presented by Moosbrugger *et al.* (1991;1993d); neglect of P_T has a significant influence on the estimates of $H_2CO_3^*$alkalinity and SCFA. If the phosphate weak acid/base is not present in the sample, P_T = zero is entered into the computer program.

Sulphide total species concentration

Analogous to the ammonium and phosphate weak acid/base subsystems, the accuracy of the $H_2CO_3^*$alkalinity and C_T estimates can be enhanced by taking into account the total species concentration of the sulphide weak acid/base subsystem (S_T). The S_T can be measured according to *Standard Methods* (1989) and is measured on the *undiluted* sample. If no measurement is available, an approximate estimate of S_T or S_T = zero is entered in the computer program. In most situations, the concentrations of sulphides will be minor compared to the carbonate subsystem (Moosbrugger *et al.*, 1991;1993a) and its neglect in estimation of $H_2CO_3^*$alkalinity and C_T will give rise to negligible error. If no sulphides are present in the sample, S_T = zero is entered into the computer program.

Total dissolved solids (TDS) or specific conductivity (SC) of undiluted sample

To calculate the apparent dissociation constants of the different weak acid/bases

(carbonate, SCFA, free and saline ammonia, inorganic phosphate and sulphide) in the computer program, the total dissolved solids (TDS) or alternatively the specific conductivity (SC) of the *undiluted* sample must be entered and hence needs to be measured. Accurate measurement of one of these parameters requires additional experimental effort which may not be justified – the algorithm developed to determine the SCFA and H_2CO_3*alkalinity acts in a compensative fashion to make the estimates of SCFA and H_2CO_3*alkalinity relatively insensitive to TDS or SC. Hence, approximation of TDS or SC is adequate in most cases. Accordingly measurement of TDS or SC may not prove necessary for each filtered sample, but may be done only daily or weekly depending on the expected variations of the operating conditions of the reactor. Whether measurement of TDS or SC for each test is necessary will depend on the accuracy desired for the determination of SCFA and H_2CO_3*alkalinity.

To illustrate the effect of errors in TDS on the calculation of H_2CO_3*alkalinity and SCFA, consider the following hypothetical example: Take a typical set of titration data for an anaerobic reactor liquid sample: V_s (diluted) = 50 mℓ, V_s (undiluted) = 10 mℓ, SCFA = 300 mg/ℓ as HAc, H_2CO_3*alkalinity = 1740 mg/ℓ as $CaCO_3$, TDS = 3340 (mg/ℓ), temperature = 21 °C (after dilution) and $N_T = P_T = S_T = 0$ mg/ℓ; SCFA and H_2CO_3*alkalinity values are calculated using various hypothetical values for TDS ranging from 1 000 to 7 000 mg/ℓ (in the undiluted sample). The results for these calculations are shown plotted in Fig 4.1. The plot indicates that SCFA and H_2CO_3*alkalinity determined with the 5 pH point titration method are not sensitive to changes in TDS (or SC).

<u>Sample preparation</u>

The undiluted sample has to be representative of the liquid to be tested. Usually a sufficiently large liquid volume is available for testing purpose. Filter the sample prior to the titration to separate the solid from the liquid phase and expel CO_2 from the sample (this has the important effect of raising the pH of the undiluted sample, a matter of particular importance in the event that the pH of the undiluted sample is below 6,7). *The ancillary measurements are done on the filtered undiluted sample.*

From the filtered undiluted sample a volume needs to be selected for titration; a choice has to be made with regard to:

- Sample size (mℓ) undiluted
- Sample size (mℓ) diluted.

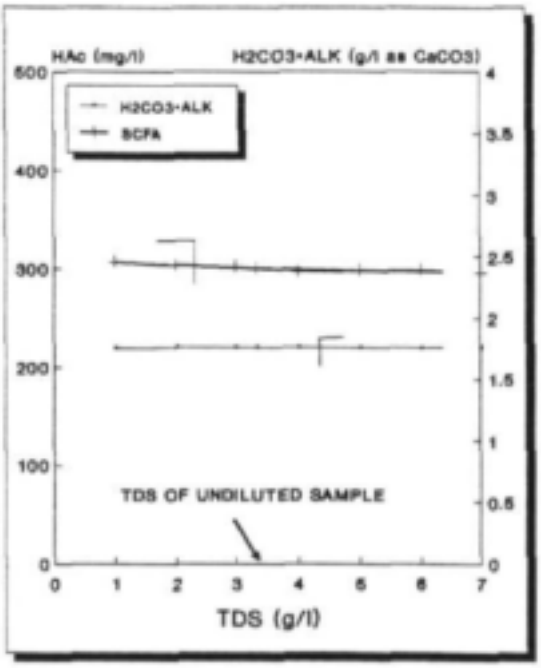


Fig 4.1: Influence of changes in the total dissolved solids concentration (TDS) on the determination of SCFA and $H_2CO_3^*$alkalinity with the aid of the 5 pH point titration method: SCFA and $H_2CO_3^*$alkalinity values for a sample containing 300 mg/ℓ of HAc and 1 740 mg/ℓ as $CaCO_3$ of $H_2CO_3^*$alkalinity are calculated with hypothetical TDS concentrations ranging from 1 000 to 7 000 mg/ℓ.

Sample size (undiluted)

The choice of undiluted sample volume is determined by the dilution ratio required and the diluted sample volume [see section *Sample size (diluted)* below]. Dilution of the sample is necessary for two reasons: (1) to achieve a total carbonate species concentration, C_T, below about 500 mg/ℓ as $CaCO_3$ to avoid undue CO_2 loss during titration; and (2) to reduce the temperature of the diluted sample to about 20 to 25 °C. Dilutions to meet these requirements are recommended for optimal accuracy.

For anaerobic reactor liquids, generally the above conditions will be satisfied using a dilution ratio of 1:4 (1 in 5 or 5 times dilution). Normally a diluted sample volume of 50 mℓ is adequate (see below); this implies an undiluted sample volume of 10 mℓ which is made up to 50 mℓ by addition of distilled water. The dilution ratio is kept as low as possible to avoid multiplication effects of titration errors: $H_2CO_3^*$alkalinity/C_T and SCFA determined by titration are for the *diluted* sample;

the respective values for the undiluted sample are obtained by multiplying the values of the diluted sample with the dilution ratio. Hence, any titration error in the diluted sample will be multiplied by the dilution ratio leading to loss of accuracy and precision.

Sample size (diluted)

The diluted sample size depends on the physical properties of the pH probe and the titration vessel. In developing the 5 pH point titration method, the pHs were measured using a combined glass electrode (Radiometer Copenhagen GK2401C). The basic physical requirement to be satisfied is that the tip and porous pin (liquid junction) are immersed in the sample below the liquid surface. With the 100 mℓ Erlenmeyer flask as titration vessel, for the Radiometer probe the tip and porous pin are well immersed using a diluted sample volume of 50 mℓ. With titration vessels greater than 100 mℓ, greater diluted sample volumes are required. Using Erlenmeyer flasks as titration vessels, in general, it should be noted that the surface (open to atmosphere) to volume ratio of the diluted sample should be small to minimize CO_2 loss; stirring time should be short and the stirring rate gentle in order to minimize CO_2 loss, yet adequate to achieve homogeneous mixing conditions. From practical experience these conditions appear to be satisfied with 50 mℓ of diluted sample in a 100 mℓ Erlenmeyer flask using a magnetic stirrer bar of 25 mm length rotating at approximately 60 rpm.

Titration procedure

The 5 pH point titration involves the following step by step procedure:

(1) Draw sample and filter using ordinary filter paper, e.g. Scheicher and Schuell 505. On the filtered sample, measure TDS (or SC), P_T, N_T and S_T.

(2) Pipette 10 mℓ of the filtered sample and 40 mℓ distilled water into a 100 mℓ Erlenmeyer flask to give a dilution ratio of 1:4 (1 in 5 or 5 times dilution). The requirement for dilution is to have C_T diluted to smaller than about 500 mg/ℓ as $CaCO_3$. (With the dilution ratio of 1:4 this condition usually will be satisfied for anaerobic digester liquids. If subsequently from the analysis it is found that $C_T > 500$ mg/ℓ as $CaCO_3$ then the test needs to be repeated at a higher dilution ratio, estimated from the initial test results).

(3) Insert thermometer and pH probe, stir gently for 15 seconds (s), take

temperature reading, remove thermometer and stop stirring.

(4) Wait a further 45 s and record initial pH (pH_0) reading (this gives the probe a total stabilization period of 60 s at pH_0).

(5) Switch on stirrer and titrate sample from pH_0 to pH_1 (6,7 ± 0,1). When pH_1 has been reached, stir for about 30 s, then switch off stirrer, record volume of titrant added from pH_0 to pH_1 and take pH_1 reading about 30 s after termination of stirring. The volume of titrant added to titrate from pH_0 to pH_1 is designated V_{x1}.

(6) Repeat step (5) to titrate from pH_1 to pH_2 (5,9 ± 0,1), from pH_2 to pH_3 (5,2 ± 0,1) and from pH_3 to pH_4 (4,3 ± 0,1). The volumes of titrant recorded at each pH point (V_{x2}, V_{x3}, V_{x4}) are the *cumulative volumes*, i.e the volume added from the initial pH point (pH_0) to reach the respective lower pH points.

Note: If the initial pH (pH_0) of the diluted sample is below 6,7 then pH_0 is recorded; strong base is added to raise pH_0 to $pH_1 = 6,7 \pm 0,1$. The volume of strong base added is V_{x1} when entered in the computer program. Acid titration commences from pH_1. The cumulative volumes for the strong acid titration, V_{x2}, V_{x3} and V_{x4} are the *sum* of strong base *and* acid volumes added to reach pH_2, pH_3 and pH_4 from the initial pH point, pH_0.

If pH_0 of the diluted sample is 6,7 ± 0,1 then pH_0 equals pH_1 and $V_{x1} = 0$ (V_{x1} is set to zero when entered into the computer program). The cumulative volumes for the strong acid titration V_{x2}, V_{x3} and V_{x4} are the cumulative strong acid volumes added to reach pH_2, pH_3 and pH_4 from the starting pH point, $pH_0 = pH_1$.

Depending on the initial pH of the diluted sample, two different types of titration data tables will be obtained which can be summarized as follows:

(1) Data table for titration with strong acid only (if initial diluted sample pH ≥ 6,7):

V_x	:	pH_x
0	:	initial diluted sample pH (pH_0) ≥ 6,7
V_{x1}	:	pH_1 (6,70 ± 0,1) ($V_{x1} = 0$ if $pH_0 = 6,7$)

V_{x2} : pH_2 (5,90 ± 0,1)
V_{x3} : pH_3 (5,20 ± 0,1)
V_{x4} : pH_4 (4,30 ± 0,1)

Note that V_{x2}, V_{x3} and V_{x4} are the cumulative volumes of strong acid added.

(2) Data table for titration with strong acid after addition of a strong base to raise the initial pH to pH_1 (if initial diluted sample pH < 6,7 ± 0,1):

V_x	:	pH_x
0	:	initial diluted sample pH (pH_0) < 6,7
V_{x1}	:	pH_1 (6,7 ± 0,1 after adding V_{x1} mℓ of strong base)
V_{x2}	:	pH_2 (5,90 ± 0,1)
V_{x3}	:	pH_3 (5,20 ± 0,1)
V_{x4}	:	pH_4 (4,30 ± 0,1)

Note that V_{x2}, V_{x3} and V_{x4} are the sum of the volume of strong base and the cumulative volume of strong acid added.

Ideally the pH values should be located within a ± 0,1 limit of the values given above (easily attainable even with little experience). In some cases the pH values pH_1, pH_2, pH_3 and pH_4 might be outside the above mentioned limit of ± 0,1 pH units, say due to "over enthusiastic" addition of titrant. However, from experience if the sample is being "over titrated" accidentally it is not necessary to repeat the titration provided the pH value is located within 0,2 pH units from the appropriate value. If the sample is being "under titrated", step (5) of the step by step procedure may be repeated to obtain pH_1, pH_2, pH_3 or pH_4 within the acceptable limit of ± 0,1 pH units from the appropriate its ideal pH value.

CALCULATION OF RESULTS

Input data for computer program

The $H_2CO_3^*$alkalinity and SCFA of the undiluted sample are calculated from the ancillary data obtained on the undiluted sample and the titration data obtained on the diluted sample; the personal computer program **TITRA5** is used for the calculations (see floppy disk and Chapter 5). The input data required from the titration for the computer program are as follows:

pH_0 – initial pH of diluted sample
pH_1 – pH after addition of V_{x1}
pH_2 – pH after addition of V_{x2}
pH_3 – pH after addition of V_{x3}
pH_4 – pH after addition of V_{x4}
V_{x1} (mℓ) – volume of strong acid or base added from pH_0 to pH_1
V_{x2} (mℓ) – Cumulative volume of strong acid (and strong base, if any) added from pH_0 to pH_2
V_{x3} (mℓ) – Cumulative volume of strong acid (and strong base, if any) added from pH_0 to pH_3
V_{x4} (mℓ) – Cumulative volume of strong acid (and strong base, if any) added from pH_0 to pH_4
Normality of strong acid titrant (mol/ℓ)
Sample size (undiluted) (mℓ)
Sample size (diluted) (mℓ)
Temperature (°C)
TDS (mg/ℓ) – Total dissolved solids, or,
SC (mS/m) – Specific conductivity
N_T (mg/ℓ as N) – Total species conc. of free and saline ammonia
P_T (mg/ℓ as P) – Total species conc. of inorganic phosphate
S_T (mg/ℓ as S) – Total species conc. of sulphides

Note that either TDS or SC needs to be entered in the program: if TDS is entered SC is calculated internally and similarly, TDS is calculated if SC is entered. The parameters TDS (or SC), N_T, P_T and S_T are measurements on the *undiluted* sample.

Output data from computer program

The computer program supplies the following data:

- H_2CO_3*alkalinity of undiluted sample (mg/ℓ as $CaCO_3$)
- SCFA of undiluted sample (mg/ℓ as acetic acid)
- Estimate of systematic pH error

Note:

(1) The systematic pH error may be due to poor pH probe calibration, residual liquid junction or any other effects on the pH electrode. The systematic pH error is taken into account automatically by the program in calculating H_2CO_3*alkalinity and SCFA.

(2) The correction for systematic pH error is subject to the condition that the carbonate weak acid/base dominates in the sample, i.e. SCFA (mg/ℓ as acetic acid) needs to be smaller than about $0{,}5 \cdot C_T$ (mg/ℓ as $CaCO_3$). This condition is tested internally by the program. If the condition is not met no correction for systematic pH error is made by the program and a message is displayed in the output data table that no correction has been made; the resulting loss in accuracy in the remaining output data will however remain within acceptable limits for the purpose of monitoring of anaerobic digesters. (This situation will develop only when the digester is showing signs of failure, in which event accurate estimates of SCFA and H_2CO_3*alkalinity no longer is essential).

(3) The maximum correction for systematic pH errors made by the program is set to ± 0,2 pH units. If the systematic pH error is greater than ± 0,2 pH units this is displayed on the screen with the recommendation that the probe should be recalibrated. From practical experience (with samples from anaerobic digesters) an average systematic pH error of about – 0,05 pH units will be encountered. It would appear therefore that with systematic pH errors of > ± 0,2 indicated by the computer program, the pH probe most likely is in error and needs to be recalibrated, and the test repeated.

(4) The H_2CO_3*alkalinity and SCFA are the concentrations present in the undiluted sample, i.e. the concentrations in the reactor. The concentration of C_T in the undiluted sample, however, is *not* equal to the concentration in the reactor due to CO_2 loss between sampling and testing. If C_T in the *reactor* is required, this is found from the reactor *in situ* pH, temperature, TDS (or SC) of the reactor liquid and the undiluted H_2CO_3*alkalinity determined with the 5 pH point titration method, see Loewenthal *et al.* (1989). Usually *in situ* C_T is of no practical importance and therefore this calculation is not included in the computer programs.

CHAPTER 5

THE COMPUTER PROGRAMS

INTRODUCTION

The experimental procedures for the 4 and 5 pH point titrations are set out in Chapters 3 and 4 respectively. Equations for calculating H_2CO_3*alkalinity or H_2CO_3*alkalinity and short–chain fatty acid total species concentration (A_T) using the data obtained from the 4 and 5 pH point titration methods respectively have been set out in detail by Moosbrugger *et al.* (1993b;1993c;1993d). Manually, calculations using these equations are laborious and tedious. To facilitate calculation and make the titration procedures more readily usable, algorithms of the calculation procedures for the 4 and 5 pH point titrations have been developed and are encoded in two computer programs, **TITRA4** and **TITRA5** respectively. From the data obtained in the 4 pH point titration, **TITRA4** calculates H_2CO_3*alkalinity and carbonate total species concentration (C_T). From the data in the 5pH point titration, **TITRA5** calculates H_2CO_3*alkalinity and short–chain fatty acid total species concentration (A_T). Both programs allow a check on the pH probe by providing an estimate of a systematic pH error where this may be present, due to poor calibration, residual liquid junction effect or any other influences on the glass electrode. The systematic pH error is taken into account automatically by the computer programs in the calculations. Also, both programs take into account the ammonium, phosphate and sulphide weak acid/bases where these may be present provided their total species concentrations are known. These considerations increase the accuracy of the parameters calculated from the titration data.

In this Chapter, details of the programs are supplied.

SYSTEM REQUIREMENTS

The programs will run on all IBM PC, XT, AT, 386, 486 or true compatible machines using DOS 3.3 or higher. At least 256K of RAM are required, a condition met by most computers. Numeric co–processors are not required. The programs do not require a graphics adapter, and will run with CGA, EGA, VGA, ATT, PC 3270 or Hercules graphics adapters.

SUPPLIED DISK

A 5¼ inch floppy disk will be found on the inside of the back cover of the manual. This distribution disk is formatted for a standard 5¼ inch 360K disk drive.

IMPORTANT NOTE !!

No attempt should be made to run the programs directly from the distribution disk. Users are advised, for their own protection, to make a back–up copy of the distribution disk and to store the original. Instructions on how to make a back–up disk follow in the section below.

BACK–UP COPIES

The distribution disk is formatted for a standard 5¼ inch 360K disk drive, and can be read by an IBM PC or compatible. The following procedure can be used to make a back–up copy of the distribution disk:

- Find a new (or unused) floppy disk.

- Boot up your computer.

- At the system prompt type **diskcopy A: B:** and press **<Enter>**. The message **Insert source diskette into drive A:** will be displayed on the screen. Remove any disk from drive A and replace it with the distribution disk.

- If your system has two floppy disk drives, the screen will say **Insert destination diskette into drive B:** . In that case remove any disk from drive B, replacing it with the blank disk. If your system has only one floppy drive then you will be swapping disks in drive A. Remember that the distribution disk is the **source** disk and the blank disk is the **destination** disk.

- Now press **<Enter>**. The computer will start reading from the source disk in drive A.

- If you have a two–drive system the computer will then write to the destination disk in drive B and continue reading from drive A and writing to drive B until copying is complete. If you have a one–drive system you will be asked to

alternatively put the destination disk and the source disk in drive A until copying is finished.

FILES ON THE DISTRIBUTION DISK

The distribution disk contains the following four files:

TITRA4.PAS
TITRA4.EXE
TITRA5.PAS
TITRA5.EXE

The files **TITRA4.EXE** and **TITRA5.EXE** are the two executable programs for the 4 and 5 pH point titration methods respectively.

The files **TITRA4.PAS** and **TITRA5.PAS** are the listed versions of the above two computer programs; the programs are written using Borland's Turbo Pascal Version 4.0 and can be listed with the Borland compiler/editor. Also, alterations to the programs can be made using this compiler/editor. [*Should the user make any alterations, the authors request that details of these alterations be forwarded to them for possible incorporation in future versions of the programs*].

SETTING UP ON A HARD DISK SYSTEM

The most convenient method for running the programs is on a hard disk system. To set up the programs to run from a hard disk, the procedure outlined below is followed:

- Assuming that the hard disk is designated as drive C, type the following commands (pressing **<Enter>** at the end of each line):

```
c:
cd c:\
mkdir titrate
```

  If the hard disk is not designated as drive C, replace C by the relevant designation code.

- Place the distribution disk in the disk drive (usually drive A).

- Change to the subdirectory **TITRATE** by entering the command

  cd c:\titrate

- At the DOS prompt on the screen (**C:>** or **C:\TITRATE>**) type the following instructions (pressing **<ENTER>** at the end of each line):

  copy a:titra4.exe
  copy a:titra5.exe

STARTING PROGRAM EXECUTION

Floppy disk system:

- Boot up the computer from a DOS disk in drive A:

- Remove the DOS disk from drive A: and replace with the back–up copy of the distribution disk.

- To initiate the execution of the program for the ***4 pH point titration***, at the DOS prompt A:> the user must type

  titra4.exe

  and then press the carriage return key.

- To initiate the execution of the program for the ***5 pH point titration***, at the DOS prompt A:> the user must type

  titra5.exe

  and then press the carriage return key.

- The program will be loaded into memory from disk and start execution.

Hard disk system:

- Boot up the system from the hard disk.

- If not done previously, follow instructions in the above section **SETTING UP ON A HARD DISK SYSTEM**.

- Change to the subdirectory **TITRATE** by entering the command

  cd c:\titrate

- To initiate the execution of the program for the ***4 pH point titration***, at the DOS prompt **C:>** or **C:\TITRATE>** the user must type

  titra4.exe

  and then press the carriage return key.

- To initiate the execution of the program for the ***5 pH point titration***, at the DOS prompt **C:>** or **C:\TITRATE>** the user must type

  titra5.exe

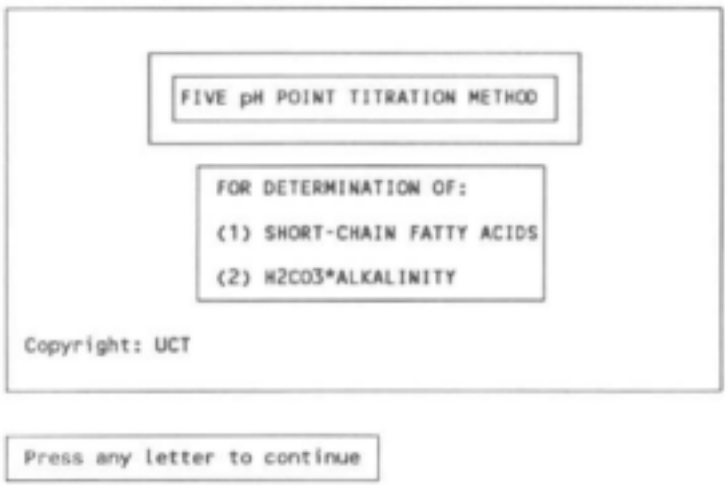
  and then press the carriage return key.

- The program will be loaded into memory from disk and start execution.

RUNNING THE PROGRAMS

Taking the 5 pH point titration program **TITRA5** as an example, execution of the program is initiated following the procedures above. The title page shown in Table 5.1 will appear on the screen.

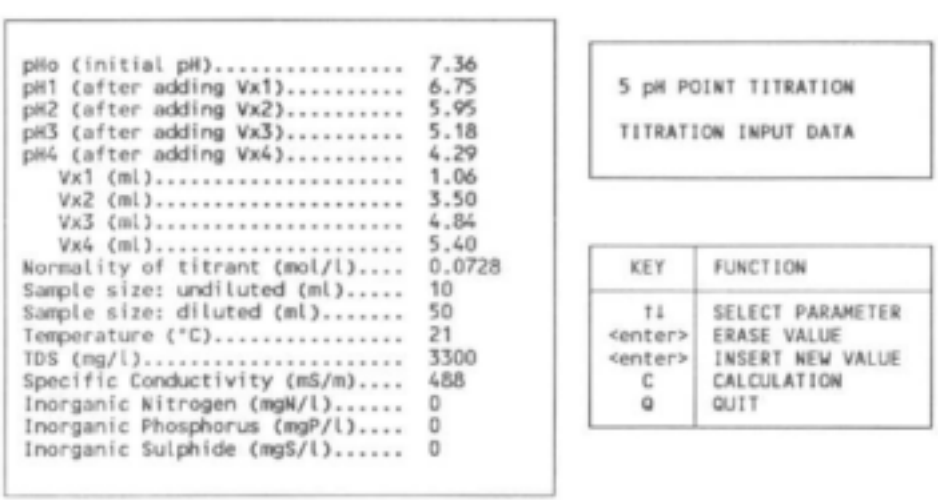
Table 5.1: Title page for the 5 pH point titration method:



Data input by the user

With the title page present on the screen, execution of the program is advanced if any letter on the keyboard is pressed. The input data table shown in Table 5.2 then will appear.

Table 5.2: Data input table for 5 pH point titration method:



The data input table contains default values for the different input parameters; the first parameter and default value (pH_0) will be highlighted. In order to change the default value (for the highlighted parameter) the user must press the carriage return key to erase the existing value, type in the new value, and press the carriage return key again. If the default or the entered value is acceptable the following or previous parameter is selected with the arrow keys: ↓ or ↑ respectively. Note that either **TDS** or **SC** need to be entered in the program; if **TDS** is entered **SC** is calculated internally, and vice versa. To invoke the calculation part of the program type the letter **C**. After termination of the calculations the output data table (table of results) will appear on the screen.

Program output

Three different output tables will be obtained: If the systematic pH error is smaller than 0,2 the output table shown in Table 5.3 will appear. If the systematic pH error is greater than 0,2 the output table shown in Table 5.4 will appear. If the short-chain fatty acid concentration (A_T) > 2·carbonate species concentration (C_T) the output table shown in Table 5.5 will appear.

The option keys (**Y/N**) or (**Q**) displayed near the bottom of the output table, enable the user to either repeat the calculations for a different set of input values or quit the program respectively.

Table 5.3: Output data table for 5 pH point titration program with a systematic pH error smaller than 0,2:

OUTPUT DATA	
H2CO3*alkalinity (undiluted sample) (mg/l as CaCO3)	1863.9
Short-chain fatty acids (undiluted sample) (mg/l as acetic acid)	195.9
Systematic pH error	-0.03

Do you wish to do a further calculation ?	Y/N
Do you wish to quit the program ?	Q

Table 5.4: Output data table for 5 pH point titration program with a systematic pH error greater than 0,2.

OUTPUT DATA	
H2CO3*alkalinity (undiluted sample) (mg/l as CaCO3)	1759.4
Short-chain fatty acids (undiluted sample) (mg/l as acetic acid)	846.1
The titration data indicate a systematic pH error > 0.2; Check pH probe calibration	
Do you wish to do a further calculation ?	Y/N
Do you wish to quit the program ?	Q

Table 5.5: Output data table for 5 pH point titration program with $A_T > 2 \cdot C_T$.

OUTPUT DATA	
H2CO3*alkalinity (undiluted sample) (mg/l as CaCO3)	1760.9
Short-chain fatty acids (undiluted sample) (mg/l as acetic acid)	1680.6
Correction for systematic pH error is not possible for this titration	0.
Do you wish to do a further calculation ?	Y/N
Do you wish to quit the program ?	Q

PROGRAM LIMITATIONS

The two computer programs have the following limitations:

- For **TITRA4**, the correction for systematic pH error is subject to the condition that the carbonate weak acid/base dominates [i.e. $C_T > 2 \cdot (N_T + P_T + S_T)$].

- For **TITRA5**, the correction for systematic pH error is subject to the condition that the carbonate weak acid/base dominates in the sample, i.e. SCFA (mg/ℓ as acetic acid) needs to be smaller than about $0{,}5 \cdot C_T$ (mg/ℓ as $CaCO_3$). This condition is tested internally by the program. If the condition is not met no correction for systematic pH error is made by the program and a message is displayed in the output data table that no correction has been made (see Table 5.5); the resulting loss in accuracy in the remaining output data will however remain within acceptable limits for the purpose of monitoring of anaerobic digesters. (This situation will develop only when the digester is showing signs of failure, in which event accurate estimates of SCFA and H_2CO_3*alkalinity no longer are essential).

- For **TITRA4** and **TITRA5**, the maximum correction for systematic pH errors is set to ± 0,2 pH units. If the systematic pH error is greater than ± 0,2 pH units this is displayed on the screen with the recommendation that the probe should be recalibrated (see Table 5.4). From practical experience (with samples from anaerobic digesters) an average systematic pH error of about – 0,05 pH units will be encountered. It would appear therefore that with systematic pH errors of > ± 0,2 indicated by the computer program, the pH probe most likely is in error and needs to be recalibrated, and the test repeated.

- For **TITRA4** and **TITRA5**, the H_2CO_3*alkalinity and SCFA respectively are the concentrations present in the undiluted sample, i.e. the concentrations in the reactor. In **TITRA4**, the concentration of C_T in the undiluted sample, however, is *not* equal to the concentration in the reactor due to CO_2 loss between sampling and testing. If C_T in the *reactor* is required, this is found from the reactor *in situ* pH, temperature, TDS (or SC) of the reactor liquid and the undiluted H_2CO_3*alkalinity determined with the 4 or 5 pH point titration methods, see Loewenthal *et al.* (1989). Usually, the reactor C_T is of no practical importance and therefore this calculation is not included in the computer programs.

CHAPTER 6

EXAMPLES

INTRODUCTION

In this Chapter operation of the computer programs **TITRA4** and **TITRA5** will be demonstrated for a 4 and 5 pH point titration respectively.

4 pH POINT TITRATION

The following example demonstrates the data input and output of **TITRA4** for a 4 pH point titration of a pure aqueous bicarbonate solution.

Titration

A solution of hydrochloric acid was made up and standardized by following the procedures set out in **Appendix A**; the standardization gave normality of the acid as 0,0728N. (This hydrochloric acid was used for both the 4 and 5 pH point titrations). A stock solution of sodium bicarbonate was made by adding 0,84g anhydrous $NaHCO_3$ to distilled water to give a final volume of 1ℓ (H_2CO_3*alkalinity $= C_T = 500$ mg/ℓ as $CaCO_3$). (At this stage in the procedure the solution should be filtered, but this was not necessary since the $NaHCO_3$ dissolved completely). The TDS of the solution can be calculated theoretically, to give TDS of the undiluted sample of 840 mg/ℓ. Since the stock solution was pure, the total species concentrations of the ammonium, phosphate and sulphide (N_T, P_T and S_T respectively) weak acid/bases in the undiluted sample were zero. A 10 mℓ sample of the stock solution was made up to 50 mℓ with distilled water, a 5 times dilution. The 4 pH point titration procedure set out in Chapter 3 was followed using standardized 0,0728N hydrochloric acid, and temperature, pH_0, pH_1, pH_2, pH_3, V_{x1}, V_{x2} and V_{x3} recorded.

Data obtained from the titration are set out overleaf.

Undiluted sample	
TDS (mg/ℓ)	840
N_T (total species conc. of free and saline ammonia, mg/ℓ as N)	0
P_T (total species conc. of inorganic phosphate, mg/ℓ as P)	0
S_T (total species conc. of sulphides, mg/ℓ as S)	0
Dilution	
Sample size (undiluted) (mℓ)	10
Sample size (diluted) (mℓ)	50
Diluted sample	
Temperature (°C)	21
pH_0 (initial pH of diluted sample)	8,00
pH_1 (pH after addition of V_{x1})	6,73
pH_2 (pH after addition of V_{x2})	5,93
pH_3 (pH after addition of V_{x3})	5,15
V_{x1} (mℓ)	0,40
V_{x2} (mℓ)	1,00
V_{x3} (mℓ)	1,30
Normality of strong acid (mol/ℓ)	0,0728

Program execution

Execution of the computer program **TITRA4** was initiated and data entered into the data input table following the procedures in Chapter 5, to give the screen in Table 6.1. Calculation was initiated (pressing **C**) and the program output screen in Table 6.2 obtained. Comparing the output from the program (H_2CO_3*alkalinity = 498,2; C_T = 507,1 both mg/ℓ as $CaCO_3$) with the known input values (H_2CO_3* alkalinity = C_T = 500 mg/ℓ as $CaCO_3$) good correlation was obtained. Also, the estimate for the systematic pH error (–0,02) was within acceptable limits (see Chapter 3).

Table 6.1: **TITRA4** input data screen for 4 pH point titration of pure $NaHCO_3$ solution (H_2CO_3*alkalinity = C_T = 500 mg/ℓ as $CaCO_3$).

pHo (initial pH).....	8.00
pH1 (after adding Vx1).....	6.73
pH2 (after adding Vx2).....	5.93
pH3 (after adding Vx3).....	5.15
Vx1 (ml).....	0.40
Vx2 (ml).....	1.00
Vx3 (ml).....	1.30
Normality of titrant (mol/l)....	0.0728
Sample size (undiluted) (ml)....	10
Sample size (diluted) (ml).....	50
Temperature (°C).....	21
TDS (mg/l).....	840
Specific Conductivity (mS/m).....	122
Inorganic Nitrogen (mgN/l).....	0
Inorganic Phosphorus (mgP/l)....	0
Inorganic Sulphide (mgS/l).....	0

4 pH POINT TITRATION

TITRATION INPUT DATA

KEY	FUNCTION
↑↓	SELECT PARAMETER
<enter>	ERASE VALUE
<enter>	INSERT NEW VALUE
C	CALCULATION
Q	QUIT

Table 6.2: **TITRA4** output data screen for 4 pH point titration of pure $NaHCO_3$ solution (H_2CO_3*alkalinity = C_T = 500 mg/ℓ as $CaCO_3$).

TABLE OF RESULTS

H2CO3*alkalinity (undiluted sample) (mg/l as CaCO3)	498.2
Total carbonate species (undiluted sample) (mg/l as CaCO3)	507.1
Estimate of systematic pH error	-0.02

Do you wish to do a further calculation ?	Y/N
Do you wish to quit the program ?	Q

5 pH POINT TITRATION

The following example demonstrates the data input and output of **TITRA5** for a 5 pH point titration of effluent from a UASB reactor treating lauter tun (brewery) waste.

Titration

Effluent was obtained from a laboratory–scale UASB reactor treating lauter tun (brewery) waste. On the filtered (Whatman's No. 1) undiluted effluent, specific conductivity and total species concentration of free and saline ammonia, phosphate and sulphide were measured (*Standard Methods*, 1989). A 10 mℓ sample of the effluent was diluted to 50 mℓ with distilled water, a five times dilution. The 5 pH point titration procedure set out in Chapter 4 was followed using standardized 0,0728N hydrochloric acid, and temperature, pH_0, pH_1, pH_2, pH_3, pH_4, V_{x1}, V_{x2}, V_{x3} and V_{x4} recorded. Data obtained from the titration are set out below:

Undiluted sample

SC (mS/m)	380
N_T (total species conc. of free and saline ammonia, mg/ℓ as N)	30
P_T (total species conc. of inorganic phosphate, mg/ℓ as P)	25
S_T (total species conc. of sulphides, mg/ℓ as S)	0

Dilution

Sample size (undiluted) (mℓ)	10
Sample size (diluted) (mℓ)	50

Diluted sample

Temperature (°C)	24
pH_0 (initial pH of diluted sample)	8,77
pH_1 (pH after addition of V_{x1})	6,80
pH_2 (pH after addition of V_{x2})	5,92
pH_3 (pH after addition of V_{x3})	5,25
pH_4 (pH after addition of V_{x4})	4,12
V_{x1} (mℓ)	1,40
V_{x2} (mℓ)	3,60
V_{x3} (mℓ)	4,56
V_{x4} (mℓ)	4,96
Normality of strong acid (mol/ℓ)	0,0728

Program execution

Execution of the computer program **TITRA5** was initiated and data entered into the data input table following the procedures in Chapter 5, to give the screen in Table 6.3. Calculation was initiated and the output screen in Table 6.4 was obtained.

Table 6.3: **TITRA5** input data screen for 5 pH point titration of effluent from a UASB reactor treating lauter tun (brewery) waste.

pHo (initial pH).....	8.77
pH1 (after adding Vx1).....	6.80
pH2 (after adding Vx2).....	5.92
pH3 (after adding Vx3).....	5.25
pH4 (after adding Vx4).....	4.12
Vx1 (ml).....	1.40
Vx2 (ml).....	3.60
Vx3 (ml).....	4.56
Vx4 (ml).....	4.96
Normality of titrant (mol/l)....	0.0728
Sample size: undiluted (ml).....	10
Sample size: diluted (ml).....	50
Temperature (°C).....	24
TDS (mg/l).....	2574
Specific Conductivity (mS/m)....	380
Inorganic Nitrogen (mgN/l).....	30
Inorganic Phosphorus (mgP/l)....	25
Inorganic Sulphide (mgS/l).....	0

5 pH POINT TITRATION

TITRATION INPUT DATA

KEY	FUNCTION
↑↓	SELECT PARAMETER
<enter>	ERASE VALUE
<enter>	INSERT NEW VALUE
C	CALCULATION
Q	QUIT

Table 6.4: **TITRA5** output data screen for 5 pH point titration of effluent from a UASB reactor treating lauter tun (brewery) waste.

OUTPUT DATA

H2CO3*alkalinity (undiluted sample) (mg/l as CaCO3)	1741.3
Short-chain fatty acids (undiluted sample) (mg/l as acetic acid)	5.7
Systematic pH error	-0.02

Do you wish to do a further calculation ?	Y/N
Do you wish to quit the program ?	Q

REFERENCES

Gran G (1952) Determination of the equivalence point in potentiometric titrations. *The Analyst*, **77**, 661.

Gujer W and Zehnder A J B (1983) Conversion processes in anaerobic digestion. *Water Sci. Technol.*, **15**, 127–167.

Jenkins S R, Morgan J M and Sawyer C L (1983) Measuring anaerobic sludge digestion and growth by a simple alkalimetric titration. *JWPCF*, **55**, 448–453.

Loewenthal R E and Marais GvR (1976) *Carbonate Chemistry of Aquatic Systems – Theory and Application.* Ann Arbor Science Publishers Inc., Michigan.

Loewenthal R E, Wiechers H N S and Marais GvR (1986) *Softening and Stabilization of Municipal Waters.* Water Research Commission, P O Box 824, Pretoria 0001, South Africa.

Loewenthal R E, Ekama G A and Marais GvR (1989) Mixed weak acid/base systems. Part I: Mixture characterization. *Water SA*, **15**(1), 3–24.

Loewenthal R E, Wentzel M C, Ekama G A and Marais GvR (1991) Mixed weak acid/base systems. Part II: Dosing estimation, aqueous phase. *Water SA*, **17**(2), 107–122.

McCarty P L (1974) *Anaerobic Processes.* International Association of Water Pollution Research, Birmingham, England. September 18, 1974.

Moosbrugger R E, Wentzel M C, Loewenthal R E, Ekama G A and Marais GvR (1991) Weak acid/bases and pH control in UASB reactors. Research Report W70, Dept. Civil Eng, Univ. of Cape Town, Rondebosch 7700, South Africa.

Moosbrugger R E, Sam-Soon P A L N S, Wentzel M C, Ekama G A, Loewenthal R E and Marais GvR (1992) Final report to the Water Research Commission on the contract "Pelletization in upflow anaerobic sludge bed (UASB) systems". Research Report W75, Dept. Civil Eng., Univ. of Cape Town, Rondebosch 7700, South Africa.

Moosbrugger R E, Wentzel M C, Ekama G A and Marais GvR (1993a) Weak acid/bases and pH control in anaerobic systems – A review. *Water SA*, **19**(1), 1–10.

Moosbrugger R E, Wentzel M C, Ekama G A and Marais GvR (1993b) Alkalinity measurement: Part 1 – A 4 pH point titration method to determine the carbonate weak acid/base in an aqueous carbonate solution. *Water SA*, **19**(1), 11–22.

Moosbrugger R E, Wentzel M C, Ekama G A and Marais GvR (1993c) Alkalinity measurement: Part 2 – A 4 pH point titration method to determine the carbonate weak acid/base in an aqueous solutions containing other weak acid/bases of known concentrations. *Water SA*, **19**(1), 23–28.

Moosbrugger R E, Wentzel M C, Loewenthal R E, Ekama G A and Marais GvR (1993d) 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. *Water SA*, **19**(1), 29–40.

Mosey F E and Fernandes X A (1989) Patterns of hydrogen in biogas from the anaerobic digestion of milk–sugars. *Water Sci.Technol.*, **21**, 187–196, Brighton.

Pohland F G and Martin J C (1969) Discussion on paper by Andrews J F, "Dynamic model of the anaerobic digestion process". *Proc.of Am.Soc.of City Eng.*, Sanitary Engineering Division.

Sam–Soon P A L N S, Loewenthal R E, Dold P L and Marais GvR (1987) Hypothesis for pelletization in the upflow anaerobic sludge bed reactor. *Water SA*, **13**(2), 69–80.

Sam–Soon P A L N S, Loewenthal R E, Wentzel M C and Marais GvR (1989) Pelletization in the upflow anaerobic sludge bed (UASB) reactor. Research Report W72, Dept. Civil Eng, Univ. of Cape Town, Rondebosch 7700, South Africa.

Sam–Soon P A L N S, Loewenthal R E, Wentzel M C and Marais GvR (1990) Growth of biopellets on glucose in upflow anaerobic sludge bed (UASB) systems. *Water SA*, **16**(3), 151–164.

Standard Methods (1989) *Standard Methods for the Examination of Water and Wastewater.* Prepared and published jointly by the American Public Health Association, American Water Works Association and Water Pollution Control Federation, Washington DC.

Stumm W and Morgan J T (1970) *Aquatic Chemistry.* Wiley – Interscience, New York.

Van Slijke D D (1922) On measurement of buffer values. *J.Biol.Chem.*, **52**, 525–590.

APPENDIX A

STANDARDIZATION OF STRONG ACID

INTRODUCTION

To obtain accurate results from the 4 and 5 pH point titration methods it is of great importance to determine the normality (concentration of H^+ ions) of the strong acid titrant accurately. The standardization method is based on the theory for $H_2CO_3^*$alkalinity in an aqueous carbonate solution. The principle of the method is to titrate a solution of known $H_2CO_3^*$alkalinity to the $H_2CO_3^*$alkalinity equivalence point (i.e. the point of zero $H_2CO_3^*$alkalinity) using the strong acid to be standardized. From the volume of strong acid required to titrate to the $H_2CO_3^*$equivalence point, the normality of the strong acid is determined (see below). Using this method one encounters the problem of identifying the $H_2CO_3^*$alkalinity equivalence point.

Because of the difficulties in identifying the $H_2CO_3^*$equivalence point the method by Gran (1952) is used which does not require endpoint identification. The theory of Gran's method, more specifically the First Gran Function, is discussed in detail by Loewenthal *et al.* (1986;1989) and will not be dealt with here; we will deal only with the practical application of the First Gran Function, i.e. calculation of the volume of strong acid added to titrate to the $H_2CO_3^*$equivalence point.

The standardization of the strong acid involves the following steps: preparation of strong acid; Gran titration of carbonate solution; application of the First Gran Function; and calculation of normality of strong acid.

PREPARATION OF STRONG ACID

In preparing the strong acid the volume of undiluted sample and the alkalinity of the undiluted sample must be kept in mind. Both these factors influence the mass of strong acid required to titrate the sample from the initial pH to pH_3 (in the 4 pH point titration) or to pH_4 (in the 5 pH point titration): If the normality is too high, small quantities of strong acid addition will cause large changes in pH and random errors in strong acid addition will become increasingly significant. If the normality

is too low, large quantities of strong acid are required to effect pH changes making the titration tedious and mixing of the sample more uncertain. For the purpose of titrating 10 mℓ of an undiluted sample from a typical anaerobic digester which has been diluted to 50 mℓ, a 0,08 N strong acid is recommended; to approximate this value one may dilute 35 mℓ of 33 percent hydrochloric acid to 5 ℓ with CO_2 free distilled water. For other samples, the most suitable concentration will have to be found by trial and error. The strong acid solution is standardized using the Gran method, as set out below.

GRAN TITRATION OF CARBONATE SOLUTION

To standardise the strong acid, a carbonate solution of known H_2CO_3*alkalinity is made up from CO_2 free distilled water and high purity anhydrous Na_2CO_3: add 5,300 g Na_2CO_3 to 5 ℓ of CO_2 free distilled water. A sample of 50 mℓ of this solution is taken and a Gran titration performed, as follows: Titrate the sample with the made–up strong acid to a pH of about 3,9 and record pH and the volume of titrant added. Titrate the sample to the final pH of about 3,4 in 4 to 5 titration steps, recording the *cumulative* volumes of titrant and pH after each step to give a table of titration data, e.g.

V_x	:	pH_x
13,32	:	3,90
13,34	:	3,80
13,37	:	3,70
13,40	:	3,60
13,44	:	3,50

Applying the First Gran Function to this set of data allows calculation of the volume of strong acid required to titrate to the H_2CO_3*equivalence point.

APPLICATION OF FIRST GRAN FUNCTION

Calculate the First Gran Function value, F_{1x}, for each of the (V_x; pH_x) pairs, from:

$$F_{1x} = -10^{-pH_x} (V_s + V_x) \qquad (A.1)$$

where

F_{1x} = First Gran Function value
pH_x = pH reading in pH region 3,9 to 3,4
V_x = volume of strong acid required to titrate to pH_x (mℓ)
V_s = initial sample volume (mℓ).

For the example, this gives the following (F_{1x}; V_x) pairs:

V_x	:	F_{1x}
13,32	:	–0,0080
13,34	:	–0,0100
13,37	:	–0,0126
13,40	:	–0,0159
13,44	:	–0,0201

Plot – F_{1x} versus V_x; a straight line should be obtained. Draw the best straight line through the data. The interception of the line with the V_x axis, V_{xe}, (i.e. F_{1x} = zero) gives the volume of strong acid required to titrate to the H_2CO_3*equivalence point, i.e. to the point where the H_2CO_3*alkalinity equals zero. Alternative to the graphical approach V_{xe} can be determined by applying a linear regression to the data set (F_{1x}; V_x); from the linear equation V_{xe} is calculated for $F_{1x} = 0$. Linear regression programs are readily available on many calculators and PC software; for the example presented here this approach was selected and V_{xe} was found to be 13,24 mℓ. Knowing the volume of strong acid that is required to titrate the carbonate solution of known H_2CO_3*alkalinity to the H_2CO_3* equivalence point (V_{xe}), the normality of strong acid can be calculated.

CALCULATION OF NORMALITY OF STRONG ACID

To calculate the normality of the strong acid note that the mass of H_2CO_3*alkalinity added to the sample as Na_2CO_3 equals the mass of strong acid required to titrate to the H_2CO_3*equivalence point:

$$Ca \cdot V_{xe} = m \cdot V_s \qquad (A.2)$$

where:

Ca = normality of strong acid (mol/ℓ)
V_{xe} = volume of strong acid to titrate to H_2CO_3*equivalence point (mℓ)

m = initial H_2CO_3*alkalinity concentration of sample (mol/ℓ)
V_s = initial sample volume (mℓ).

Rearranging Eq (A.2):

$$Ca = m \cdot \frac{V_s}{V_{xe}} \tag{A.3}$$

For the above example of 5,300 g Na_2CO_3/(5 ℓ distilled water), initial sample size 50 mℓ and V_{xe} = 13,24 mℓ, Ca can be calculated as follows:

$$Ca = 2 \cdot \frac{\text{mass of } Na_2CO_3 \text{ (5,3 g)}}{\text{Volume of dist. water (5 ℓ)} \quad \text{molecular weight of } Na_2CO_3 \text{ (106 g/mol)}} \cdot \frac{V_s \text{ (50 mℓ)}}{V_{xe} \text{ (13,24 mℓ)}}$$

$$= 0{,}0755 \text{ mol/ℓ}$$

Note that 1 mol of Na_2CO_3 mol/ℓ added yields 2 moles of H_2CO_3*alkalinity.