WEAK ACID/BASES AND pH CONTROL IN UPFLOW ANAEROBIC SLUDGE BED REACTORS

by

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DECLARATION BY CANDIDATE

I, RICHARD ENGELBERT MOOSBRUGGER, hereby declare that this thesis is my own work and that it has *not* been submitted for a degree at another University.

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SYNOPSIS

Since its discovery in the early 1970's the upflow anaerobic sludge bed (UASB) reactor system has become a well established technology for treatment of soluble high strength organic wastes. Successful application hinges on the generation of a sludge aggregating into pellets. Despite the widespread application of the UASB system, until recently the cause for pelletisation has been but ill understood.

Sam–Soon *et al.* (1987) proposed an hypothesis for pelletisation which, to date, appears to provide the best explanation for this phenomenon. They ascribe pelletisation to the action of a hydrogenotrophic microorganism, *Methanobrevibacter arboriphilus* (earlier known as *Methanobacterium* strain AZ, *M* strain AZ), a pH neutrophile that can synthesize all its amino acids except cysteine. With a deficiency in cysteine, in a high hydrogen partial pressure environment with an adequate supply of inorganic nitrogen this hydrogenotroph is stimulated to produce amino acids for growth, but because some of the protoplasmic protein cannot be synthesized completely due to inadequate cysteine supply, the excess amino acids generated disrupt the equilibrium conditions in the cell; to reestablish internal equilibrium the excess amino acids are extruded from the cell as polypeptides; these bind the anaerobic microorganisms together in pellets.

Sam–Soon *et al.* (1987) put forward 4 basic prerequisites for optimal pellet formation in a UASB system; (1) the feed substrate must give rise to a high hydrogen partial pressure, (2) inorganic nitrogen must be available in an amount in excess of that for normal anaerobic fermentation, (3) the feed substrate must be deficient in the amino acid cysteine, and (4) the pH in the sludge bed must be near neutral. In the UASB system they showed that the flow regime is essentially plug flow. Investigating apple juice waste, a carbohydrate substrate, they found that along the line of flow there develops partial separation of the anaerobic fermentation reactions acidogenesis, acetogenesis, acetoclastic and hydrogenotrophic methanogenesis. In particular the acidogenic phase dominates in the lower part of the bed leading to an increase in short–chain fatty acids (SCFA) and the development of a high hydrogen partial pressure, the latter creating an environment conducive to pelletisation. However, the presence of the SCFA induces a decline in pH. If the pH declines below about pH 6,6 the methanogens

are inhibited, including *M* strain AZ, and pelletisation is adversely affected. Consequently, the maintenance of a near neutral pH is of pivotal importance for successful operation of the system.

The pH established in an anaerobic fermentation system is a result of the interaction of the weak acid/base systems present, the main ones being the SCFA and the carbonate systems (the latter characterized by the $H_2CO_3^*$alkalinity and pH, or, the total carbonate species and pH). The SCFA reduce the $H_2CO_3^*$alkalinity and induce a decline in pH. In normal anaerobic fermentation, i.e. completely mixed systems, the SCFA generated are utilized immediately and SCFA are low throughout the reactor and the net $H_2CO_3^*$alkalinity reduction is relatively small - consequently the $H_2CO_3^*$alkalinity required to maintain a near neutral pH also is relatively small. In a UASB system, substantial concentrations of SCFA are generated in the lower region of the sludge bed reducing the $H_2CO_3^*$alkalinity - accordingly the $H_2CO_3^*$alkalinity required to maintain a near neutral pH is relatively large. In the upper part of the bed the SCFA are converted to methane and CO_2, and $H_2CO_3^*$alkalinity is regenerated; in effect the $H_2CO_3^*$alkalinity supplied to maintain a near neutral pH in the lower part of the bed is now in excess and wasted in the effluent. Thus, in the UASB system the mass of $H_2CO_3^*$alkalinity to be supplied is controlled by the transient high concentration of SCFA in the lower part of the sludge bed.

Prior to the work of Sam-Soon *et al.* virtually no information was available regarding the $H_2CO_3^*$alkalinity requirements when treating wastes in UASB systems. Sam-Soon *et al.* did a semi quantitative study into the $H_2CO_3^*$alkalinity requirements of apple juicing waste and found that with a *flow through system* the alkalinity requirement was so high that it could render the UASB system uneconomic. However, they established that by recycling the reactor effluent back to the influent, the $H_2CO_3^*$alkalinity in the effluent formed an $H_2CO_3^*$alkalinity supplementation to the influent. In this manner the mass of $H_2CO_3^*$alkalinity to be added to the influent, to buffer against pH decline in the lower region of the sludge bed, could be reduced substantially.

The study of Sam-Soon *et al.* (1991) exposed the alkalinity problem, but the solution proposed was of a semi-quantitative nature; the economic implications associated with $H_2CO_3^*$alkalinity supplementation in UASB systems appeared to be of such importance that a detailed investigation was merited: The apple juice waste studied by Sam–Soon *et al.* (1991) represents a category of wastes which contains or generates only insignificant $H_2CO_3^*$alkalinity and virtually all the $H_2CO_3^*$alkalinity needs to be supplied from an external source. Other wastes may generate substantial alkalinity in anaerobic fermentation systems. This opens up questions such as: To what extent can this internally generated $H_2CO_3^*$alkalinity be utilized to control the pH in the sludge bed and how much alkalinity still needs to be supplied from an external source ? What operational measures must be taken to make full use of the internally generated alkalinity ? Questions such as these prompted an enquiry into alkalinity, its generation and mass requirements for different wastes to maintain a near neutral minimum bed pH, effect of recycles, and, monitoring and control of $H_2CO_3^*$alkalinity and SCFA in UASB systems.

One may distinguish two basic categories of wastes on the basis of $H_2CO_3^*$alkalinity; (1) wastes which *do not* generate significant amounts of $H_2CO_3^*$alkalinity during anaerobic fermentation, and (2) wastes that generate significant amounts of $H_2CO_3^*$alkalinity during fermentation, e.g. due to deamination of proteins to inorganic nitrogen or conversion of organic salts to methane and carbon dioxide. Accordingly, in this investigation the following two wastes were selected to represent these two categories: Lauter tun (brewery) waste which generates very little internal $H_2CO_3^*$alkalinity and wine distillery waste which generates a substantial amount of internal $H_2CO_3^*$alkalinity. In addition to these two wastes, $H_2CO_3^*$alkalinity generation from deamination was studied using a pure proteinaceous substrate, casein.

Prior to the investigation into $H_2CO_3^*$alkalinity, each waste (substrate) was studied with respect to its potential for pellet formation. During these feasibility studies, the need emerged for a simple, reliable and accurate method to monitor the $H_2CO_3^*$alkalinity and SCFA concentration in the reactor effluent.

Against the background described above, the following tasks were set:

- Development of a simple method for simultaneous determination of the $H_2CO_3^*$alkalinity (carbonate system alkalinity) and SCFA concentration in anaerobic systems to be used in, (1) assessing the $H_2CO_3^*$alkalinity requirements of different types of wastes when treated in UASB systems, (2) monitoring process stability when treating these wastes under different operating conditions, e.g. different recycle ratios.

- Assessment of H_2CO_3*alkalinity requirements for lauter tun (brewery) waste to maintain a near neutral minimum bed pH in UASB systems. Because this waste generates very little H_2CO_3*alkalinity internally, virtually all H_2CO_3*alkalinity has to be supplied externally. It was of special interest to evaluate the effect of recycling the effluent to the influent in order to recover the effluent H_2CO_3*alkalinity and to dilute the base influent COD to an effective influent COD, COD_e, defined as: base influent COD/(1 + recycle ratio).

- Assessment of H_2CO_3*alkalinity requirements for wine distillery waste to maintain a near neutral minimum bed pH in UASB systems. This waste generates a substantial mass of H_2CO_3*alkalinity internally due to deamination of proteins to ammonium/ammonia, reduction of sulfates to sulfides and removal of organic acid salts such as potassium bitartrate. Similar to the lauter tun waste it was of interest to evaluate the effect of recycling on process performance and on the requirements of H_2CO_3*alkalinity at different recycle ratios, i.e. different COD_e concentrations.

- Assessment of a pure proteinaceous waste, casein: This substrate provides the opportunity to study the H_2CO_3*alkalinity generation from deamination and the effect of pH changes on process performance of systems with high levels of inorganic nitrogen. With high levels of inorganic nitrogen generated in the reactor liquid due to deamination the likelihood increases of inhibitory effects developing due to increased ammonia (NH_3) levels at higher than neutral pH values. It was of interest to evaluate the effect of pH change on process performance due to the NH_3 inhibition.

Because of the differing nature of these tasks each will be dealt with separately, describing the problems encountered and the solutions achieved.

Measurement of H_2CO_3*alkalinity and SCFA

In the literature a number of methods had been proposed to measure, (1) some form of alkalinity which approximates the H_2CO_3*alkalinity only, (2) the SCFA concentration only, and (3) some form of alkalinity approximating the H_2CO_3*alkalinity *and* the SCFA by using strong acid/base titrations. Since the objective in this investigation was to measure alkalinity *and* SCFA concentration, only methods measuring both these parameters needed to be considered. Two approaches to quantify the SCFA *and* approximate forms of the H_2CO_3*alkalinity concentrations in anaerobic digestor liquids had been proposed, one by Powell and Archer (1989) and one by Colin (1984). Both methods involve strong acid *and* strong base titrations over a large pH range which imposes a rather cumbersome titration procedure, increases uncertainty in the correctness of the pH readings, and may give rise to precipitation phenomena, all these resulting in loss of accuracy of the derived values.

In this investigation a 5 pH point acid titration was developed for determining the SCFA (as acetic acid) and H_2CO_3*alkalinity in aqueous solutions also containing known concentrations of other weak acid/bases such as the phosphate, ammonium or sulfide weak acid/bases. The method requires only an acid titration over the middle range of pH (initial pH to pH 6,7; 5,9; 5,2 and 4,3) so that the problems of adequate calibration of the pH probe is overcome and precipitation phenomena are unlikely. 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 task is only to increase the pH to 6,7, i.e. the mass of strong base added does not need to be known for the calculations and consequently there is no need to standardize the strong base. The need for initial adjustment of pH to 6,7 with strong base in anaerobic digestor liquids should be the exception rather than the rule because pH neutrality is required for optimal operation of anaerobic processes.

Besides the carbonate and SCFA weak acid/bases the most common additional weak acid/bases in anaerobic digestion are phosphate and ammonium which can be accounted for in the 5 pH point titration method if the total species concentration of each one is known. In some events the the total species concentrations of these two weak acid/bases might not be known: It was shown that if the concentration of the ammonium weak acid/base is neglected, the errors induced in the determination of the SCFA and H_2CO_3*alkalinity are very small and usually negligible. However if the concentration of the phosphate weak acid/base is neglected, the error in the determination of the SCFA always will be minor but the error in the H_2CO_3*alkalinity can be substantial, being high if the phosphate concentration is high and small if the phosphate concentration is small.

Besides estimating the H_2CO_3*alkalinity and SCFA, the method allows a check on the pH probe in that it provides an estimate of the 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 estimate of the systematic pH error, however, requires that the carbonate subsystem dominates over the SCFA system, i.e. the total species concentration of the SCFA subsystem must not exceed half that of the carbonate subsystem.

The method was tested extensively on made up solutions of acetic acid and H_2CO_3*alkalinity (sodium bicarbonate); both the acetic acid and H_2CO_3*alkalinity concentrations were always within a standard deviation of 8 percent of the input values.

For monitoring the process performance via SCFA and H_2CO_3*alkalinity and for pH control of anaerobic systems, it is believed that the 5 pH point titration method has decided advantages over existing methods in, (1) attainable accuracy, (2) testing time required, and (3) simplicity of testing procedure.

Feasibility study and assessment of H_2CO_3*alkalinity requirements for lauter tun (brewery) waste

The study of lauter tun waste in a laboratory scale UASB reactor at 30^0 C was undertaken with three principal objectives in mind:

- to investigate the potential for pelletisation in a UASB system in a feasibility study,
- to study the H_2CO_3*alkalinity requirements to maintain a near neutral minimum sludge bed pH when recycling the reactor effluent back to the influent (H_2CO_3*alkalinity would be measured in the effluent using the 5 pH point titration method) and,
- to investigate the effect of recycling on process performance, i.e. SCFA concentration in the effluent and COD removal (SCFA in the effluent would be monitored using the 5 pH point titration method).

The feasibility study was done on a single UASB reactor operated in flow through mode with an influent COD concentration of 4000 mg/ℓ and seeded with pelletised sludge from a UASB system treating wine distillery waste. During the feasibility study the COD loading rate was increased from 2 to 25 kg COD/(m^3 sludge bed.d).

Studies involving the recycle ratios were done at a presumed operational COD loading rate of 9 kg/(m^3 sludge bed.d). This COD loading rate was substantially lower than the maximum COD loading rate applied during the feasibility study to ensure stable operating conditions throughout this experimental period.

From the experimental study the following conclusions were drawn:

- Lauter tun waste is amenable to treatment in a UASB system and the waste develops a pelletised sludge bed. The pattern of product formation along the line of flow of the reactor is very similar to that observed under similar conditions when treating a pure carbohydrate type substrate, e.g. glucose or apple juice concentrate.

- The pellets produced were smaller and less compact than with glucose. This contributed to the pellets being lifted by the escaping gas to the gas seperator and the settler at higher COD loading rates. The maximum COD loading rate at which the pellet loss became unacceptable was 15 kg/(m^3 sludge bed.d), i.e. the maximum rate was set by the physical rather than biochemical behaviour. The operational COD loading rate was accepted at 9 kg/(m^3 sludge bed.d).

- Lauter tun waste generates no, or only insignificant, internal pH buffer measured as $H_2CO_3^*$alkalinity; pH buffer needs to be supplied from an external source to control the minimum pH in the reactor to acceptable levels (approx. $6{,}8 < pH > 7{,}2$). In this study when supplying $H_2CO_3^*$alkalinity via a strong base (e.g. NaOH) to the base feed flow, the pH in the influent increased to such high levels that apparently some of the trace elements precipitated and became unavailable to the microorganisms, and gave rise to complete failure of the process. Hence, the dosing point needs to be selected such that a drastic pH increase at the dosing point is avoided. In this study an appropriate dosing point was found to be the recycle stream; the presence of dissolved CO_2 and $H_2CO_3^*$alkalinity in the recycle stream buffered the pH downstream of the point of strong base addition to a pH < 8,5, instead of a pH of > 11 when NaOH was added to the base influent flow.

- Dilution of the base influent COD from 13 000 mg/ℓ to an effective influent COD of 570 mg/ℓ, by applying a recycle ratio of 22:1, appeared to have no adverse effect on process performance, in COD removal and SCFA conversion to methane and carbon dioxide (the percentage COD removal never declined below 90 percent). Thus it would seem that the lower limit of the effective influent COD of 2500 mg/ℓ, tested by Sam–Soon et al. (1991), can be substantially lowered.

- With the target minimum bed pH of ≃ 7 the pH profile in the bed exhibited only a slight depression to its minimum value for a recycle ratio of 6:1 (base influent COD = 13 000 mg/ℓ diluted by the recycle to 1860 mg/ℓ) and no significant depression at higher recycle ratios. This tendency to smooth out the "dip" in the pH profile when the effective influent COD is reduced, conforms with the observations of Sam–Soon et al. (1991).

- The alkalinity requirement (mg H_2CO_3*alkalinity/ℓ base influent) to maintain a selected minimum pH in the bed, can be reduced by imposing a recycle. Sam–Soon et al. (1991) formulated the alkalinity requirement/ℓ influent as C · (base influent)/(1 + recycle ratio) where C was accepted to be more or less constant for all recycle ratios. This study shows that for a specific COD loading rate, C was not constant but increases as the recycle ratio, r, increased, from C = 1,5 (r = 6) to C = 2,4 (r = 22) for the selected operational COD loading rate of 9 kg/(m^3 sludge bed.d) and the selected minimum pH ≃ 7.

- The effect of lowering the effluent H_2CO_3*alkalinity (i.e. the H_2CO_3*alkalinity generated per litre of base influent), by adding HCl to the base influent flow, was evaluated at a constant COD loading rate of 9 kg/(m^3 sludge bed.d). This experiment showed that, at a constant COD loading rate: (1) for the same COD_e the minimum bed pH increases with increase of effluent H_2CO_3*alkalinity, and (2) for the same minimum bed pH, the higher the COD_e the higher the effluent H_2CO_3*alkalinity requirements.

- To maintain a minimum sludge bed pH ≃ 7, at a COD loading rate of 9 kg/(m^3 sludge bed.d), a base influent COD concentration of 13 000 mg/ℓ and a recycle ratio of 22:1, the pH buffer requirements, expressed as H_2CO_3*alkalinity as $CaCO_3$, were 1350 mg/ℓ per litre of base influent flow; with the recycle ratio 6:1, the requirement was 2980 mg/ℓ as $CaCO_3$. Virtually all of the pH buffer needed to be supplied from an external source.

- The TKN/COD ratio of the lauter tun waste was 0,011 mgN/mgCOD; for unimpeded pelletisation when treating glucose in a UASB system, Sam-Soon *et al.* (1990) suggested a TKN/COD ratio of 0,02 mgN/mgCOD. In this study the feed was supplemented with NH_4Cl to give a TKN/COD ratio of 0,024; the observed TKN uptake was 0,015 mgN/mg undiluted influent COD. Thus it appears that lauter tun waste needs to be supplied with nitrogen when treated in UASB system to achieve unimpeded pelletisation. The lower TKN/COD uptake compared to glucose substrate may be due to the fact that in lauter tun waste carbohydrates form only a fraction of the COD whereas in glucose the carbohydrates constitute 100 percent of the COD [the carbohydrates generate a high hydrogen partial pressure during acidogenesis, which according to Sam-Soon *et al.* (1987) provides the basis for pelletisation and concomitantly a high uptake of inorganic nitrogen per mass of COD removed]. Besides the requirement for nitrogen augmentation there was a "suspicion" that lauter tun waste may be deficient of some trace elements. For this study, to ensure that such a deficiency positively was not present, trace elements were added. Because this aspect has not been clarified it would be advisable in design to take cognizance of a possible need for trace element supplementation.

Feasibility study and assessment of H_2CO_3*alkalinity requirements for wine distillery waste

The study of wine distillery waste in a laboratory scale UASB reactor at 30^0 C, similar to the study on lauter tun waste, was undertaken with three principal objectives in mind:

- to investigate the potential for pelletisation in a UASB system in a feasibility study,

- to study the H_2CO_3*alkalinity required to maintain a near neutral minimum sludge bed pH when recycling the reactor effluent back to the influent (the $H_2CO_3{}^*$alkalinity would be measured with the 5 pH point titration method),

- to investigate the effect of recycling on process performance, i.e. SCFA concentration in the effluent and COD removal (SCFA in the effluent would be monitored using the 5 pH point titration method).

The feasibility study was done on a single UASB reactor operated in flow through mode with an influent COD concentration of 5500 mg/ℓ and seeded with pelletised sludge from a UASB system treating glucose substrate. During the feasibility study the COD loading rate was increased from 27 to 41 kg COD/(m^3 sludge bed.d). At 41 kgCOD/(m^3 sludge bed.d) the pellets were being lifted into the gas separator and settling section and in this manner established the maximum COD loading rate. The bed behaviour did not show any signs of biochemical failure.

Studies involving the recycle ratios and $H_2CO_3{}^*$alkalinity requirements were done at a presumed operational COD loading rate of 9 kg/(m^3 sludge bed.d). This COD loading rate was substantially lower than the maximum COD loading rate applied during the feasibility study to ensure stable operating conditions throughout this experimental period.

From the experimental study the following conclusions were drawn:

- Wine distillery waste is amenable to treatment in a UASB system and develops a pelletised sludge bed. The pattern of product formation along the line of flow of the reactor was very similar to that observed under similar conditions treating a pure carbohydrate type substrate e.g. glucose or apple juice concentrate.

- The pellets produced were smaller, less compact than with glucose and appeared to have a sightly filamentous surface texture. This contributed to the pellets being lifted by the escaping gas to the gas seperator and the settler (see above).

- The TKN/COD ratio of the wine distillery waste was about 0,014 mgN/mgCOD; for unimpeded pelletisation when treating glucose in a UASB system Sam-Soon *et al.* (1990) suggested a TKN/COD ratio of 0,02 mgN/mgCOD. However, in this study the average mass of TKN uptake per mass of COD for wine distillery waste was 0,01 mgN/mgCOD. This reduced TKN uptake may be ascribed to the nature of the waste: Part of the COD (short chain fatty acids and other organic acids) did not induce high hydrogen partial pressure conditions; hence, only reduced biopolymer production would take place. From the measured TKN uptake of about 0,01 mgN/mgCOD it would appear that in most cases wine distillery waste would require no addition of nitrogen, or only a little.

- Pellet production in the high hydrogen partial pressure region of the reactor was 0,14 mgVSS/(mgCOD removed). This pellet yield is significantly lower than that reported by Sam-Soon *et al.* (1987), 0,36 mgVSS/(mgCOD removed), when treating apple juicing wastes. This observation is in agreement with the reduced TKN uptake and lends further support to the conclusion above that wine distillery waste would not induce pelletisation to the same extent as pure carbohydrate substrates.

- When pH buffer was added in the form of NaOH to the undiluted feed, with addition of 1 gNaOH per litre feed the pH did not increase above 8,0 because the waste pH was very low (pH $\simeq$ 4) due to the presence of short chain fatty acids and other organic acids. Wine distillery waste generated significant internal buffer, H_2CO_3*alkalinity, due to the interaction of OH^- ions with dissolved CO_2; the OH^- ions were generated by the removal of H^+ ions due to deamination of proteins and the removal of organic weak acid/base salts. The mass of H_2CO_3*alkalinity generated could not be predicted *ab initio* because the concentrations of the proteins and various organic acid/base salts could not be determined. The H_2CO_3*alkalinity generated was experimentally determined to be about 0,1 mgH_2CO_3*alkalinity as $CaCO_3$ per mg base influent COD. Imposing a recycle from the effluent to the influent, the H_2CO_3*alkalinity generated in the bed, and appearing in the effluent, is recycled to the influent; the dilution due to the recycle reduces the base influent COD to an effective influent COD, COD_e [COD_e = base influent COD/(1 + recycle ratio)]. In the measure the recycle ratio increases, the effective influent COD concentration decreases, but the effluent (i.e. recycled) H_2CO_3*alkalinity remaining constant (because the H_2CO_3*alkalinity generated per base influent COD remains constant). Consequently the H_2CO_3*alkalinity/COD_e ratio increases, causing the minimum pH to increase.

- The base influent COD concentration ranged from 20 000 to 30 000 mg/ℓ. Dilution of the base influent COD to an effective influent COD (COD_e) as low as 900 mg/ℓ, by applying a recycle ratio of 33:1, appeared to have no adverse effect on the process performance (the percentage COD removal never declined below 90 percent). Thus it would seem that the lower limit of the effective influent COD of 2500 mg/ℓ, tested by Sam–Soon *et al.* (1991) with satisfactory operation, can be substantially lowered.

- In a UASB system with a recycle, in assessing the H_2CO_3*alkalinity supplementation to maintain a selected minimum bed pH, the effluent H_2CO_3*alkalinity must serve as a reference parameter because this H_2CO_3*alkalinity includes any H_2CO_3*alkalinity generated in the bed and accordingly reduces the H_2CO_3*alkalinity to be supplied externally.

- The effect of different effective influent COD (COD_e) concentrations on the minimum bed pH was evaluated at the constant operational COD loading rate of 9 kg/(m^3 sludge bed.d), a base influent COD of 27 000 mg/ℓ and an effluent H_2CO_3*alkalinity of about 3700 mg/ℓ as $CaCO_3$, by applying three different recycle ratios of 33:1, 20:1 and 7:1 giving COD_e concentrations of 790 mg/ℓ, 1290 mg/ℓ and 3380 mg/ℓ respectively. The minimum bed pH decreased from 7,5 with COD_e = 790 mg/ℓ to 7,3 with COD_e = 1290 mg/ℓ and to 6,8 with COD_e = 3380 mg/ℓ. Hence, by changing COD_e via the recycle the minimum bed pH changed considerably and indicates that the minimum pH $\simeq$ 7 can be readily controlled by the recycle. COD removal was not significantly affected by the change in COD_e.

- The effect of lowering the effluent H_2CO_3*alkalinity (i.e. the H_2CO_3*alkalinity generated or present per litre of base influent), by adding HCl to the base influent flow, was evaluated at a constant COD loading rate of 9 kg/(m^3 sludge bed.d). This experiment showed that, at a constant COD loading rate:

  (1) for the same COD_e the minimum bed pH increases with increase of effluent H_2CO_3*alkalinity, and,

(2) for the same minimum bed pH, the higher the COD_e (the lower the recycle ratio) the higher the effluent H_2CO_3*alkalinity requirements.

- The effect of different COD loading rates on the minimum bed pH was evaluated by using a constant base influent COD concentration (29 000 mg/l) and changing the base influent flow. The recycle ratio was kept constant at 12:1 giving a COD_e of 2230 mg/ℓ. The effluent H_2CO_3*alkalinity was constant at 3100 mg/ℓ (as $CaCO_3$). When the COD loading rate was increased from 7 to 19 kg/(m^3 sludge bed.d) by increasing the base flow, the minimum bed pH decreased from 7,1 to 6,8. It would appear that for the same base influent COD *concentration* and a constant recycle ratio the minimum bed pH remained relatively stable despite an almost threefold change in COD loading rate.

- The pH profiles in the bed exhibited only a slight depression (to the minimum pH) for recycle ratios of 33:1 and 20:1 (base influent COD of 27 000 mg/ℓ and COD_e values of 790 and 1290 mg/ℓ). This tendency to smooth out the "dip" in the pH profile at low effective influent CODs, conforms with the observations of Sam–Soon *et al.* (1991). It would seem, therefore, that provided the effective influent COD is maintained in the range, say, 1000 to 1500 mg/ℓ the pH up the bed will be substantially constant and can be monitored at any point in the bed.

- From the experiments on recycling carried out in this laboratory scale study, it appears that the base influent COD should be diluted by the recycle to an effective influent COD range of about 1500 to 2000 mg/ℓ. Within this range of COD_e, for a COD loading rate of about 10 kg/(m^3 sludge bed.d) the different batches of wastes generated sufficient internal H_2CO_3*alkalinity to maintain a near neutral minimum sludge bed pH.

Feasibility study for a pure proteinaceous substrate, casein, and effects of pH changes on process performance

Sam–Soon *et al.* (1987 and 1990) investigated two basic types of organic substrates with regard to their potential to form pellets in a UASB system; carbohydrates (glucose) and fats and oils (oleic acid). They found that pelletisation occurred with glucose but did not occur with oleic acid. Besides these two basic types of organic substrates there is a third - proteins. To date there has been but little information available on the behaviour of UASB systems receiving pure proteinaceous substrates. To investigate the behaviour of a proteinaceous substrate in a UASB system, casein was fed to laboratory scale reactors. The objectives of the study were to:

- study the feasibility of treatment of casein in a UASB system, i.e. to investigate its potential for pelletisation,
- measure sludge production and,
- investigate the response of the process to changes in pH. Depending on the concentration of proteins, deamination may generate high concentrations of ammonium/ammonia. The species concentration of ammonium and ammonia is dependent on the pH, the concentration of ammonia increasing with an increase in pH. From the literature, methanogenic organisms are inhibited even at low ammonia concentrations. It was of interest therefore to study possible inhibition effects due to increased levels of ammonia at pH levels above neutral.

The feasibility study was done on a single reactor unit, that is, the sludge bed that included both the high and low hydrogen partial pressure regions. The study on sludge production and inhibition effects was done on a two in-series reactor systems, the first reactor containing the high hydrogen partial pressure region, and the second reactor containing the low hydrogen partial pressure region of the sludge bed respectively. From the study on the treatment of the proteinaceous substrate, casein, in these two laboratory UASB systems the following conclusions were formed:

- A UASB system treating the proteinaceous substrate casein developed a pelletised bed.
- Up to the highest loading rate applied (65 kgCOD/m^3 sludge bed.d) the COD removal remained above 95 per cent.
- The system could be operated without alkalinity addition to the influent.

- The profiles of product formation along the line of flow of the reactor were similar to those reported by Sam Soon *et al.* (1987) when treating a carbonaceous substrate in a UASB reactor.

- Uptake of nitrogen was well in excess of that observed in "normal anaerobic fermentation" – Sam Soon's conclusion that this was due to pellet formation appears to be supported.

- The specific sludge yield obtained in a high hydrogen partial pressure reactor, under the prevailing low pH conditions (minimum pH ≃ 6,2) was 0,26 mgVSS/mgCOD utilized. In the first reactor the VSS retained as pellets was 38 per cent of the VSS produced; the remaining 62 per cent was lost from the bed to the effluent of the first reactor.

- The overall sludge yield of the high and low hydrogen partial pressure reactors combined (with a minimum bed pH ≃ 6,2 in the first reactor) was estimated at 0,11 mgVSS/mgCOD utilized.

- When the pH in the system was raised (minimum pH ≃ 7,0) by addition of alkalinity to the influent, the specific sludge yield in the high hydrogen partial pressure reactor declined to 0,17 mgVSS/COD utilized. The VSS retained as pellets was 11 percent and the remaining 89 per cent was lost to the effluent.

- The lower specific sludge yield measured under near neutral pH conditions was contradictory to Sam Soon's hypothesis on pelletisation, which predicts a higher sludge yield at neutral pH levels because of increased activity of the hydrogenotrophs. The decrease in sludge production at near neutral pH levels was ascribed to inhibitory effects on the hydrogenotrophic organisms of the increased NH_3 species concentration as pH neutrality was approached, see below.

- On addition of alkalinity to raise the minimum pH from 6,2 to 7 in the first reactor the concentration of HAc decreased, the COD removal increased but there was now an increase in HPr in the profile and decrease in VSS production from 0,26 to 0,17 mgVSS/mgCOD utilized in the high $\bar{p}H_2$ reactor. Accepting the hypothesis for pelletisation by Sam–Soon *et al.* (1987), i.e. increased VSS production due to the action of the hydrogenotroph M strain

AZ, it was concluded that the reduced VSS production was due to inhibition of the hydrogenotrophs. Inhibition of the hydrogenotrophic microorganisms is further supported by the fact that the HPr advanced higher up the sludge bed. HPr can only be converted to HAc and H_2 at low hydrogen partial pressure. Inhibition of hydrogenotrophs reduced the rate of H_2 utilization thereby extending the region of high hydrogen partial pressure up the sludge bed, in this manner retarding the conversion of HPr to HAc and H_2.

- The cause of the inhibition appeared to be the increase in NH_3 species concentration when the pH was raised to pH 7. The higher NH_3 concentrations appeared to inhibit primarily the hydrogenotrophs, not acetoclastic organisms.

- With time the hydrogenotrophs appeared to adapt, to a large degree, to the increased NH_3 concentrations. When the ammonium/ammonia concentration was raised in steps from 900 to 1400 to 2400 mgN/ℓ influent with pH maintained within the reactor between 7,0 to 7,5, the system's overall COD removal showed only temporary loss in COD conversion at each step. On termination of ammonium and alkalinity addition the system reverted rapidly back to the response observed before these additions were made.

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SYMBOL	DESCRIPTION
A^-	Dissociated weak acid/base
Ac^-	Acetate
acetyl CoA	Acetyl Coenzyme A
ADP	Adenosine diphosphate
Alk HA	Weak acid/base subsystem alkalinity (mg/ℓ as $CaCO_3$)
Alk HAc	Acetate subsystem alkalinity (mg/ℓ as $CaCO_3$)
ALK $H_2CO_3^*$	Carbonate subsystem alkalinity (mg/ℓ as $CaCO_3$)
ALK $H_2PO_4^-$	Phosphate subsystem alkalinity (mg/ℓ as $CaCO_3$)
Alk H_2O	Water subsystem alkalinity (mg/ℓ as $CaCO_3$)
Alk NH_4^+	Ammonium subsystem alkalinity (mg/ℓ as $CaCO_3$)
A_T	Total acetate species concentration (mg/ℓ)
ATP	Adenosine triphosphate
ba	Mass of strong base (mol)
Br^-	Butyrate
B_T	Total butyrate species concentration (mol/ℓ)
°C	Degree Celsius
ca	Mass of strong acid (mol)
Ca	Normality of titration acid (mol/ℓ)
$CaCO_3$	Calcium carbonate
CoASH	Coenzyme A
COD	Chemical oxygen demand (mg/ℓ)
COD_b	Base (= undiluted) influent COD (mg/ℓ)
COD_e	Effective (= diluted by recycle) influent COD (mg/ℓ)
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
CH_4	Methane
C_T	Total carbonate species concentration (mol/ℓ)
f_m	Monovalent activity coefficient
f_d	Divalent activity coefficient
F_{1x}	First Gran Function

H^+	Hydrogen ion
H_2	Molecular hydrogen
HA	Undissociated weak acid/base
HAc	Undissociated acetic acid
HBr	Undissociated butyric acid
HCO_3^-	Bicarbonate ion
H_2CO_3	Undissociated carbonic acid
H_2CO_3*	Sum of molecularly dissolved carbon dioxide and undissociated carbonic acid
$H_2PO_4^-$	Hydrogen orthophosphate ion
HPO_4^-	Dihydrogen orthophosphate ion
H_3PO_4	Orthophosphoric acid
HPr	Undissociated propionic acid
IAWPRC	International Association for Water Pollution Research and Control
inorg-N	Soluble inorganic nitrogen (in the context of this thesis referring to free and saline ammonia)
K_a, K'_a	First thermodynamic and apparent dissociation equilibrium constants
K_{aa}, K'_{aa}	Thermodynamic and apparent dissociation equilibrium constants for the acetate weak acid/base
K_{ac1}, K'_{ac1}	First thermodynamic and apparent dissociation equilibrium constants for the carbonate weak acid/base
K_{ac2}, K'_{ac2}	Second thermodynamic and apparent dissociation equilibrium constants for the carbonate weak acid/base
K_{an}, K'_{an}	First thermodynamic and apparent dissociation equilibrium constants for the ammonia weak acid/base
K_{ap1}, K'_{ap1}	First thermodynamic and apparent dissociation equilibrium constants for the phosphate weak acid/base
K_{ap2}, K'_{ap2}	Second thermodynamic and apparent dissociation equilibrium constants for the phosphate weak acid/base
K_{ap3}, K'_{ap3}	Third thermodynamic and apparent dissociation equilibrium constants for the phosphate weak acid/base

K_{as1}, K'_{as1}	First thermodynamic and apparent dissociation equilibrium constants for the sulfide weak acid/base
K_{as2}, K'_{as2}	Second thermodynamic and apparent dissociation equilibrium constants for the sulfide weak acid/base
K_w, K_w'	Thermodynamic and apparent ion product constants respectively for the water weak acid/base
MAlk HA	Mass of weak acid/base subsystem alkalinity (mol)
MAlk HAc	Mass of acetate subsystem alkalinity (mol)
MALK $H_2CO_3^*$	Mass of carbonate subsystem alkalinity (mol)
ALK $H_2PO_4^-$	Mass of phosphate subsystem alkalinity (mol)
MAlk H_2O	Mass of water subsystem alkalinity (mol)
MAlk NH_4^+	Mass of ammonium subsystem alkalinity (mol)
M strain AZ	*Methanobacterium* strain AZ
N	Nitrogen
NAD^+	Nicotinamide adenine dinucleotide (oxidized form)
NADH	Nicotinamide adenine dinucleotide (reduced form)
NH_3	Free ammonia (unionized form)
NH_4^+	Saline ammonium (ionized form)
NH_3-N	Inorganic nitrogen
N_T	Total inorganic nitrogen species concentration (mg/ℓ)
org-N	Soluble organic nitrogen
P	Phosphorus
pCO_2	Partial pressure of carbon dioxide (atm)
pH	Negative log (activity of hydrogen ions)
$\bar{p}H_2$	Hydrogen partial pressure (atm)
pK_a	Negative log (thermodynamic dissociation constant)
pK'_a	Negative log (apparent dissociation constant)
pK_{aa}	Negative log (K'_{aa})
pK'_{aa}	Negative log (K'_{aa})
pK_{ac1}	Negative log (K_{ac1})
pK'_{ac1}	Negative log (K'_{ac1})
pK_{ac2}	Negative log (K_{ac2})
pK'_{ac2}	Negative log (K'_{ac2})
pK_{an}	Negative log (K_{an})
pK'_{an}	Negative log (K'_{an})
pK_{ap1}	Negative log (K_{ap1})

pK'_{ap1}	Negative log (K'_{ap1})
pK_{ap2}	Negative log (K_{ap2})
pK'_{ap2}	Negative log (K'_{ap2})
pK_{ap3}	Negative log (K_{ap3})
pK'_{ap3}	Negative log (K'_{ap3})
pK_{as1}	Negative log (K_{as1})
pK'_{as1}	Negative log (K'_{as1})
pK_{as2}	Negative log (K_{as2})
pK'_{as2}	Negative log (K'_{as2})
PO_4^{3-}	orthophosphate ion
P_T	Total inorganic phosphate species concentration (mol/ℓ)
Q	Influent flow (ℓ/d)
Q_r	Recycle flow (ℓ/d)
r	Recycle ratio
R_s	Sludge age (d)
SC	Specific conductivity (mS/m)
SCFA	Short–chain fatty acids
S_T	Total sulfide species concentration (mg/ℓ)
TDS	Total dissolved solids (mg/ℓ)
TKN	Total Kjeldahl nitrogen concentration
TSS	Total suspended solids (mg/ℓ)
UASB	Upflow anaerobic sludge bed
V_s	Sample volume (mℓ)
VSS	Volatile suspended solids (mg/ℓ)
V_x	Volume of titrant (mℓ)
μ	ionic strength (mol/ℓ)
Z	ionic charge
4 ppt	four pH point titration
5 ppt	five pH point titration

CHAPTER 1

INTRODUCTION

The upflow anaerobic sludge bed (UASB) reactor was developed in the Netherlands in the early 70's and has found wide application for treatment of industrial wastes. Suitability of a waste for treatment in a UASB reactor was established wholly by experiment. One key requirement established for successful treatment was that the waste must give rise to the formation of a granular (pelletised) sludge bed, to ensure retention of the biomass in the reactor. From laboratory and full scale experience it appeared that pelletisation took place readily with waste flows that contain a high fraction of carbohydrates, e.g. glucose starch, maize starch, beet root, potato and other similar wastes. Poor pellet formation was observed in cases where the waste flow was principally short-chain fatty acids (SCFA).

An explanation for the pelletisation phenomenon was proposed by Sam-Soon *et al.* (1987). They hypothesized that pelletisation was due to the action of *Methanobacterium* strain AZ (*Methanobrevibacter arboriphilus*). This organism utilizes H_2 as its sole energy source; it can produce all its amino acids except cysteine which needs to be supplied from an external source and it is a pH neutrophile. In an environment of high H_2 partial pressure (high $\bar{p}H_2$), with free and saline ammonium available, the organism produces large quantities of amino acids but protoplasm synthesis is limited by the cysteine supply; any excess amount of amino acids produced is excreted as extracellular polypeptide; this polymer binds the organisms together to form pellets. Other anaerobic bacteria may have similar characteristics to that of *M.*strain AZ and also contribute to pellet formation. Sam-Soon *et al.* concluded that the following prerequisites need to be satisfied to ensure pellet formation:

(1) a deficiency of the amino acid cysteine,

(2) adequate ammonium supply (in excess of that required for 'normal' anaerobic fermentation),

(3) build up of a high $\bar{p}H_2$ zone within the reactor,

(4) a near neutral pH, ranging from 6,6 to 7,4.

With regard to prerequisite (1), deficiency in cysteine supply usually appears to be present in most wastes treatable in UASB systems. Sam–Soon *et al.* found that *with* addition of cysteine to a made up glucose substrate, the pellet yield in the high $\bar{p}H_2$ zone of the UASB reactor declined significantly compared to the yield obtained *without* addition of cysteine.

With regard to prerequisite (2), from the nitrogen content of the pellet mass generated when treating a glucose substrate, Sam Soon *et al.* (1990) suggested a minimum nitrogen level in the influent of 0,02 mgN/mgCOD removed. 'Normal' anaerobic digestion processes require about 0,004 mgN/mgCOD removed so that the nitrogen requirements in UASB systems appear to be about 5 times that of a 'normal' digestor system.

With regard to prerequisite (3), to generate an environment of high $\bar{p}H_2$, H_2 is generated principally during the acidogenic phase where carbohydrates are converted to SCFA and H_2. In a semi plug or plug flow system, e.g. the UASB system, the substrate enters the reactor at the bottom and passes through the sludge bed in semi–plug or plug flow fashion, leading to a partial phase separation of the acidogenic and methanogenic phases. Under normal loading conditions of, say, a carbohydrate type substrate, in the lower part of the sludge bed production of SCFA and H_2 exceeds the removal of SCFA (by acetoclastic methanogenesis) and H_2 (by hydrogenotrophic methanogenesis), causing increases in SCFA and H_2; in this fashion a high $\bar{p}H_2$ is built up in this bed region, satisfying prerequisite (3). The increase in SCFA, however, has a side effect in that it causes a decline in pH in this region. To satisfy prerequisite (4), this decline in pH needs to be controlled to not less than about 6,6, by ensuring that adequate pH buffering is present in the influent.

When treating a carbohydrate substrate, under stable operating conditions the SCFA generated in the lower part of the sludge bed are converted to methane and CO_2 in the upper part of the sludge bed, to give an effluent substantially free of SCFA. The SCFA generated in the lower part of the sludge bed reduce the pH buffer present in the influent but as the SCFA are removed in the upper part of the sludge bed so the buffer is regenerated. In this way the generation of SCFA and its conversion to methane and carbon dioxide causes that there is very little loss of pH buffer from influent to effluent. The only losses are due to incorporation of ammonium in amino acids for protoplasm synthesis and extracellular biopolymer formation; these are relatively small quantities. In a sense, in a UASB system the high $\bar{p}H_2$ environment is created at the 'cost' of accumulation of SCFA in the lower part of the reactor with an associated pH decline.

In the literature, information on the pH buffer necessary to contain the pH decline due to SCFA accumulation is sparse, mainly qualitative, rarely quantitative. Sam–Soon *et al.* (1991) enquired quantitatively into the problem of pH buffering in UASB systems. With pure carbohydrate waste (apple juice) as influent substrate, they found that about 1,2 mg of carbonate alkalinity (as $CaCO_3$) per 1 mg influent COD concentration were required to prevent the minimum pH in the lower part of the sludge bed declining below 6,6. This mass of alkalinity per mg COD influent is very high; addition of buffering chemicals to the influent waste of this order of magnitude, would make the UASB process uneconomical. Young and McCarty (1967) in their studies on upflow anaerobic filters treating protein–carbohydrate wastes, also encountered the problem of low pH in the lower part of the filter bed and found that approximately 0,5 to 1 mg carbonate alkalinity (as $CaCO_3$) was necessary to maintain the pH > 6,6. Capri (1973) and Cronje (1973), treating wine distillery and glucose–starch wastes respectively in upflow anaerobic filters, successfully used recycles to maintain a near neutral pH in the lower part of the filter bed without addition of buffering chemicals. Sam–Soon *et al.* (1991) in their studies on UASB systems also applied a recycle with the objective of reducing the mass of buffer addition to the influent. Their reasons for installing a recycle were as follows: In a normally operated UASB system the buffer concentration of the effluent is closely equal to that in the influent; if a recycle is instituted from the effluent to the influent flow, the buffer concentration of the combined recycle + influent flow will remain constant; the recycle flow will reduce the COD concentration in the combined recycle + influent flow, in this manner increasing the buffer to substrate (COD) ratio. Sam–soon *et al.* concluded that the base buffer requirement (i.e buffer requirement without recycle) could be reduced by the multiplicative factor, (influent flow)/(influent + recycle flow) if a recycle is implemented. In this way the mass of buffer chemicals to be added could be reduced to an economically viable level.

In using the recycle, Sam–Soon *et al.* (1991) found that the recycle introduces an element of instability to the UASB system: If the system approaches overload, the

SCFA generated in the lower part of the sludge bed will be removed only partially in the upper part of the sludge bed and the remaining fraction will carry over into the effluent; with a recycle, this SCFA fraction will be added to the influent causing a further increase in the SCFA level in the reactor, and an associated decline in pH. In this fashion a recycle could accelerate the rate of deterioration of process performance, finally causing process failure. Hence, for safe operation of UASB systems, and in particular UASB systems with a recycle, the effluent must be monitored for SCFA.

From the discussion above it would appear that there are two principal parameters for *monitoring* and *control* of UASB systems:

- *pH buffering* for pH control and,
- *SCFA* for process stability.

With regard to pH buffering in UASB systems, two main categories of wastes can be identified: The first category are wastes that do not generate internally any weak acid/base buffer subsystem which is effective at near neutral pH; the total buffer requirements must be supplied externally, that is, the mass of buffer to be added equals the mass of buffer required in the influent. In this regard, the mass of buffer required to establish a desired minimum pH (under stable operating conditions) needs to be determined by experiment. With unstable operating conditions, which give rise to an increase in SCFA, the mass of buffer in the influent needs to be increased to counter a pH decline.

The second category of wastes are those containing organic salts, proteins or sulfates: removal of organic salts, deamination of proteins to inorganic nitrogen or reduction of sulfates to sulfides generates buffer internally. The mass of internal buffer generated varies depending on the type of waste; in some instances the buffer generated will be sufficient to prevent a decline of the minimum pH below 6,6; in other instances the buffer generated will reduce the mass supplementation of buffering chemicals.

When some of the buffer is generated internally, or, when the pH needs to be adjusted during unstable operating conditions, the mass of buffer chemicals to be added externally (to control the pH to a desired level) may be established by trial, using the pH as feed back parameter. Such an approach demands a high degree of experience and skill from the operator in managing the particular process and is essentially a trial and error approach. To overcome this problem a more methodical and direct approach to pH control would be invaluable:

> The dominating pH buffering system in anaerobic digesters is the carbonate weak acid/base system; one of its associated alkalinities (the H_2CO_3*alkalinity) is commonly used to quantify the buffering present in anaerobic digesters. The minimum mass of H_2CO_3*alkalinity required to maintain the minimum pH in a UASB system depends on the type of waste treated under *specified, stable operating conditions*; this must be determined experimentally. Knowing the minimum H_2CO_3*alkalinity requirements for the specific waste, pH control can be based on the H_2CO_3*alkalinity in the effluent as follows; the H_2CO_3*alkalinity in the reactor effluent is measured and compared to the experimentally determined H_2CO_3*alkalinity required to maintain the minimum pH. The difference between the measured and required alkalinities then is supplied externally, the mass of buffer chemicals being calculated from the difference between measured and required H_2CO_3*alkalinities.

This more direct approach to pH control, set out above, requires (1) knowledge of the mass concentration of the H_2CO_3*alkalinity to maintain a desired pH in the reactor effluent (used as a substitute indicator for the minimum bed pH) and, (2) measurement of the H_2CO_3*alkalinity present in the reactor effluent.

With regard to (1), H_2CO_3*alkalinity *requirements* for treatment of a waste in a UASB system, little quantitative information is available for the different waste categories. With regard to (2), the *measurement* of the H_2CO_3*alkalinity in anaerobic liquids, two prominent weak acid/base systems are present, carbonate and SCFA. There has always been difficulty in separating out experimentally the alkalinities associated with these two weak acid/bases. Of the methods available to determine the H_2CO_3*alkalinity in anaerobic liquids, the more elaborate (and accurate) are cumbersome and necessarily include independent direct determination of the SCFA. The less elaborate methods have lower accuracy and either neglect the effect of the SCFA on the determination of the H_2CO_3*alkalinity or include it in an approximate fashion only.

Apart from the need to account for the SCFA in experimentally determining the

H_2CO_3*alkalinity, measurement of the SCFA also is important in monitoring of the stability of the UASB systems. Thus for pH control *and* stability monitoring, measurements of both H_2CO_3*alkalinity *and* SCFA are necessary. Clearly a simple but accurate method to measure both would be of great practical value in monitoring and control of UASB systems, and in general for all anaerobic systems.

From the background set out above, the following objectives were set for this thesis:

- Development of a simple method for simultaneous determination of the H_2CO_3*alkalinity and SCFA concentrations in anaerobic systems, to be used in (1) assessing the H_2CO_3*alkalinity requirements for stable operation of UASB systems treating different types of wastes, (2) monitoring UASB system stability when treating these wastes under different operating conditions, e.g. different recycle ratios.

- Assessment of H_2CO_3*alkalinity requirements for lauter tun (brewery) waste to maintain a near neutral minimum bed pH in UASB systems. This waste generates very little H_2CO_3*alkalinity internally, virtually all H_2CO_3*alkalinity has to be supplied externally. It is of special interest to evaluate the effect of recycling the effluent to the influent to recover the effluent H_2CO_3*alkalinity and dilute the base influent COD to an effective influent COD (COD_e) defined as: COD_e = base influent COD/(1 + recycle ratio).

- Assessment of H_2CO_3*alkalinity requirements for wine distillery waste to maintain a near neutral minimum bed pH in UASB systems. This waste generates a substantial mass of H_2CO_3*alkalinity internally due to deamination of proteins to ammonium/ammonia, reduction of sulfates to sulfides and removal of organic acid salts such as potassium bitartrate. Similar to the lauter tun (brewery) waste, it is of interest to evaluate the effect of recycling on UASB system performance and the requirements of H_2CO_3*alkalinity at different recycle ratios, i.e. different COD_e concentrations.

- Assessment of a pure proteinaceous waste, casein: This substrate provides the opportunity to study H_2CO_3*alkalinity generation from deamination and the effects of pH changes on process performance of systems with high levels of inorganic nitrogen. With high levels of inorganic nitrogen generated in the reactor liquid due to deamination the likelihood of inhibitory effects developing increases due to increased ammonia (NH_3) levels at higher than neutral pH values. It is of interest to evaluate the effect of pH change on process performance due to the NH_3 inhibition.

In this thesis, Chapter 2 reviews the existing methods for determination of $H_2CO_3^*$alkalinity and SCFA and their application to monitoring and control of anaerobic systems. Chapter 3 to 6 describe the development of a simple acid titration method for measuring the $H_2CO_3^*$alkalinity in aqueous solutions containing only the carbonate system, the $H_2CO_3^*$alkalinity in aqueous solutions containing the carbonate system plus *known* concentrations of other weak acid/base systems, and, the $H_2CO_3^*$alkalinity *and* SCFA unknown in solutions containing also other weak acid/bases of known concentrations, e.g. inorganic nitrogen, phosphate and sulfides. Chapter 7 and 8 describe studies on the feasibility of treating lauter tun and wine distillery wastes in UASB systems and the influence of a recycle on the $H_2CO_3^*$alkalinity requirements and system performance; lauter tun waste being virtually completely dependent on an external alkalinity source, the wine distillery waste being completely independent of an external alkalinity supply if operated at an appropriate recycle ratio. In Chapter 9 the treatment of a pure proteinaceous substrate, casein, in a UASB system is investigated.

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CHAPTER 2

WEAK ACID/BASES AND pH IN ANAEROBIC SYSTEMS - A REVIEW

ABSTRACT

This chapter briefly reviews the practical approaches that have been developed to evaluate and control anaerobic fermentation processes. Practical parameters considered are the H_2CO_3*alkalinity, short–chain fatty acid concentrations (SCFA) and pH. Various methods have been developed to determine either (1) the H_2CO_3*alkalinity or SCFA, (2) both the H_2CO_3*alkalinity and SCFA in a more or less approximate form, or, (3) an approximate ratio of the H_2CO_3*alkalinity and SCFA. From a critical review, it would appear that these methods are either too approximate or too elaborate in their analytical procedures to serve as routine monitoring or control parameters. With the increased understanding of mixed weak acid/base chemistry, the potential is there to develop a relatively simple acid titration procedure to give both the H_2CO_3*alkalinity and SCFA concentration reasonably accurately.

2.1 INTRODUCTION

In anaerobic fermentation a number of different microbial species contribute to the breakdown of soluble organic compounds to carbon dioxide and methane. The main groups of bacterial species are the following:

- acidogens
- acetogens
- hydrogenotrophic methanogens
- acetoclastic methanogens

Each of these groups has a specific pH region for optimal growth; for acidogens a pH ≃ 6, for acetogens, hydrogenotrophic and acetoclastic methanogens a pH ≃ 7 (Gujer and Zehnder, 1983). The relative rates of growth of these groups changes with pH.

Under normal operating conditions, in anaerobic digestion, Mosey and Fernandes (1989) report the following average doubling times : acidogens – 30 min, acetogens – 1,4 days, hydrogenotrophic methanogens – 6 hours, acetoclastic methanogens – 2,6 days. To ensure optimal conversion one condition that must be satisfied is to provide optimal pH conditions for the slowest growing organism group. From Mosey's work, the acetoclastic methanogens are the rate limiting species. 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. However, near neutral pH by itself does not necessarily ensure effective performance – the hydrogen partial pressure ($\bar{p}H_2$) also has a crucial effect on fermentation. If the $\bar{p}H_2$ in the reactor is high, this inhibits conversion of propionic acid (HPr) to acetic acid (HAc) by the acetogenic organisms; this gives rise to an increase in HPr and consequentially to an overall increase in SCFA (and hence in the COD concentration) in the effluent, a decline in gas production, and a change in gas composition.

To manage and control an anaerobic system, information on pH, $\bar{p}H_2$, HPr, HAc, gas production and composition should be sufficient. However, at present measurement of $\bar{p}H_2$ requires a rather sophisticated technique, and separate measurement of HAc and HPr depends on the availability of a gas chromatograph, both not feasible in most full scale anaerobic installations. As a result there has been a resort to indirect practical approaches to obtain indicators of reactor performance and malfunction.

Assuming steady state conditions in a system treating a particular substrate, with normal operation one would expect a stable low level of SCFA, a stable pH between 6,8 – 7,4 and a stable methane/carbon dioxide ratio. With deviant behaviour one would expect a rise in the SCFA level, a reduction in the methane/carbon dioxide ratio and a decline in pH. The change in pH would be due principally to the rise in SCFA, but the pH change may be insubstantial due to the "buffering" agents in the reactor which would dampen the change. Accordingly, indirect estimation of the principal buffering agent, the carbonate system, was developed, via measurement of "alkalinity". Changes in alkalinity then were linked in various ways to estimate changes in SCFA; these together with the pH and the gas production rate and composition allowed the "health" of the system to be assessed.

In this chapter the intention is to review the practical approaches that have been developed to measure the parameters used to evaluate and control anaerobic fermentation systems. In order to do this properly it is necessary to sketch briefly the relevant background relating to pH and its control in anaerobic digestion.

2.2 pH BUFFERING IN ANAEROBIC DIGESTION

In the digester liquid the pH is established by interaction between strong and weak acid/bases. The pH that is established will depend on the mixture of weak acid/bases and strong acid or base, and the mass concentrations of each of these. The weak acid/bases most commonly found in anaerobic fermentation are the carbonate, ammonium, phosphate, sulfide and SCFA, e.g. acetate and propionate, Pohland *et al.* (1969). Under 'normal' operating conditions the carbonate weak acid/base is the dominant one. However, 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 increase in SCFA concentration and the pH buffering due to *all* the weak acid/bases present.

Buffer index

The buffering action of a weak acid/base in solution is demonstrated practically by titrating the solution with a strong acid or a strong base. By plotting the cumulative amounts of strong acid or base added versus pH, a titration curve is obtained. The slope of this curve (dca/dpH), at any pH, defines the buffer index β (Loewenthal and Marais, 1976):

$$\beta = dca/dpH = -dcb/dpH \tag{2.1}$$

where ca, cb = mass of strong acid or strong base added per litre respectively, (mol/ℓ),

β = buffer index, mol/(ℓ.ΔpH).

An aqueous solution containing a weak acid/base can be looked upon as a *system* that is made up of two *subsystems*, water and the weak acid/base (Loewenthal *et al.*, 1991). Theoretically β at any pH is the sum of the buffer indices of the two subsystems. These can be formulated as follows:

Weak acid/base subsystem:

For a monoprotic weak acid/base, HA, buffering arises from the change in the proportions of its constituent species, HA and A^-, due to different levels of dissociation between two pH values. The dissociation and equilibrium equations can be formulated as follows:

$$HA \rightarrow A^- + H^+ \tag{2.2}$$

$$\frac{[A^-]\ (H^+)}{[HA]} = K_a/f_m = K_a' \tag{2.3}$$

$$A_t = [HA] + [A^-] \tag{2.4}$$

where [ ] = concentration,(mol/ℓ),
( ) = activity, (mol/ℓ),
K_a, K_a' = thermodynamic and apparent dissociation constants respectively, (mol/ℓ),
f_m = monovalent activity coefficient (see Appendix A),
A_t = total species concentration of the weak acid/base, (mol/ℓ).

For a monoprotic weak acid/base subsystem its buffer index, β_a, can be formulated in terms of A_t, (H^+) and K_a as follows (Loewenthal and Marais, 1976):

$$\beta_a = dca/dpH = 2{,}303\ [A_t\ K_a\ (H^+)/f_m]\ /\ [K_a+(H^+)/f_m]^2 \tag{2.5}$$

For a diprotic weak acid/base, with dissociation constants, K_{a1} and K_{a2}, provided 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 (2.5) (Loewenthal and Marais, 1976).

Water subsystem:

For the water subsystem, the equilibrium expression is given by Loewenthal *et al.* (1976):

$$(H^+)\ [OH^-] = K_w/f_m = K_w' \tag{2.6}$$

where K_w and K_w' = thermodynamic and apparent ionic product constants respectively for the water subsystem, K_w is temperature dependent and equal to 10^{-14} $(\mathrm{mol}/\ell)^2$ at 25° C.

For the water subsystem the dissociation reaction offers buffering at very low and high pH's. The buffer index for water is related to its thermodynamic ion product constant, K_w, the hydrogen ion activity, (H^+), and the hydrogen ion activity coefficient, f_m, as follows:

$$\beta_w = 2{,}303\ \{(H^+)/f_m + K_w/(H^+)/f_m\} \tag{2.7}$$

At a fixed temperature K_w is constant, and the buffer index of the water subsystem is dependent only on the pH and f_m.

The buffer index of the solution containing one weak acid/base, β, at any pH is given by

$$\beta = \beta_a + \beta_w \tag{2.8}$$

<u>Species concentration:</u>

In evaluating the various methods, proposed later, to estimate the the carbonate and the SCFA subsystems, the following relationships, defining the species concentrations at any pH, are useful.

From Eqs (2.3 and 2.4) the individual species concentrations of a weak acid/base are expressed in terms of A_t and (H^+) as follows:

$$[A^-] = \frac{A_t\ K_a'}{K_a' + (H^+)} \tag{2.9}$$

$$[HA] = A_t\,(1 - \frac{K_a'}{K_a' + (H^+)}) \tag{2.10}$$

where $(H^+) = 10^{-pH}$

Changes in $[A^-]$ and $[HA]$ with pH can be plotted from Eqs (2.9 and 2.10).

The water subsystem species can be written in terms of pH as follows:

$$[H^+] = 10^{-pH}/f_m \tag{2.11}$$

rearranging Eq (2.6)

$$[OH^-] = 10^{(pK_w'-pH)} \tag{2.12}$$

where $pK_w' = -\log K_w'$

Species concentration and buffer index – pH diagrams

Graphical representations of the species concentrations vs pH (log–species diagram) and the associated buffer index curves for the water and weak acid/bases usually present in anaerobic digestion, are shown in Fig 2.1(a,b,c,d,e,f). The SCFA are represented by acetic acid because the pK_a values of the various SCFA, typically present in the digester liquid (acetic, propionic and butyric), differ only slightly.

Between any two pH points the area under the buffer index curve gives the mass of H^+ ions to be added or removed to bring about the pH change, termed the buffering capacity (or proton accepting/donating capacity, or, positive and negative alkalinity) between the two pH points. The buffer index diagrams can be used to illustrate the following points:

- The buffer index for a weak acid/base subsystem is at its maximum where the pH equals the dissociation constant pK_a, where the component weak acid/base species are in equal concentration.

- The buffer index decreases rapidly on either side of the pK_a value and becomes negligible within two pH units, giving rise to a bell shaped buffering index curve centered around the pK_a value.

- The buffer index is proportional to the total species concentration of the weak acid/base subsystem. Hence increasing the total species concentration increases the height of the bell shaped buffer index curve and accordingly increases the buffering capacity against pH change.

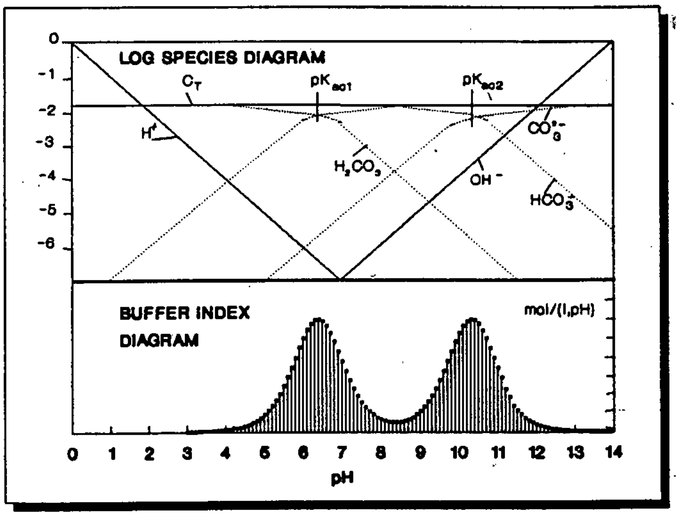

Fig 2.1a: Log species diagram for the carbonate weak acid/base system in aqueous solution and the buffer index diagram for the carbonate subsystem. Note that pH as used in the term [mol/(l.pH)] refers to a unit change in pH.

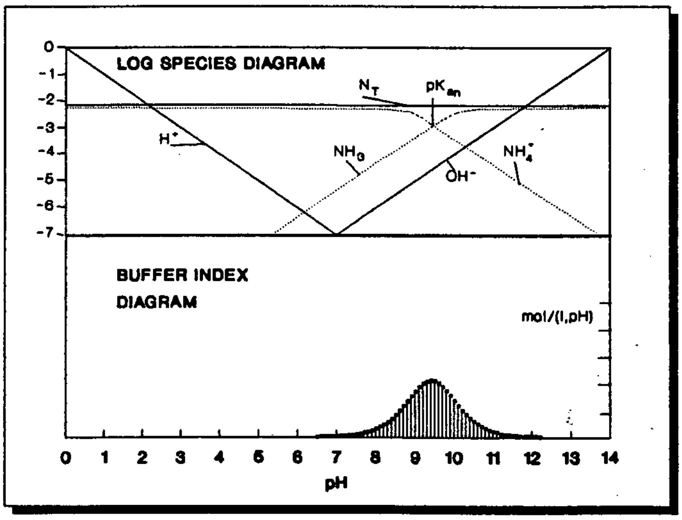

Fig 2.1b: Log species diagram for the ammonium weak acid/base system in aqueous solution and the buffer index diagram for the ammonium subsystem. Note that pH as used in the term [mol/(l.pH)] refers to a unit change in pH.

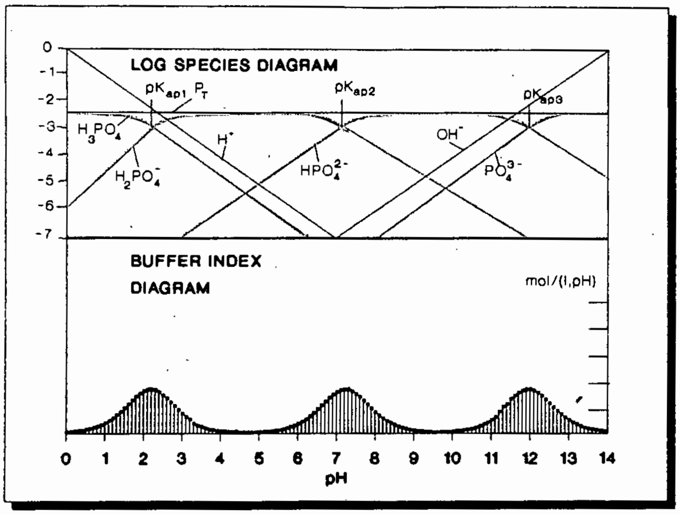

Fig 2.1c: Log species diagram for the phosphate weak acid/base system in aqueous solution and the buffer index diagram for the phosphate subsystem. Note that pH as used in the term [mol/(l.pH)] refers to a unit change in pH.

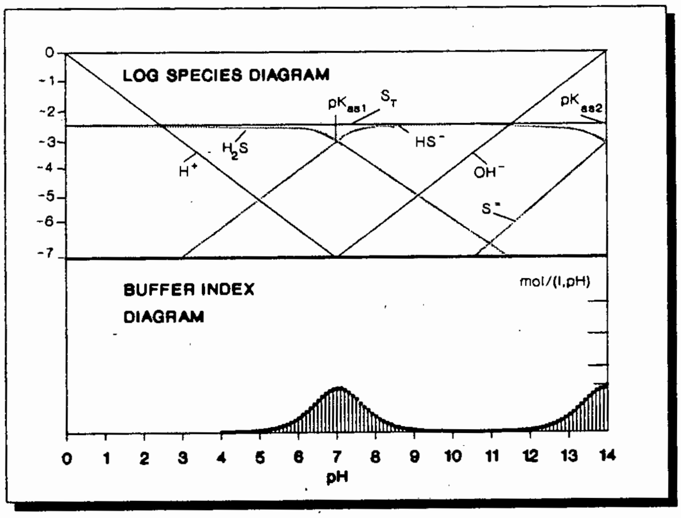

Fig 2.1d: Log species diagram for the sulfide weak acid/base system in aqueous solution and the buffer index diagram for the sulfide subsystem. Note that pH as used in the term [mol/(l.pH)] refers to a unit change in pH.

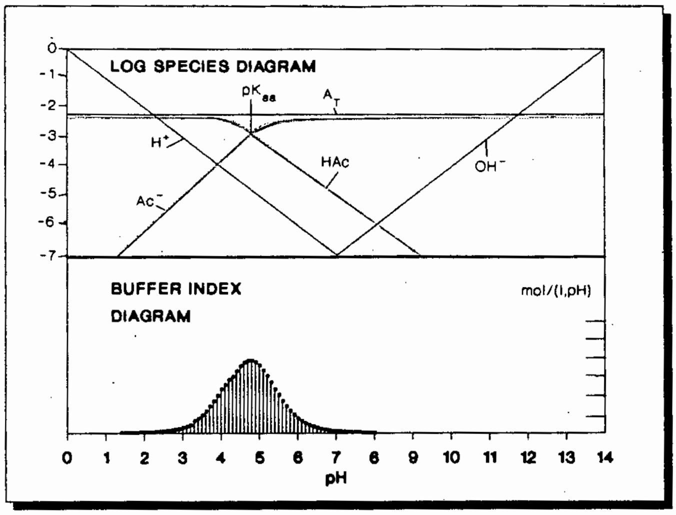

Fig 2.1e: Log species diagram for the acetate weak acid/base system in aqueous solution and the buffer index diagram for the acetate subsystem. Note that pH as used in the term [mol/(l.pH)] refers to a unit change in pH.

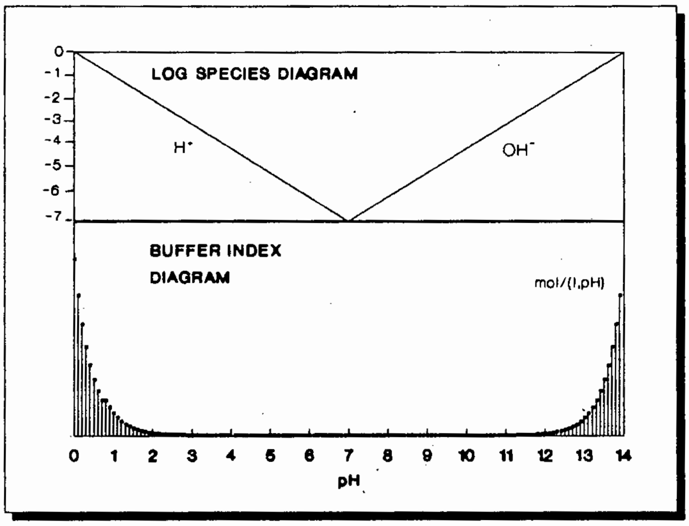

Fig 2.1f: Log species diagram and buffer index diagram for the water subsystem. Note that pH as used in the term [mol/(l.pH)] refers to a unit change in pH.

In the pH range of normal digester operation, pH 6,6 to 7,4, the buffering against pH change by the different weak acid/base systems is as follows:

- Sulfide, phosphate and carbonate subsystems have pK_a values near to the pH range 6,6 to 7,4 and therefore potentially can provide significant buffering against pH change. The measure of buffering contributed by each weak acid/base subsystem will depend on its total species concentration. Usually the sulfide subsystem concentration is very small compared to the carbonate subsystem so that the buffering contribution of the sulfide subsystem is negligible relative to that of the carbonate subsystem. The phosphate subsystem sometimes may be present at concentrations sufficiently high to make a significant contribution to buffering.

- The ammonium subsystem has a pK_a value well outside the pH range 6,6 to 7,4 ($pK_{an} \simeq 9,4$). In this pH range the ammonium subsystem is virtually completely in the ionized (NH_4^+) form and affords virtually no buffering against pH change even when present in high concentrations (> 500 mgN/l). If NH_3 is added with the pH remaining in the range 6,6 to 7,4, the NH_3 will change virtually completely and immediately to NH_4^+ thereby abstracting H^+, i.e. NH_3 acts as a strong base.

- The SCFA subsystem, as represented by the acetic acid, also has a pK_a value well outside the pH range of 6,6 to 7,4 ($pK_{aa} \simeq 4,75$) and accordingly, like the ammonium subsystem, contributes little to the pH buffering in this pH range. If acetic *acid* is added with the pH remaining in the range 6,6 to 7,4, it dissociates virtually completely to acetate and H^+ i.e. acts as a strong acid.

2.3 QUANTIFICATION OF WEAK ACID/BASE SYSTEMS

Minor weak acid/bases

Methods of quantification of the weak acid/base systems, present in digester liquid, differ greatly between the weak acid/bases. Measurements of the total species of the phosphate, ammonium and sulfide subsystems can be done by conventional wet chemical methods without undue difficulties. Even though under normal circumstances these weak acid/bases are of minor importance in pH buffering in the pH range 6,6 to 7,4, they need to be determined for two reasons, to safeguard against nutrient deficiency or inhibition effects (usually from increased concentrations of sulfides and ammonia), and, to enhance the accuracy of the determination of the total species concentration of the carbonate subsystem, see later.

Short chain fatty acids

Quantification of the SCFA system is a complex problem, not easily resolvable by conventional chemical methods. The SCFA total species can be measured by straight distillation, steam distillation, chromatographic separation (Standard Methods, 1989) or by a colorimetric technique as set out by Montgomery *et al.* (1962). These methods cannot differentiate individual SCFA but measure this group of weak acid/bases as a whole. If identification and quantification of the individual SCFA is required, this needs to be done by gas chromatography. All these methods tend to be time consuming and the last three involve considerable analytical skill and expensive equipment.

Carbonate subsystem only in solution:

Quantification of the carbonate subsystem presents difficulties because of its nature: In solution the carbonate subsystem consists of four species (1) CO_2 dissolved (2) carbonic acid, H_2CO_3 (3) bicarbonate, HCO_3^- and (4) 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.

$$[H_2CO_3^*] = [CO_2\ \text{dissolved}] + [H_2CO_3] \tag{2.13}$$

The total species concentration C_T is given by

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \tag{2.14}$$

The ratio CO_2 (dissolved) : H_2CO_3 is fixed and equal to 99,76 : 0,24, 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. If the sample is acidified to convert the carbonate species to H_2CO_3*, the solution partial pressure of CO_2 is high and the CO_2 species can be removed by sparging with nitrogen gas or air. The CO_2 exchange is also evident in anaerobic digestion liquid: In the digester the partial pressure of dissolved CO_2 is much higher than that of CO_2 in the atmosphere; 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. Because of this loss of CO_2 (in sample preparation), it is not possible to measure C_T of the digester liquid accurately by means of an inorganic carbon analyzer. To avoid the difficulties in determination of C_T due to CO_2 loss, an alternative approach to quantifying the carbonate system was developed via pH and the concept of proton capacity (Loewenthal *et al.*, 1989), described below.

If either CO_2 (gas), HCO_3^- or CO_3^{2-} species (called reference species) are added to pure water the solution is called an $H_2CO_3^*$, HCO_3^- or CO_3^{2-} equivalent solution. This solution (system) is made up of two subsystems; the water and carbonate subsystems. The pH established is called the $H_2CO_3^*$, HCO_3^- or CO_3^{2-} equivalence point respectively. These equivalence points serve as reference pH's for the respective solutions. The $H_2CO_3^*$ and CO_3^{2-} equivalence points are established by the respective concentrations of reference species $[H_2CO_3^*]$ 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 the equivalent solutions the pH increases above the respective equivalence points. The mass of strong base added generates a proton accepting capacity (H^+ accepting capacity) relative to the respective equivalence point; this capacity can be measured by titrating back to the equivalence point using a standard strong acid. If a strong acid is added to the equivalent solutions the pH will decrease below the equivalence point giving rise to a proton donating capacity relative to the respective equivalence points and this can be measured by titrating back to the respective equivalence point using a strong base. Note, the proton accepting or donating capacity to an equivalence point is equal to the strong base or strong acid added and independent of the mass of reference species present. Conventionally, the proton accepting capacity (given to the liquid by addition of strong base) is taken as positive. On this basis the proton *donating* capacity is in effect a negative proton *accepting* capacity.

Historically the proton accepting capacity between two pH points has been called *alkalinity* and the proton donating capacity the *acidity*. As both refer to the proton capacity, the old nomenclature creates a measure of confusion and should not continue to be used. 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; the proton donating capacity is then a negative alkalinity, thereby making the term acidity redundant.

The proton accepting capacity between the initial pH and the $H_2CO_3^*$, HCO_3^- and CO_3^{2-} equivalence points give the $H_2CO_3^*$alkalinity, HCO_3^- alkalinity, CO_3^{2-} alkalinity respectively. These alkalinities and C_T are interrelated; if one of these alkalinities can be measured, together with the initial pH of the sample or *in situ*, the other alkalinities and C_T can be calculated (Loewenthal *et al.*, 1989).

From a practical point of view the alkalinity associated with the $H_2CO_3^*$ equivalent solution – the $H_2CO_3^*$alkalinity – has been found the most useful. The $H_2CO_3^*$alkalinity is not affected by gain or loss of CO_2 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. Subsequently C_T in the *in situ* liquid can be calculated from the measured sample $H_2CO_3^*$alkalinity and the *in situ* pH; thus CO_2 loss between sampling and testing of the sample does not prevent the determination of *in situ* C_T. However, the experimental measurement of $H_2CO_3^*$alkalinity presents a problem in that the $H_2CO_3^*$equivalence point depends on C_T which is not known *a priori*. Fortunately this equivalence point lies in a region of low buffering capacity so that a slight error in the equivalence point estimation (based on rules developed from experience) do not give rise to significant errors in $H_2CO_3^*$alkalinity (indeed it was because of this feature that the $H_2CO_3^*$alkalinity concept has been developed). If accurate determination of the $H_2CO_3^*$alkalinity is required, a method developed by Gran (1952) allows quantification of the $H_2CO_3^*$alkalinity without the knowledge of the equivalence point, thereby avoiding errors resulting from incorrect equivalence point identification.

The reference species alkalinities are special ones in that they are theoretically linked to each other and C_T and have specific endpoints. Alkalinity, in general, arises from titration between *any* two pH points; such titrations from an initial and any selected endpoint, allow the reference species alkalinities to be determined, but, the relationships are quite complex – practical application requires the assistance of a personal computer or programmable calculator. This approach has received little attention in the past and the accuracy and precision of such estimates have not been investigated in depth.

Mixtures of the carbonate and other weak acid/base subsystems

In anaerobic digestion the determination of the $H_2CO_3^*$alkalinity, by titrating to the $H_2CO_3^*$ equivalence point virtually always will give an incorrect result. This arises from the presence of other weak acid/base subsystems, i.e. SCFA, phosphate, sulfide and ammonium. Depending on the starting pH of the titration, these weak acid/bases will influence, in a greater or lesser degree, the amount of acid required to titrate to the $H_2CO_3^*$ equivalence point and thus lead to an incorrect $H_2CO_3^*$alkalinity estimation. To overcome this problem, Loewenthal *et al.* (1989) proposed a modified Gran Function for mixtures of weak acid/bases that include the carbonate system. However, this approach requires that the total species concentrations of the ammonium, phosphate, sulfide and SCFA subsystems are known accurately in order to isolate the carbonate subsystem in the mixture. Moreover from a practical point of view the Gran titration is a relatively complex exercise, so also the independent accurate determination of the SCFA; consequently, in many operational situations this approach has not found ready application.

2.4 PRACTICAL CONTROL PARAMETERS

In the section above we have noted the difficulties in characterizing the constituent mixed liquor parameters of importance for controlling anaerobic fermentation systems. These difficulties have prompted the development of practical parameters and quantitative or semi–quantitative estimates of these, for control.

It was noted earlier that in anaerobic digestion, in general, the SCFA as a group are the principal agent inducing a pH decline and the carbonate subsystem the principal agent resisting such a decline. Therefore it is to be expected that a practical method for control of an anaerobic fermentation system would include a parameter relating to the carbonate subsystem or the SCFA subsystems, or both. The following categories of approaches have been proposed:

(1) Measurement of $H_2CO_3^*$alkalinity only
  - DiPinto *et al.* (1990) without titration
  - Jenkins *et al.* (1983) using titration

(2) Measurement of total(H_2CO_3*+SCFA) alkalinity by titration and separate measurement of SCFA total species, to give the H_2CO_3*alkalinity and a SCFA alkalinity
- McCarty (1974)

(3) Measurement of ratios of approximate alkalinities of the solution of carbonate and SCFA species
- Ripley *et al.* (1986)

(4) Measurement of total species concentrations of the carbonate and SCFA subsystems by titration

- Colin (1984)
- Powell and Archer (1989)

Measurement of H_2CO_3*alkalinity only

The H_2CO_3*alkalinity (which is the system alkalinity) can be written as the sum of the alkalinity contributions by the carbonate and the water *subsystems* (Loewenthal *et al.*, 1991), i.e.

$$\begin{aligned} H_2CO_3^*\text{alkalinity} &= \text{Alk } H_2CO_3^* + \text{Alk } H_2O \\ &= \{[HCO_3^-] + 2\,[CO_3^{2-}]\} + \{[OH] - [H^+]\} \end{aligned} \tag{2.15}$$

Note: The subsystem alkalinities are written with the alkalinity terms preceding the H_2CO_3* and H_2O.

In the pH region 7,0 to 8,3, the carbonate subsystem is present virtually totally as HCO_3^- species. This species is converted virtually totally to H_2CO_3* when titrated to the H_2CO_3*equivalence point (pH ≃ 4,2 to 5,0) and the HCO_3^- species is virtually the sole contributor to the H_2CO_3*alkalinity (see Fig 2.1a); the proton accepting capacity of the water subsystem can be neglected because of its minor influence on a titration to the H_2CO_3* equivalence point. Hence, the H_2CO_3*alkalinity can be closely approximated by:

$$H_2CO_3^*\text{alkalinity} \simeq HCO_3^- \text{ concentration}$$

DiPinto *et al.* (1990) proposed determining the H_2CO_3*alkalinity of the digester liquid by measuring the CO_2 over pressure created when acidifying a sample, as follows: A fixed volume of sample is introduced into a vessel of specified volume; the sample is purged with CO_2 to achieve CO_2 saturation. The sample is sealed and acidified to convert virtually totally the HCO_3^- to $H_2CO_3^*$. The CO_2 generated causes an over pressure in the sealed vessel; this over pressure is related to the HCO_3^- converted, and, equals the H_2CO_3*alkalinity. This approach has the merit that it measures the H_2CO_3*alkalinity independently of the presence of other weak acid/bases in the solution.

Another approach to measuring the H_2CO_3*alkalinity was proposed by Jenkins *et al.* (1983): By titrating from the initial pH of the sample to pH 5,75 about 80 per cent of the H_2CO_3*alkalinity is titrated, but 20 per cent of the alkalinity due to the SCFA is also included in such a titration (see Fig 2.1a,e). Because the SCFA is *low* in a stable operating system, the influence of the SCFA on the alkalinity measurement will be correspondingly low and they proposed that it be neglected. Accordingly the H_2CO_3*alkalinity[1] can be formulated as:

$$H_2CO_3^*\text{alkalinity} = ALK_{5,75}/\ 0{,}8 \tag{2.16}$$

where $Alk_{5,75}$ is the alkalinity obtained from titration to $pH_{5,75}$.

Clearly if the SCFA should be high, for example, where unstable conditions develop, this method would overestimate the H_2CO_3*alkalinity because the method does not take into account the significant buffering effect due to the SCFA in the titration.

In both approaches above, process deviation from stable steady state conditions is indicated by a change (decline) in H_2CO_3*alkalinity. The cause for the deviation is not explicitly evident but is inferred, say, to be due to accumulation of SCFA. However, other causes may give rise to changes in the H_2CO_3*alkalinity. For example, in winery wastes, the protein content of the

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[1] Jenkins *et al.* (1983) call the H_2CO_3*alkalinity the TBA or "true bicarbonate"; McCarty (1974) uses the term "bicarbonate alkalinity". Both these terms are based on the assumption that the proton accepting capacity afforded during the titration of a digester sample to a selected end point is due to the change of the HCO_3^- species to $H_2CO_3^*$.

waste can vary appreciably depending on the operation of the distillery plant; a reduced protein content will cause a decline in H_2CO_3*alkalinity (due to reduced deamination) without an increase in SCFA. Raising the alkalinity by chemical dosing would also upset the use of this method. Successful application of the two approaches, therefore, would require the history of the fermentation process, and, depends to a degree on the experience of the operator.

Measurement of total (H_2CO_3*+SCFA)alkalinity with separate SCFA determination to give H_2CO_3* alkalinity and SCFA alkalinity

McCarty (1974) proposed an alkalinity titration to approximately the H_2CO_3* equivalence point, pH 4,0, and direct measurement of the SCFA. A titration to pH 4 would include virtually 100 per cent of the proton accepting capacity of the carbonate subsystem but also about 85 per cent of that of the SCFA subsystem (see Fig 2.1e). Knowing the SCFA concentration (as acetic acid) the proton accepting capacity (alkalinity) contribution of the SCFA to pH 4,0, can be calculated from the total species concentration as: 0,85·(Total SCFA as acetic acid), see later. Because the H_2CO_3*alkalinity is expressed as mg/ℓ as $CaCO_3$, the unit of the SCFA has to be adjusted from mg/ℓ as acetic acid to mg/ℓ as $CaCO_3$, the factor to calculate the proton accepting contribution of the SCFA changes from 0,85 to 0,71. Hence the H_2CO_3*alkalinity can be calculated as:

$$H_2CO_3^*\text{alk} = \text{TOT.ALK}_{4,0} - 0{,}71\ \text{SCFA} \tag{2.17}$$

where:

$\text{TOT.ALK}_{4,0}$ = the total alkalinity including all weak acid/base subsystems (mg/ℓ as $CaCO_3$),

SCFA = the sum of the concentrations of all SCFA (mg/ℓ as acetic acid)

McCarty's method separates out the SCFA and the H_2CO_3*alkalinities, however, the accuracy of the H_2CO_3*alkalinity is dependent on a reasonably accurate measurement of the SCFA subsystem. Furthermore, errors may be introduced by neglecting the proton accepting contributions due to the minor weak acid/bases.

Measurement of ratios of approximate alkalinities of the carbonate and SCFA systems

Ripley *et al.* (1986) suggested roughly separating out the SCFA and carbonate systems and to base control on a ratio of the two; the sample is titrated to a fixed pH of 5,75 and thereafter to pH 4,3. The mass of acid to titrate to pH 5,75 is termed the partial alkalinity (PA) indicating that only a part of the total alkalinity is covered by titrating to this pH, principally the carbonate subsystem alkalinity. The mass of acid to titrate from pH 5,75 to 4,3 is termed the intermediate alkalinity (IA) and is mainly due to the buffering of the SCFA subsystem. Ripley argues that for stable digester operation adequate buffering due to the carbonate subsystem is necessary and excessive SCFA concentrations must be avoided. Consequently he introduces a ratio made up of a parameter mainly representing the alkalinity contribution due to the SCFA subsystem (IA) and a parameter mainly representing the alkalinity contribution due to the carbonate subsystem (PA), i.e.:

$$r = IA/PA \tag{2.18}$$

Ripley *et al.* (1986) monitored an anaerobic digester fed with poultry manure and found that the ratio served as a good indicator of stress conditions in the process, when $r > 0,3$.

> The method requires a simple analytical procedure. The parameters IA and PA are fuzzy in that both are made up of SCFA and carbonate subsystem alkalinities, the first dominating in IA and the second in PA. Very likely the critical r values would differ between wastes so that application as a control measure on a plant will require a build up of experience. Ripley *et al.*'s method identifies deviant behaviour but would not supply information from which to calculate, say, corrective chemical dosing.

Measurement of the total species concentrations of the carbonate and SCFA subsystems by titration

In the approaches of McCarty and Jenkins *et al.* the basic parameter selected to characterize the carbonate subsystem is the $H_2CO_3^*$alkalinity (in an approximate form). One may obtain the $H_2CO_3^*$alkalinity in two ways: (1) directly by titrating a sample to the $H_2CO_3^*$ equivalence point, or, (2) indirectly by determining C_T and measuring the initial pH of the sample which allows the calculation of the $H_2CO_3^*$alkalinity. McCarty and Jenkins *et al.* both used direct titration to obtain approximate estimates of the $H_2CO_3^*$alkalinity. We shall now review indirect approaches that estimate C_T in a solution also containing the SCFA subsystem, by titration. Having estimated C_T, together with the initial pH of the sample the H_2CO_3*alkalinity is derived.

DiLallo and Albertson (1961) proposed that a decanted or centrifuged digester sample be titrated from the initial pH to pH 4,0 to estimate a total alkalinity. This titration includes the proton accepting capacity of the carbonate, SCFA and minor weak acid/bases. The sample is then titrated to pH 3,3 to ensure complete conversion of HCO_3^- species to (H_2CO_3 + dissolved CO_2) species; these carbonate species are now removed from the sample by boiling lightly for 3 minutes. The sample is back titrated with strong base and the amount of base added between pH 4,0 and 7,0 forms an estimate of the "volatile acid alkalinity" which is the proton accepting capacity between these two pH points exerted by the SCFA and minor weak acid/bases, because the carbonate species have been removed from the sample (see Fig 2.1c,d,e). From the "volatile acid alkalinity" the SCFA concentration is then calculated using conversion factors specified by DiLallo and Albertson (1961).

Powell and Archer (1989) modified and extended DiLallo and Albertson's approach and developed it into an automated procedure to estimate the total carbonate species (C_T) and SCFA concentrations. The sample pH is raised to pH > 11 using a strong base. Following this they measure, a "carbonate" alkalinity by titrating from pH 11 to pH 9,4: They insert pH = 11 and 9,4 in Eq (2.9) which yields two equations relating the concentration of the CO_3^{2-} species at each pH to C_T; to calculate C_T, they note that the molar mass difference in CO_3^{2-} species at the two pHs equals the mass of protons added in the titration to bring about the change in the carbonate subsystem and subtract the two equations to solve for C_T. The sample pH is then lowered to 6,9 and titrated from pH 6,9 to 4,0; between these two pHs the titration gives a combined proton accepting capacity due to the carbonate and SCFA weak acid/bases. After this the sample pH is lowered to pH 2,2 and the sample is sparged with air, expelling virtually all of carbonate system species in the form of CO_2. Following this the sample is back titrated between pH 4,0 and 6,9. This titration provides a measure of the proton donating capacity due to the SCFA subsystem between these two pH values; the molar mass of titrant added equals the change in mass of the undissociated species of the SCFA subsystem. Via Eq (2.9), analogous to the determination of C_T in the pH range 11 to 9,4, the total species concentration of the SCFA system is derived. Having the data from the titration from pH 6,9 to 4,0 and the total SCFA species concentration, the proton accepting capacity of the SCFA between pH 6,9 and 4,0 is determined by subtraction (via Eq

2.9); this quantity is subtracted from the combined proton accepting capacity measured by titration. This gives the proton accepting capacity of the carbonate system between these two pH values (6,9 and 4,0) which, in this pH range, closely equals the change in HCO_3^- species concentration; via Eq (2.9) two equations relating the HCO_3^- species concentration to C_T at pH 6,9 and 4,0 can be established, and, a second C_T value is estimated again by subtracting the two equations, noting that the change in HCO_3^- concentrations between the two pHs equals the known (measured) proton accepting capacity of the carbonate subsystem. Thus two C_T values become available and the mean of these two values is accepted as the best estimate of C_T. The method was tested on solutions of pure carbonate, pure acetate and mixtures of these. The results give estimates within about 1 mmol of the true values (at 95 % confidence) for concentration ranges from 5 mmols to 50 mmols. No data is supplied on the performance of this procedure on anaerobic digester liquids. The following comments are pertinent:

> Raising the pH to > 11 may cause carbonate species precipitation thereby leading to an underestimate of the proton accepting capacity of the carbonate system in the subsequent titration between pH 11 to 9,4. Additionally in this pH range the water and ammonium systems have significant proton accepting capacities [see Figs 2.1(f) and 2.1(b)], both if not accounted for, giving rise to an overestimate of C_T. In the back titration from pH 4,0 to 6,9 the phosphate and sulfide systems may exert significant buffering capacities thereby causing an overestimate of the SCFA. However, if the ammonium, phosphate and sulfide systems are measured by conventional methods then their buffering effect can be evaluated via Eq (2.9) and the titrations duly corrected to give closer estimates of the carbonate and SCFA systems. Other difficulties foreseen would be the problem with pH calibration over the pH range of 4 to 11.
>
> Powell and Archer's approach breaks new ground but the method of application is still cumbersome, particular the need for stripping the CO_2 and requirement for both acid and base titrations.

Colin (1984) also proposed an automated method using acid and base titrations to different end pH points and inserting the titration results in appropriate equilibrium equations, defining the ammonium, SCFA and carbonate systems. Colin's method differs from those of Powell *et al.* (1989) and DiLallo and Albertson (1961) in that there is no need to remove the carbonate system (by aerating or boiling the sample at a low pH). Insufficient detail on the experimental requirements and calculation procedures is supplied to make an assessment of the method.

2.5 DISCUSSION

It is clear from the review presented here that the SCFA and the carbonate subsystems have achieved importance in monitoring the performance of anaerobic fermentation systems. Various methods have been proposed to estimate the carbonate system only, or the carbonate and SCFA systems via titration. In these methods different approaches have been adopted to isolate the carbonate and SCFA systems; by empirical factors, measurement of the SCFA with wet chemical methods or by stripping the carbonate system and measuring the SCFA system via titration. Of all these methods Powell and Archer's method appears to have the best potential for further development, but attention must be given to the following shortcomings of this method. It,

- neglects the effect of the phosphate, sulfide, ammonium and water subsystems,
- requires both acid and base titrations over a wide pH range which,
- introduces uncertainty in pH calibration,
- introduces titration errors due to precipitation at high pH, and,
- may introduce errors due to sparging of the sample.

In the following chapters a titration method will be presented for determining the SCFA and carbonate systems that overcomes the shortcomings in the Powell and Archer approach. Its development is based on the theoretical behaviour of mixtures of weak acid/bases; its application requires the availability of programmable calculators or personal computers. It has the following features: It,

- takes account of the phosphate, sulfide, ammonium and water subsystems,

- uses only strong acid in titration for quantification of C_T, SCFA and H_2CO_3*alkalinity,

- has a narrow titration range to minimize pH calibration errors,

- minimizes influence of systematic pH measurement errors by correct choice of pH titration points,

- allows a measure of flexibility in selecting the pH endpoints, and,

- dispenses with sparging of the sample.

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CHAPTER 3

A 4 PH POINT TITRATION METHOD TO QUANTIFY THE CARBONATE SUBSYSTEM IN AN AQUEOUS CARBONATE SOLUTION

ABSTRACT

Theory and method of a 4 pH point acid titration is presented, to measure the H_2CO_3*alkalinity and/or the total carbonate species, C_T, in aqueous solutions containing only the carbonate weak acid/base. The influence of systematic pH measurement errors due to faulty calibration, residual liquid junction effect, temperature effects, salt errors etc. on the calculation of C_T and H_2CO_3*alkalinity is examined theoretically and experimentally and methods presented to minimize the influence of the systematic pH error, together with a procedure to approximately quantify the systematic pH error. The influence of CO_2 loss during titration on C_T and H_2CO_3*alkalinity estimates is shown to be negligible if the sample C_T is kept below 500 mg/ℓ as $CaCO_3$ and the titration completed within 10 min. Comparative tests using the 4 pH point titration and First Gran Function methods, on aqueous $NaHCO_3$ solutions ranging from 10 to 50 mg/ℓ as $CaCO_3$, to determine the H_2CO_3*alkalinity and C_T, correlated very closely (r = 0,99). For aqueous $NaHCO_3$ solutions ranging from 100 to 500 mg/ℓ as $CaCO_3$, the 4 pH point titration method has high accuracy, with an inprecision having a standard deviation of < 2 percent.

3.1 INTRODUCTION

In this chapter, a 4 pH point titration method will be developed to determine the total carbonate species concentration, C_T, (and hence the H_2CO_3*alkalinity) in aqueous solutions containing only the carbonate weak acid/base. In the next chapter, a 4 pH point titration method will be extended to allow the determination of C_T in an aqueous solution of unknown carbonate and *known* concentrations of the ammonium and phosphate weak acid/bases. In Chapter 5, the 4 pH point titration is further extended to a 5 pH point titration method that allows the determination of C_T *and* the total short chain fatty acids concentration, SCFA, in an aqueous solution containing the carbonate, SCFA and known concentrations of the ammonium and phosphate weak acid/bases.

A feature of these proposed methods is that an estimate is provided of the pH measurement error due to poor pH calibration, and/or residual liquid junction and salt effects. This estimate is then included in the calculation of C_T, SCFA and H_2CO_3*alkalinity leading to improved accuracy in the determination of these parameters.

One may ask why another method for determination of the carbonate system parameters should be deemed desirable particularly when the Gran method for the aqueous solution containing the carbonate system only (Gran, 1952), and the Modified Gran method for aqueous solutions containing unknown concentrations of carbonate and known concentrations of other weak acid/bases (Loewenthal *et al.*, 1989), are available. This can be answered as follows:

> The Gran method for aqueous solutions containing only the carbonate subsystem allows an accurate estimate of the H_2CO_3*alkalinity without having to titrate to the $H_2CO_3^*$ equivalence point. Determination of the initial pH point of the sample, however, may be affected by a systematic pH measurement error (see below) and this would cause an error in the calculation of C_T; in normal practice this should not be considered a serious deficiency. The modified Gran method similarly is an effective method for determining the H_2CO_3*alkalinity but requires independent accurate determination of the SCFA, ammonium, phosphates and sulfides total species concentrations to derive an accurate value for the H_2CO_3*alkalinity; furthermore should there be a systematic error in the measurement of the initial pH, this will introduce an error in the estimate of C_T. Also, for routine monitoring the Gran methods are too tedious and time consuming.

It was to overcome the problems with the Gran Function method identified above, that new methods were developed. The proposed methods focus on the determination of C_T as the primary parameter, from which the H_2CO_3*alkalinity and other alkalinities can be derived subsequently. As with the Gran methods, titration to the H_2CO_3*equivalence point is not required. Instead, the sample is titrated from its initial pH to 3 or 4 further pH points, selected such that (1) the error in C_T due to systematic errors in pH measurement is largely eliminated, and, (2) the systematic pH measurement error can be estimated. Furthermore, importantly, in aqueous solutions of the carbonate and SCFA subsystems the 5 pH point titration method allows C_T *and* the SCFA total species concentration to be estimated from the titration data; this is not possible with the Gran method. Finally, by having only 3 or 4 pH points to titrate to from the initial pH, the method is less tedious than the Gran method. The main disadvantage of the method is that it requires the aid of a personal computer or programmable calculator; however, these are becoming widely available.

3.2 THEORY

The basic equations defining the carbonate subsystem in aqueous solution are as follows (Loewenthal *et al.*, 1989):

$$\frac{[HCO_3^-]\ (H^+)}{[H_2CO_3]} = K_1/f_m = K_1' \tag{3.1}$$

$$\frac{[CO_3^{2-}]\ (H^+)}{[HCO_3^-]} = K_2\, f_m/f_d = K_2' \tag{3.2}$$

$$(H^+)\,[OH^-] = K_w/f_m = K_w' \tag{3.3}$$

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \tag{3.4}$$

where:

(H^+), $[H^+]$ = hydrogen ion activity (measured via pH) and hydrogen ion concentration respectively (mol/ℓ),

K_1, K_1' = first thermodynamic and apparent dissociation constants respectively for the carbonate subsystem (mol/ℓ),

K_2, K_2' = second thermodynamic and apparent dissociation constants respectively for the carbonate subsystem (mol/ℓ),

K_w, K_w' = thermodynamic and apparent ionic product constants $(mol/\ell)^2$, respectively for water subsystem

f_m, f_d = mono- and di- valent activity coefficients (see Appendix A)

$[H_2CO_3^*]$ = sum of molecularly dissolved carbon dioxide $[CO_2]_{aq}$, and carbonic acid, $[H_2CO_3]$, (mol/ℓ), these two having a virtually fixed ratio with regard to each other thereby allowing expression in terms of the composite $H_2CO_3^*$ (Loewenthal *et al.*, 1976).

[ ], ( ) = molar mass and active mass (activity) respectively, (mol/ℓ).

The above four equations contain 6 unknowns; hence two unknowns need to be measured. Of these, pH [to give (H^+)], and C_T are the only feasible ones to measure, but, measurement of C_T presented practical difficulties. Accordingly, additional parameters that have the potential for measurement, have been defined to replace C_T, i.e. $H_2CO_3^*$, HCO_3^-, and CO_3^{2-} alkalinities, where:

$$H_2CO_3^*\text{alkalinity} = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+] \tag{3.5}$$

$$HCO_3^-\text{ alkalinity} = -\,[H_2CO_3] + [CO_3^{2-}] + [OH^-] - [H^+] \tag{3.6}$$

$$CO_3^{2-}\text{ alkalinity} = -\,2\,[H_2CO_3] - [HCO_3^-] + [OH^-] - [H^+] \tag{3.7}$$

Knowing any one of these alkalinities and the pH of the sample, C_T, *inter alia*, can be calculated and the carbonate subsystem in aqueous solution is completely defined.

The alkalinity parameter most commonly measured is the $H_2CO_3^*$alkalinity. To measure it the sample is titrated to the $H_2CO_3^*$equivalence point. This pH endpoint, however, changes with the concentration of C_T and therefore is not known *ab initio*. Hence, a titration to a preselected pH end point using a colour indicator or potentiometric titration, invariably introduces a measure of uncertainty as to the accuracy of the $H_2CO_3^*$alkalinity. This approach usually has a relatively minor effect on the $H_2CO_3^*$alkalinity, except if the $H_2CO_3^*$alkalinity is low, because the endpoint selected (from experience) is in a region of low buffer capacity. If a *systematic* error in pH measurement is present (faulty pH calibration, residual liquid junction effect, salt error), the approach may give rise to a substantial error in calculating C_T from the measured $H_2CO_3^*$alkalinity, because the calculation requires the initial sample pH, which may be in a region of high buffer index.

An alternative method to obtain C_T directly via a pH titration in an aqueous solution containing the carbonate subsystem only, will now be presented. This method does not rely on the H_2CO_3*alkalinity endpoint titration.

Relationship between carbonate system parameters

System and subsystem parameters:

An aqueous solution containing the carbonate subsystem can be subdivided into two subsystems,the carbonate subsystem and the water subsystem Loewenthal *et al.* (1991):

$$H_2CO_3^*alk = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+] \qquad (3.8)$$

$$= Alk\ H_2CO_3^* + Alk\ H_2O \qquad (3.9)$$

where

$$H_2CO_3^*alk = H_2CO_3^*alkalinity$$

$$Alk\ H_2CO_3^* = [HCO_3^-] + 2\,[CO_3^{2-}] \qquad (3.10)$$

$$Alk\ H_2O = [OH^-] - [H^+] \qquad (3.11)$$

The species $[HCO_3^-]$ and $[CO_3^{2-}]$ and hence Alk $H_2CO_3^*$ can be expressed as functions of C_T and pH and Alk H_2O as a function of pH, as follows:

HCO_3^- as function of C_T and pH:

Rearranging Eq (3.4),

$$C_T = [HCO_3^-]\left[\frac{[H_2CO_3]}{[HCO_3^-]} + 1 + \frac{[CO_3^{2-}]}{[HCO_3^-]}\right] \qquad 3.12)$$

Inserting Eq (3.1 and 3.2) in Eq (3.12),

$$C_T = [HCO_3^-]\left[\frac{(H^+)}{K_1'} + 1 + \frac{K_2'}{(H^+)}\right] \qquad (3.13)$$

Letting

$$A = \left[\frac{(H^+)}{K_1'} + 1 + \frac{K_2'}{(H^+)}\right] \qquad (3.13a)$$

and rearranging Eq (3.13), then

$$[HCO_3^-] = \frac{Ct}{A} \qquad (3.14)$$

CO_3^{2-} as a function of C_T and pH:
Rearranging Eq (3.4),

$$C_T = [CO_3^{2-}]\left[\frac{[H_2CO_3]}{[HCO_3^-]}\frac{[HCO_3^-]}{[CO_3^{2-}]} + \frac{[HCO_3^-]}{[CO_3^{2-}]} + 1\right] \qquad (3.15)$$

Inserting Eq (3.1 and 3.2) in Eq (3.15),

$$C_T = [CO_3^{2-}]\left[\frac{(H^+)^2}{K_1' K_2'} + \frac{(H^+)}{K_2'} + 1\right] \qquad (3.16)$$

Letting,

$$B = \left[\frac{(H^+)^2}{K_1' K_2'} + \frac{(H^+)}{K_2'} + 1\right] \qquad (3.16a)$$

and solving for $[CO_3^{2-}]$ in Eq (3.16) and inserting B from Eq (3.16a),

$$[CO_3^{2-}] = \frac{C_T}{B} \qquad (3.17)$$

Alk H_2CO_3* as a function of C_T and pH:
Equations (3.14 and 3.17) link the HCO_3^- and CO_3^{2-} species respectively to C_T and pH (through A and B respectively). Hence, Alk H_2CO_3* at any pH point can be written as a function of C_T and pH:

From Eq (3.10),

$$\text{Alk } H_2CO_3^* = \frac{C_T}{A} + 2\frac{C_T}{B} \qquad (3.18)$$

Alk H_2O as a function of pH:

From Eq (3.11), the alkalinity contribution of the water subsystem (Alk H_2O) is expressed in terms of pH as follows:

$$\text{Alk } H_2O = [OH^-] - [H^+] \tag{3.19}$$

Considering $[H^+]$,

$$[H^+] = (H^+)/f_m \tag{3.20}$$

$$pH = -\log (H^+) \tag{3.21}$$

$$\text{i.e.} \quad (H^+) = 10^{-pH} \tag{3.22}$$

Hence,

$$[H^+] = 10^{-pH}/f_m \tag{3.23}$$

Considering $[OH^-]$,

$$(H^+)(OH^-) = K_w \tag{3.24}$$

Replacing (OH^-) with $[OH^-]$,

$$(H^+)[OH^-] = K_w/f_m = K_w' \tag{3.25}$$

$$[OH^-] = \frac{K_w'}{(H^+)} = 10^{pH-pK_w'} \tag{3.26}$$

From Eqs (3.23 and 3.26), inserting for $[H^+]$ and $[OH^-]$ in Eq (3.19),

$$\text{Alk } H_2O = 10^{pH-pK_w'} - \frac{10^{-pH}}{f_m} \tag{3.27}$$

H_2CO_3*alk in terms of C_T and pH:

Inserting in Eq (3.9) for Alk H_2CO_3* and Alk H_2O from Eqs (3.18 and 3.27),

$$H_2CO_3^*alk = \frac{C_T}{A} + 2\,\frac{C_T}{B} + 10^{pH-pK'_w} - \frac{10^{-pH}}{f_m} \tag{3.28}$$

Determination of C_T in a sample by titration between two pH points

Equation (3.28) expresses H_2CO_3*alk in terms of C_T and pH. However, the problem of measuring either C_T or H_2CO_3*alk remains. It will now be shown that, provided the titration results between any two pH points have been obtained, C_T can be determined. Then, knowing the initial pH of the sample, the state of the carbonate system in solution (i.e. carbonate + water subsystems) can be completely defined.

Assume the sample is titrated between two pH points. The amount of titrant required to titrate from the first pH point (pH_1) to the second pH point (pH_2) equals the area under the buffer index curves for the carbonate and water subsystems between these two points [see Fig 2.1(a,f)]; this total area represents the *change* in H_2CO_3*alkalinity. From this *change* in H_2CO_3*alkalinity and the two pH points, C_T is calculated as follows:

The H_2CO_3*alkalinities before and after the titration are $H_2CO_3^*alk_1$ and $H_2CO_3^*alk_2$ respectively. The change in H_2CO_3*alkalinity ($\Delta H_2CO_3^*alk_{1,2}$) due to addition of the specific amount of titrant is therefore:

$$\Delta\, H_2CO_3^*alk_{1,2} = H_2CO_3^*alk_1 - H_2CO_3^*alk_2 \tag{3.29}$$

$$= \Delta\, Alk_{1,2}H_2CO_3^* + \Delta\, Alk_{1,2}H_2O \tag{3.30}$$

where

$$\Delta\, Alk_{1,2}H_2CO_3^* = Alk_1H_2CO_3^* - Alk_2H_2CO_3^* \tag{3.31}$$

$$\Delta\, Alk_{1,2}H_2O = Alk_1H_2O - Alk_2H_2O \tag{3.32}$$

If Ca is the normality of the strong acid and V_x the volume of strong acid added, the mass of acid added to the sample is:

$$\text{mass of acid added} = Ca\ V_x \tag{3.33}$$

$$Ca\ V_x = \Delta\ MH_2CO_3{}^*alk_{1,2} \tag{3.34}$$

$$= \Delta\ MAlk_{1,2}H_2CO_3{}^* + \Delta\ MAlk_{1,2}H_2O \tag{3.35}$$

Now the two terms in the RHS of Eq (3.35) need to be determined:

(1) $\Delta MAlk_{1,2}H_2CO_{3*}$. The mass change (mol) in H_2CO_3*alkalinity on acid titration due to the *carbonate* subsystem can be written as:

$$\Delta\ MAlk_{1,2}H_2CO_3{}^* = V_s\ Alk_1H_2CO_3{}^* - (V_s+V_x)\ Alk_2H_2CO_3{}^* \tag{3.36}$$

where V_s is the sample size and
V_x is the volume of strong acid added to the sample

From Eq (3.18), $Alk_1H_2CO_3{}^*$ and $Alk_2H_2CO_3{}^*$ can be expressed in terms of $C_{T1,\,2}$ (C_T of sample), pH_1 and pH_2, and inserting in Eq (3.36):

$$\Delta\ MAlk_{1,2}H_2CO_3{}^* = V_s\ C_{T1,\,2}\,(\frac{1}{A_1} + 2\frac{1}{B_1})$$

$$- (V_s+V_x)\ \frac{V_s\ C_{T1,2}}{(V_s+V_x)}\ (\frac{1}{A_2} + 2\frac{1}{B_2})$$

$$= V_s\ C_{T1,\,2}\left[(\frac{1}{A_1} + 2\frac{1}{B_1}) - (\frac{1}{A_2} + 2\frac{1}{B_2})\right] \tag{3.37}$$

where subscripts 1 and 2 refer to first and second pH.

Letting

$$X_{1,2} = (\frac{1}{A_1} + 2\frac{1}{B_1} - \frac{1}{A_2} - 2\frac{1}{B_2}) \tag{3.38}$$

then Eq (3.37) becomes

$$\Delta MAlk_{1,2}H_2CO_3^* \quad = V_s\, C_{T1,\,2}\, X_{1,2} \tag{3.39}$$

Note: $C_{T1,\,2}$ is the total carbonate species concentration of the sample prior to the titration, i.e. C_T of sample.

(2) Δ*MAlk* H_2O: The mass change of H_2CO_3*alkalinity due to the *water* subsystem can be written as:

$$\Delta MAlk_{1,2}H_2O \;= V_s\, Alk_1H_2O - (V_s + V_x)\, Alk_2H_2O \tag{3.40}$$

From Eq (3.27),

$$\begin{aligned}\Delta MAlk_{1,2}H_2O \;&= V_s\,(10^{pH_1-pK'_w} - 10^{-pH_1}/f_m)\\ &\quad - (V_s+V_x)\,(10^{pH_2-pK'_w} - 10^{-pH_2}/f_m)\end{aligned} \tag{3.41}$$

In Eq (3.35), we may now substitute for $\Delta MAlk_{1,2}H_2CO_3^*$ and $\Delta MAlk_{1,2}H_2O$ from Eqs (3.39 and 3.41) respectively. This is done as follows; make the substitution for $\Delta MAlk_{1,2}H_2CO_3^*$ and solve for $C_{T1,\,2}$ (C_T of sample),

$$C_{T1,\,2} \quad = (Ca\, V_x - \Delta MAlk_{1,2}H_2O)/\,(V_s\, X_{1,2}) \tag{3.42}$$

In Eq (3.42), the terms $\Delta MAlk_{1,2}\ H_2O$ and $X_{1,2}$ both can be calculated from Eqs (3.41 and 3.38) knowing only pH_1 and pH_2; V_s is the sample volume, the term ($Ca\ V_x$) is the mass of titrant added to change the pH from pH_1 to pH_2 and both these terms are measured. Hence, $C_{T1,\,2}$ can be calculated. Knowing C_T and the initial pH of the sample the carbonate system is completely defined.

Errors in C_T determination

The method developed above for the determination of C_T involves acid titration between two pH points. There are two potential sources of errors when carrying out such a titration between two pH points:

- Systematic pH measurement errors resulting from poor calibration of the pH probe and residual liquid junction effect (caused by the difference in ionic strength and constitution between the calibration solution and that of the sample when using a glass electrode) and other effects, Linder *et al.* (1984).

- Exchange of CO_2 during titration between the liquid–gas interface at the sample surface: Such exchange of CO_2 would cause a change in C_T as the titration proceeds. From Eq (3.39), calculation of C_T is based on the assumption that the mass of C_T in the sample remains constant at these two pH points, consequently, the titration has to be carried out in a way that minimizes exchange of CO_2.

Effect of systematic pH errors on C_T

From Eq (3.42), a systematic error in pH will cause an error in calculation of the terms $\Delta MAlk_{1,2}H_2O$ and $X_{1,2}$. With regard to the error induced in $\Delta MAlk_{1,2}H_2O$, assuming that titrations are only carried out from approximately pH 7 to approximately pH 4, systematic pH measurement errors will have a negligible effect because the buffering capacity of the water subsystem is very small around these two pH points. With regard to the error induced in $X_{1,2}$, it should be noted that an error in $X_{1,2}$ induces an error in $\Delta MAlk_{1,2}H_2CO_3^*$ (Eq 3.39) which in turn gives rise to an error in calculation of $C_{T1,2}$ (Eq 3.42). Accordingly, the effect of a systematic pH error on the calculation of $\Delta MAlk_{1,2}H_2CO_3^*$ needs further investigation.

From Eq (3.37),

$$\begin{aligned}\Delta MAlk_{1,2}H_2CO_3^* &= V_s\, C_{T1,2}\left[\left(\frac{1}{A_1} + 2\frac{1}{B_1}\right) - \left(\frac{1}{A_2} + 2\frac{1}{B_2}\right)\right] \\ &= MAlk_1H_2CO_3^* - MAlk_2H_2CO_3^* \qquad (3.43)\end{aligned}$$

From Eq (3.43), it follows that an error in $\Delta MAlk_{1,2}H_2CO_3^*$ arises from an error in calculation of either $MAlk_1H_2CO_3^*$ or $MAlk_2H_2CO_3^*$, or both of these terms. Hence, it is necessary to elucidate the effect of pH error on the calculation of MAlk $H_2CO_3^*$ over the pH titration range of the sample. Assuming that V_s and C_T are ***both unity***, at any pH point MAlk $H_2CO_3^*$ can be written as,

$$MAlk\ H_2CO_3^* = \frac{1}{A} + 2\frac{1}{B} \qquad (3.44)$$

A deviation of the observed pH from its true value can be written as,

$$\Delta pH = pH_{true} - pH_{obs} \qquad (3.45)$$

$$pH_{true} = pH_{obs} + \Delta pH \qquad (3.46)$$

For the purpose of demonstrating the effect of ΔpH on MAlk H_2CO^* we assume that ΔpH is known. Hence, MAlk $H_2CO_3^*$ can be calculated from Eq (3.44) for two cases:

- using pH_{obs} giving MAlk $H_2CO_3^*(pH_{obs})$ and,
- using pH_{true} giving MAlk $H_2CO_3^*(pH_{true})$.

Subtracting these two alkalinities,

$$\Delta \text{MAlk } H_2CO_3^*(\Delta pH) = \text{MAlk } H_2CO_3^*(pH_{obs}) - \text{MAlk } H_2CO_3^*(pH_{true}) \quad (3.47)$$

In Fig 3.1, ΔMAlk $H_2CO_3^*(\Delta pH)$ is shown plotted for C_T and V_s equal to unity and $\Delta pH = -0{,}04$. The plot illustrates the following points:

- The magnitude of ΔMAlk $H_2CO_3^*(\Delta pH)$ is dependent on ΔpH.
- The bell shaped curve has a maximum at $pH = pK_{ac1}(6{,}3)$.
- ΔMAlk $H_2CO_3^*(\Delta pH)$ decreases sharply on either side of pK_{ac1}.
- If $\Delta pH = 0$, then ΔMAlk $H_2CO_3^*(\Delta pH) = 0$, and MAlk $H_2CO_3^*$ is at its true value.

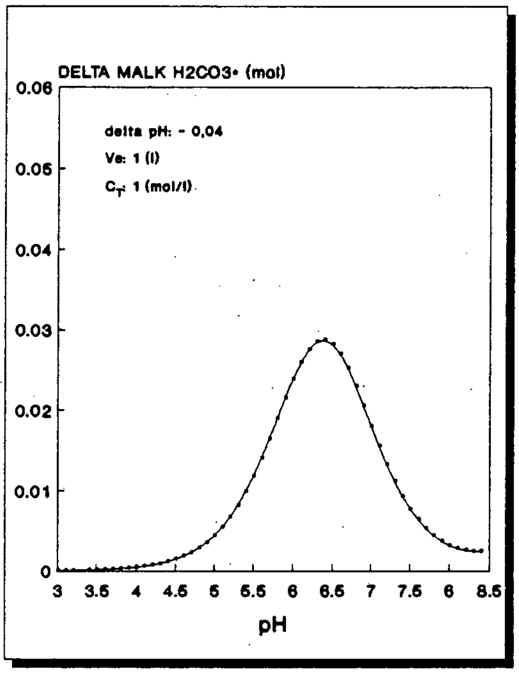

Fig 3.1: Theoretical error in MAlk $H_2CO_3^*$ (mass of Alk $H_2CO_3^*$ of sample) at any pH over the pH range 3,0 to 8,5 due to a systematic pH measurement error (ΔpH), ΔMAlk $H_2CO_3^*(\Delta pH)$, calculated for a specific $\Delta pH = -0{,}04$ with C_T and V_s equal to unity.

When titrating a sample between pH_1 and pH_2, if the measured pH differs from the true pH, the error, ΔpH, at these two pH points respectively are not known. Hence only $MAlk_1H_2CO_3{}^*(pH_{1obs})$ and $MAlk_2H_2CO_3{}^*(pH_{2obs})$ can be calculated. Both these terms deviate from their respective true values as follows:

$$MAlk_1H_2CO_3{}^*(pH_{1true}) = MAlk_1H_2CO_3{}^*(pH_{1obs}) - \Delta MAlk_1H_2CO_3{}^*(\Delta pH) \quad (3.48)$$

$$MAlk_2H_2CO_3{}^*(pH_{2true}) = MAlk_2H_2CO_3{}^*(pH_{2obs}) - \Delta MAlk_2H_2CO_3{}^*(\Delta pH) \quad (3.49)$$

In Eqs (3.48 and 3.49) neither $\Delta MAlk_1H_2CO_3{}^*(\Delta pH)$ nor $\Delta MAlk_2H_2CO_3{}^*(\Delta pH)$ can be calculated. Hence, to minimize the influence of ΔpH, the titration points have to be chosen such that the effect of ΔpH on the calculation of $\Delta MAlk_{1,2}H_2CO_3{}^*$ is canceled out: From Eq (3.43) it can be seen that $MAlk_2H_2CO_3{}^*$ is subtracted from $MAlk_1H_2CO_3{}^*$ to calculate $\Delta MAlk_{1,2}H_2CO_3{}^*$ from which $C_{T1,\,2}$ is finally obtained. Subtracting Eq (3.48 and 3.49),

$$\begin{aligned}\Delta MAlk_{1,2}H_2CO_3{}^* &= MAlk_1H_2CO_3{}^*(pH_{1true}) - MAlk_2H_2CO_3{}^*(pH_{2true}) \\ &= MAlk_1H_2CO_3{}^*(pH_{1obs}) - MAlk_2H_2CO_3{}^*(pH_{2obs}) - \\ &\quad \Delta MAlk_1H_2CO_3{}^*(\Delta pH) + \Delta MAlk_2H_2CO_3{}^*(\Delta pH) \qquad (3.50)\end{aligned}$$

From Fig 3.1, if pH_1 and pH_2 are chosen symmetrical around pK_{ac1} their respective $\Delta MAlk\ H_2CO_3{}^*(\Delta pH)$ values are equal, and, if inserted in Eq (3.50), cancel out. In that event the correct $\Delta MAlk_{1,2}H_2CO_3{}^*$, and consequently also the correct $C_{T1,\,2}$, can be obtained.

Estimate of systematic pH error

It was shown above that with appropriate choice of the titration points pH_1 and pH_2, errors in calculation of $C_{T1,\,2}$ can be minimized. However, to estimate the $H_2CO_3{}^*$ alkalinity from C_T [via Eq (3.28)] requires the initial pH of the sample; but the initial pH measurement will contain a systematic pH error, ΔpH, in the same way as pH_1 and pH_2 so that an error is introduced in estimating the $H_2CO_3{}^*$alkalinity even if C_T is error free. It is necessary therefore to form an estimate of ΔpH. Then the initial pH can be corrected for ΔpH and $H_2CO_3{}^*$alkalinity calculated more accurately.

To establish a procedure to estimate ΔpH, consider a titration from an initial pH point, say pH_1 = 8,3 to pH_2 = 6,0 and pH_3 = 4,8. From Eqs (3.44 and 3.47) the error in MAlk $H_2CO_3^*$ at *any* pH due to ΔpH, [ΔMAlk $H_2CO_3^*$(ΔpH) for ΔpH = – 0,04, V_s = 1, C_T = 1] has been calculated and is plotted in Fig 3.1. The plot demonstrates the theoretical effect of a systematic pH measurement error, ΔpH (= –0,04 for this example), on the calculation of MAlk $H_2CO_3^*$ at any pH. Evidently the error in ΔMAlk $H_2CO_3^*$(ΔpH) is greater at pH 6,0 than at 4,8. We now consider the pH pairs (8,3; 6,0) and (8,3; 4,8); for each one we calculate $\Delta MAlk_{1,2}H_2CO_3^*$ using Eq (3.50) with $C_{T1,\,2}$ and V_s equal to unity and assuming that ΔpH = – 0,04. This allows the calculation of an error free $\Delta MAlk_{1,2}H_2CO_3^*$ for both pH pairs because ΔpH has been included in the calculation. However, the true value for ΔpH is as yet *unknown*; the pH is the observed one containing the unknown ΔpH. To determine ΔpH, we now examine its effect on the calculation of $\Delta MAlk_{1,2}H_2CO_3^*$ from Eq (3.50) using the pH pair (8,3; 4,8) with V_s and $C_{T1,\,2}$ unity:

> Since ΔpH is unknown the terms $\Delta MAlk_1H_2CO_3^*(\Delta pH)$ and $\Delta MAlk_2H_2CO_3^*(\Delta pH)$ cannot be calculated. However, from Fig 3.1 we notice that for this particular pH pair these two terms virtually cancel out; from this it follows that $\Delta MAlk_{1,2}H_2CO_3^*$ for pH pair (8,3; 4,8) is closely error free. From Eq (3.39) for V_s and $C_{T1,\,2}$ equal to unity, $\Delta MAlk_{1,2}H_2CO_3^*$ is equal to $X_{1,2}$. This example demonstrates that $X_{1,2}$ for any titration between pH pair (8,3; 4,8) can be obtained closely error free (despite the fact that ΔpH is unknown) and, hence, a closely error free $C_{T1,\,2}$, related to pH pair (8,3; 4,8), can be calculated via Eq (3.42).

Considering pH pair (8,3; 6,0), C_T can be obtained analogously to pH pair (8,3; 4,8). In this case, however, the terms $\Delta MAlk_1H_2CO_3^*(\Delta pH)$ and $\Delta MAlk_2H_2CO_3^*(\Delta pH)$ do *not* cancel out in Eq (3.50); this leads to an incorrect estimate of $X_{1,2}$ and, consequently, the C_T calculated via this pH pair, $C_{T1,\,3}$, will contain an error due to ΔpH. From this we see that to avoid errors in the calculation of C_T the pH pair must be chosen such that the terms $\Delta MAlk_1H_2CO_3^*(\Delta pH)$ and $\Delta MAlk_2H_2CO_3^*(\Delta pH)$ are closely equal and cancel out in Eq (3.50), or, ΔpH must be taken into account.

To form an estimate of ΔpH we make use of the fact that ΔpH produces different C_T values ($C_{T1,\,2}$; $C_{T1,\,3}$) for, say pH pair (8,3; 4,8) and pH pair (8,3; 6,0) respectively. It has been stated that $C_{T1,\,2}$ closely represents the true C_T value because the effect of ΔpH on its calculation cancels out. The true value for $C_{T1,\,3}$

will be found if the observed pH measurements of pH pair (8,3; 6,0) are adjusted to the true pH values. The true pH values can be identified by that adjusted pH where $C_{T1,2}$ equals $C_{T1,3}$, i.e. the difference between the observed pH and the adjusted (true) pH equals ΔpH.

Hence the following procedure is used to estimate ΔpH:

- Assume the sample has been titrated from its initial pH (pH_0) to three appropriately selected pH points pH_1, pH_2 and pH_3.

- For data pair (pH_1, pH_2) symmetrically located, and data pair (pH_1, pH_3) unsymmetrically located around pK_{ac1}, $C_{T1,2}$ and $C_{T1,3}$ respectively are calculated.

- $C_{T1,2}$ and $C_{T1,3}$ are compared and the measured pH_1, pH_2, pH_3 are then adjusted incrementally until $C_{T1,2}$ equals $C_{T1,3}$; when $C_{T1,2}$ equals $C_{T1,3}$, the adjusted pH values equal their respective true pH values and ΔpH is then obtained from Eq (3.45).

The above calculations for these parameters are done by means of a computer program with the experimental data as input parameter, see Appendix T.

Error due to CO_2 loss during titration

The algorithm for calculating C_T and the H_2CO_3*alkalinity, set out above, assumes that the mass of C_T in the sample remains constant during titration. This would imply that there is no exchange of CO_2 between the sample and atmosphere at the liquid/gas interface. Such a transfer at the liquid/gas interface depends primarily on the difference in partial pressure of CO_2 in the water and air, water temperature and mixing conditions.

Loss of CO_2 from the sample decreases C_T and from the basic theory on the carbonate system this can be shown to give rise to an increase in pH (Loewenthal and Marais, 1976). With a gain in CO_2 by the sample, the opposite occurs. Through Eq (3.42), C_T is linked to pH_1 and pH_2. If CO_2 is lost while titrating with a strong acid from pH_1 to pH_2, this will cause that pH_2 is attained with more titrant than if there was no CO_2 loss and will result in an error in calculation of $C_{T1,2}$ [the calculated C_T will show a higher value than the initial (true) value of the sample].

In the section below, amongst others, the experimental procedure to minimize loss of CO_2 is discussed.

3.3 EXPERIMENTAL INVESTIGATION

The experimental investigation can be divided into three sections:

- systematic pH measurement errors,
- CO_2 loss during titration, and,
- results from 4 pH point titration method.

Systematic pH measurement errors

As stated earlier, when using a glass electrode systematic pH measurement errors can be present; these are discussed in greater detail below:

(1) Poor calibration of the pH probe

With regard to calibration, care should be taken that the buffer solutions are chosen such that the buffer pHs bracket the titration pH points required to determine C_T. Furthermore, the buffer solutions (usually of NBS standard) need to be stored as indicated by the manufacturer; CO_2 entrainment from the air into the buffer solution placed in the calibration vessel means that daily replacement of the buffer solution is required.

(2) Salt error

When measuring the pH with a glass electrode, a potential is set up by the response of the glass membrane to ions other than the H^+ ions. This potential may differ between the standard buffer solution and the sample, and may give rise to a pH measurement error if the ionic matrix of the buffer solution and the sample differ greatly. This potential cannot be readily measured, but fortunately, it has been estimated to be relatively small compared with the residual liquid junction potential, and usually is neglected (Plummer and Busenberg, 1982).

(3) Residual liquid junction effect

A liquid junction is a heteroionic boundary between two dissimilar solutions, across which ions migrate (Jones and Williams 1987). The liquid junction potential is set up because of the difference in the mobilities of the positive and negative ions in the solutions and the physical nature of the junction path. This causes a net positive charge to be established in one solution and a negative in the other, resulting in an electrical potential between the two solutions. When calibrating a particular pH probe, standard buffers (say NBS buffers) are used and the pH is set to the correct values. When the probe is inserted in a liquid with a different ionic matrix to that of the buffer, the liquid junction potential across the junction will differ, affecting the pH reading. This difference in potential between the standard buffer and test solution is termed the residual liquid junction potential, RLJP, and is one possible cause for pH measurements containing a systematic error.

Four different classes of liquid junction systems are used in various pH probes: (1) continuous mixture junction, (2) constrained diffusion junction, (3) free diffusion junction, and, (4) flowing junctions. Most electrodes available for analytical use are of the "constrained diffusion junction" type and this was the type used in this investigation: It consists of a ceramic (porous) plug between the saturated KCl solution of the probe and the test solution; a small flow of KCl leaks through this plug from the probe into the test solution.

Theoretically no definite evaluation of the liquid junction potential has been developed. Henderson (1961) put forward a theoretical model, but this is only valid at low ionic strength for certain ionic constitutions, and hence is of restricted value (Cavalcanti, 1981). Loewenthal and Marais (1983) proposed a semi-empirical method which has been verified to give reasonable estimates of the residual liquid junction effect for ionic strengths up to that of seawater (μ = 0,7). However, this method requires accurate evaluation of the ionic constitution of the solution; for general use the method is too complex.

From the theory developed earlier in this chapter, it would appear that by titrating an aqueous solution containing only the carbonate subsystem to selected pH points, one may form an estimate of a systematic pH measurement error. Three sets of experiments were set up, to (1) verify the existence of a systematic pH error, (2) quantify the systematic pH error and show that it may be due to the RLJP, and, (3) test different methods to minimize the effect of the systematic pH error.

Effect of a systematic pH error on calculation of C_T

To assess the effect of a systematic pH measurement error on the calculation of C_T and H_2CO_3*alkalinity, a set of aqueous solutions with increasing concentrations of $NaHCO_3$ (250, 500, 750 and 1000 mg/ℓ as $CaCO_3$) were made up. For each solution the H_2CO_3*alkalinity and C_T were determined using the following titration procedure: Titration from the initial pH (approximately 8,3) to a second (lower) pH, i.e. from 8,3 to 6,0; 5,8; 5,6; 5,4; 5,2; 5,0 and 4,8. Each test was repeated five times. The pH probe (glass electrode supplied by Radiometer, Copenhagen) was calibrated against a Radiometer NBS buffer (0,05 M potassium hydrogen phthalate for pH 4,00 at 25°C; 0,0275 M Disodium hydrogen phosphate and 0,025 M potassium dihydrogen phosphate for pH 7,00 at 25°C). The apparatus for this experiment is described in Appendix B.

For each $NaHCO_3$ concentration from the five replica titrations five sets of C_T and H_2CO_3*alkalinity values were determined from the initial and second (lower) pH values (pH_1, pH_2 respectively), using Eqs (3.42 and 3.28). The individual results and the averages of each set are given in Appendix C .The results, when plotted against pH, all showed a similar trend, the C_T and H_2CO_3*alkalinity plots for each $NaHCO_3$ concentration being virtually identical. Hence, only the results for C_T of the $NaHCO_3$ solution of 1000 mg/ℓ as $CaCO_3$, μ = 0,02 mol/ℓ are shown in Fig 3.2. The plot shows that as the second (lower) pH value of the titration decreases from 6,0 to 4,8 so the value of C_T also decreases, indicating that the estimates show a systematic error, probably due to a systematic error in pH.

To verify the hypothesis that the observed decrease in C_T and H_2CO_3*alkalinity values is a result of a systematic pH measurement error, C_T and H_2CO_3*alkalinity were recalculated from the titration data obtained on the $NaHCO_3$ solutions described above, applying a correction factor, ΔpH, to pH_1 and pH_2. ΔpH was established by trial and error; starting with Δ pH = – 0,01 an new set of values for C_T and H_2CO_3*alkalinity was calculated; ΔpH was increased incrementally, eventually to – 0,07; with this correction all the C_T and H_2CO_3*alkalinity values approximated their expected values, irrespective of pH_2. Fig 3.3 shows the effect of the pH correction of ΔpH = – 0,07 on C_T for the $NaHCO_3$ solutions (1000 mg/ℓ as $CaCO_3$). The data for this experiment are listed in Appendix C .

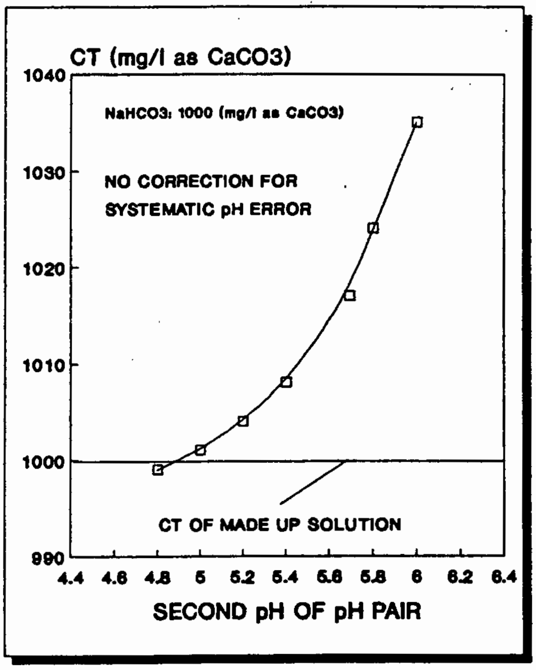

Fig 3.2: Error in determining C_T in aqueous solutions containing only the carbonate subsystem using pH pairs located symmetrically and unsymmetrically around pK_{ac1} of the carbonate subsystem *without* correcting for systematic pH measurement error, ΔpH. The first pH of all pH pairs is 8,3.

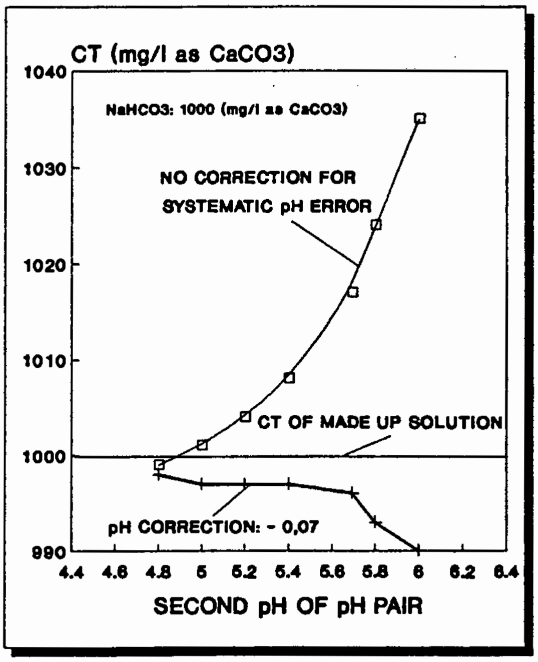

Fig 3.3: Error in determining C_T in aqueous solutions containing only the carbonate subsystem (made up $NaHCO_3$ solutions) using pH pairs located symmetrically and unsymmetrically around pK_{ac1} of the carbonate subsystem using two approaches (1) *without* correcting for systematic pH measurement error, ΔpH, and, (2) correcting for an estimated systematic pH measurement error of ΔpH = -0,07. The first pH of all pH pairs is 8,3.

The conclusions that can be drawn from this experiment are:

- A systematic pH measurement error appears to be present in the titration between the initial pH and the selected set of second (lower) pH points causing corresponding errors in the calculation of C_T and the H_2CO_3*alkalinity.
- The choice of the second (lower) pH point has a significant influence on the magnitude of the error induced in C_T and H_2CO_3*alkalinity, i.e. in the pH range of 6,0 to 4,8 this error decreases consistently as the second (lower) pH approaches pH 4,8.
- The observed differences in the values of C_T and H_2CO_3*alkalinity (when titrating to different second pH points) can be largely eliminated by correcting the initial and second pH using a pH correction factor. In this experiment this pH correction factor was estimated empirically to be about – 0,07.

At this stage it was speculated as to what might be the cause of this apparent systematic pH error. Since great care had been taken in the calibration of the pH probe using NBS buffer solutions and in frequently changing the buffer solution, a pH measurement error from faulty calibration was unlikely. This left the possibility of a systematic error caused by the RLJP, which was then investigated.

Systematic pH error at different levels of ionic strength in test solutions

If the error in pH was due to a RLJP then, since the RLJP arises from a difference in ionic concentration and composition between two solutions, such a difference must have been present between the pH standard buffer solution and the sample. The ionic strength of a solution can be calculated if the individual concentrations and charges of the ions making up the ionic matrix of the solution are known. If the ionic matrix is not known it is often approximated via measurement of total dissolved solids, TDS, or, specific conductivity (see Appendix A). The ionic strength of the NBS buffer solutions was about 0,10 mol/ℓ at pH = 7,0 and about 0,05 at pH = 4,0. In an experiment, if an aqueous solution of 1000 mg$NaHCO_3$/ℓ as $CaCO_3$ was made up, it would give an ionic strength of 0,02 mol/ℓ. If the solution then was tested for C_T and the H_2CO_3*alkalinity, using the above 2 pH point titration method (initial and lower pH points between 4,8 and 6,0), a systematic pH measurement error could be expected. Furthermore, if a series of solutions were used in the experiment with increasing concentrations of $NaHCO_3$, then the systematic pH error due to the RLJP should decrease as the ionic strength of the $NaHCO_3$ solution approaches that of the buffer solution, eventually to near zero when the ionic strength of the NBS buffer solution equals that of the $NaHCO_3$ plus background electrolyte solution. To test this hypothesis the following experiment was carried out:

> Five different stock solutions of different ionic strength were made up by adding to distilled water $NaHCO_3$, to give C_T and H_2CO_3*alkalinity of 1000 mg/ℓ as $CaCO_3$, and different masses of NaCl, i.e. 0,0; 4,0; 7,0; 10,5 and 14 gNaCl/ℓ, to give respective ionic strengths of the samples of 0,02, 0,09, 0,14, 0,20 and 0,26 mol/ℓ. Each solution was tested as follows: The sample was titrated from the initial pH ≃ 8,3 to pH ≃ 5,4 and thereafter to pH ≃ 4,8. From these titration data two values for C_T could be calculated [from Eq (3.42)] using pH pair (8,3; 4,8) for calculation of the first value, C_{T1}, and pH pair (8,3; 5,4) for calculation of the second value, C_{T2}. The C_{T1} value was accepted as the true C_T value since previously (above) it was shown that the effect of a systematic pH error would cancel out using pH pair 8,3 and 4,8 (because $\Delta MAlk_1H_2CO_3^*(\Delta pH)$ and $\Delta MAlk_2H_2CO_3^*(\Delta pH)$ are closely equal, see Fig 3.1). Depending on ΔpH, C_{T2} would differ from C_{T1} because $\Delta MAlk_1H_2CO_3^*(\Delta pH)$ and $\Delta MALK_2H_2CO_3^*(\Delta pH)$ would not cancel out in the calculation of C_{T2}. However, by adjusting the observed pH via ΔpH to the true pH, C_{T2} can be corrected to the true C_T. Hence, the second pH pair was adjusted incrementally, C_{T2} recalculated and compared to C_{T1}. At the point where the recalculated C_{T2} equaled C_{T1} the iteration was stopped since hypothetically the observed second pH pair had been adjusted to its true pH values. The difference between the observed pH value and the adjusted pH value can be taken as the systematic pH measurement error, ΔpH. The experimental data and results are for the different solutions are listed in Appendix D.

For each of the five different solutions an average ΔpH value was determined from the three repetitive tests. These values are plotted in Fig 3.4, relating the ionic strength of the various samples to ΔpH. Figure 3.4 shows an almost linear relationship between the ionic strength and ΔpH; furthermore ΔpH is zero at an ionic strength of about 0,15 mol/ℓ. The fact that ΔpH is influenced by the change in ionic strength of the sample (due to addition of NaCl) lends support to the hypothesis that *the systematic pH error observed in the 2 point titration is caused mainly by the RLJP*. From the data available from this experiment it cannot be established if the estimated ΔpH is exclusively caused by the RLJP and hence the results do not necessarily represent a quantitative analysis of the RLJP. The aim of this experiment was not to quantify the RLJP, but to find a possible explanation for the observed systematic pH error. To attempt a quantification of the RLJP with this method more sophisticated methods, incorporating ion pairing effects etc., to determine the activity coefficients (in order to determine the apparent equilibrium constants with greater accuracy) would be required, Loewenthal and Marais (1983). For practical purposes an accurate determination of the RLJP is not necessary; from a practical point of view, the value of an estimate of ΔpH is that it allows detection of systematic pH errors, and, hence may serve as an indicator of faulty pH measurements.

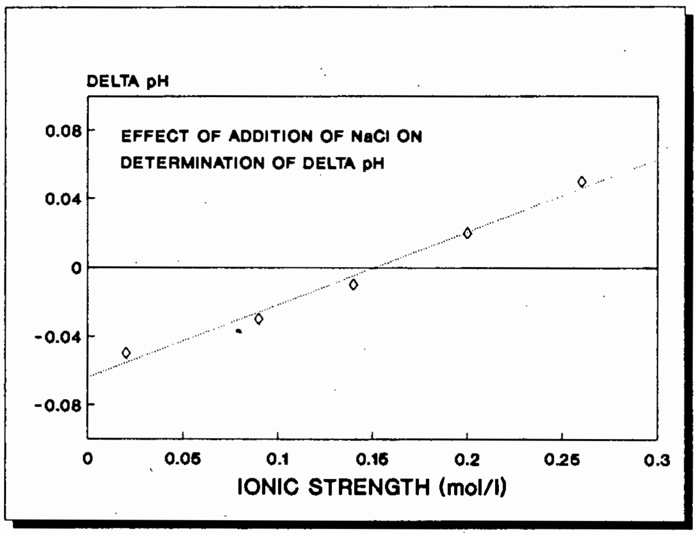

Fig 3.4: Estimation of systematic pH measurement error, ΔpH, at different levels of ionic strengths in aqueous $NaHCO_3$ solutions (1000 mg/ℓ as $CaCO_3$) also containing additions of 0, 4,0; 7,0; 10,5 and 14 g/ℓ of NaCl to give respective ionic strengths of the solutions of 0,02, 0,09, 0,14, 0,20 and 0,26 mol/ℓ; ΔpH was estimated using a symmetrical and an unsymmetrical pH pair located around pK_{ac1} of the carbonate subsystem.

Having identified a possible cause of the systematic pH measurement error, strategies were investigated to eliminate its influence on the calculation of C_T and H_2CO_3*alkalinity.

Elimination of the effect of ΔpH on the calculation of C_T

Three possible approaches can be suggested to eliminate the effect of a systematic pH error, ΔpH, on the calculation of C_T:

- application of an empirical pH correction factor,
- addition of background electrolyte to the sample to adjust the ionic strength to that of the pH buffer solution,
- choice of pH pairs to minimize or eliminate the *effect* of the systematic pH error on C_T.

The application of an empirical correction factor has been demonstrated earlier, Fig 3.3; provided the correct ΔpH is chosen the error induced in the calculation of C_T can be largely eliminated. However, because ΔpH would differ with the ionic strengths of the sample and buffer solution, and the condition of the pH probe, the choice of the appropriate ΔpH is difficult.

With regard to addition of background electrolyte to the sample to adjust the ionic strength to that of the pH buffer solution in order to eliminate the RLJP, and consequently ΔpH, the work reported above has shown that the addition of NaCl, to increase the ionic strength of the sample to about 0,15 mol/ℓ should eliminate the RLJP[1]. Hence, if an aqueous $NaHCO_3$ solution of, say, 1000 mg/ℓ as $CaCO_3$ containing 7800 mg/ℓ of NaCl as background electrolyte is titrated from its initial pH (≃ 8,3) to a series of second (lower) pH values in the pH range of 6,0 to 4,8, the calculation of C_T should be independent of the choice of the second (lower) pH value. To test this hypothesis, four $NaHCO_3$ solutions of the concentration 250, 500, 750 and 1000 mg/ℓ as $CaCO_3$ were made up and the ionic strength of each of these was increased to about 0,15 mol/ℓ by addition of NaCl. Titration of each solution was repeated five times as follows: The sample is titrated from its initial pH (≃ 8,3) to a set of lower (second) pH values of 6,0; 5,8; 5,6; 5,4; 5,2; 5,0 and 4,8. From this

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[1] It is evident that the ionic strength of the NaCl plus $NaHCO_3$ solution of 0,15 mol/ℓ, apparently required to eliminate the RLJP, is considerably higher than that of the pH buffer solutions (0,1 and 0,05 mol/ℓ). This may be due to the different nature of the electrolytes in the test solution (NaCl) and the electrolytes of the pH buffer solutions. Another reason may be the inaccurate determination of the apparent dissociation constants (pK_{ac1}, pK_{ac2}) of the carbonate weak acid/base when using the 3 pH point titrations to estimate ΔpH.

titration data, 7 pH pairs (pH_1,pH_2) are formed all using the initial pH as pH_1 and one of the lower pH values as pH_2. The C_T values calculated from these titration data are listed in Appendix D. For the purpose of illustration, the data obtained for C_T, with and without NaCl addition to the $NaHCO_3$ solution (1000 mg/ℓ as $CaCO_3$), are shown in Fig 3.5. Comparing the C_T values from the titrations with and without NaCl addition, with addition of NaCl all C_T values approach their expected (true) value irrespective of the choice of the second pH point. This finding lends further support to the hypothesis that the systematic error is due mainly to the RLJP. However, the method of adding background electrolyte to the sample is not of much practical value since the ionic strength of the sample and of the pH buffer solution, has to be known before this can be done.

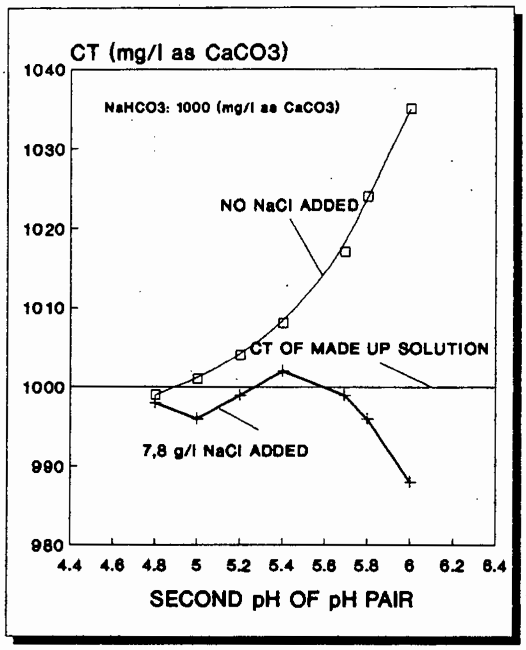

Fig 3.5: Determination of C_T in aqueous solutions containing only the carbonate subsystem (made up $NaHCO_3$ solution: 1000 mg/ℓ as $CaCO_3$) using pH pairs located symmetrically and unsymmetrically around pK_{ac1} of the carbonate subsystem, using two approaches (1) *without* adding NaCl to the sample, and (2) adding 7800 mg/ℓ of NaCl to the sample.

With regard to the choice of the pH pair (pH_1, pH_2), from examining Fig 3.1 it can be seen that for pH values located symmetrically around pK_{ac1} the value of the error in alkalinity, ΔMAlk $H_2CO_3^*(\Delta pH)$ is the same. Hence, by choosing a pH pair (pH_1, pH_2) symmetrical about pK_{ac1}, such that $\Delta MAlk_1 H_2CO_3^*(\Delta pH)$ and

$\Delta MAlk_2H_2CO_3^*(\Delta pH)$ are equal and these two terms cancel out in Eq (3.50); hence, theoretically the true $\Delta MAlk_{1,2}H_2CO_3^*$ can be calculated without knowing ΔpH. Thus a value for C_T can be obtained free from any error due to ΔpH.

The data pairs used in the plots shown in Figs 3.2, 3.3 and 3.5 were all unsymmetrically located with respect to pK_{ac1} except for pH pair (8,3; 4,8). This pH pair also gave the best estimate of C_T. It was now of interest to find out whether symmetrical pH pairs located closer around pK_{ac1}, such as (7,3; 5,4) and (6,7; 5,9), would yield C_T values as good as those of pH pair (8,3; 4,8).

$NaHCO_3$ solutions were made up to C_T concentrations of 50, 100, 150, 200, 250 and 500 mg/ℓ as $CaCO_3$, giving associated ionic strengths of 0,001, 0,002, 0,003, 0,004, 0,005 and 0,01 mol/ℓ respectively. These solutions were titrated from pH $\simeq$ 8,3 to a set of lower pH points 7,3; 6,7; 5,9; 5,4 and 4,8. From these titration data the following pH values were paired because they are approximately symmetrical around pK_{ac1}: (8,3; 4,8), (7,3; 5,4) and (6,7; 5,9). The individual results and averages for C_T and $H_2CO_3^*$alkalinity calculated from the three pH pairs (for the different solutions) are listed in Appendix E. In Fig 3.6 the average percentage errors of C_T [(C_T expected − C_T measured)/C_T expected * 100] for each solution are plotted for the pH pairs (8,3; 4,8), (7,3; 5,4) and (6,7; 5,9). The expected value for C_T is known from the make up of the solution. It appears that the optimal choice of a pH pair is (8,3; 4,8); except for the 50 and 100 mg$NaHCO_3$/ℓ as $CaCO_3$ solutions, the pH pair closest to the pK_{ac1} value (6,7; 5,9) produced less accurate results than the remaining pH pairs. The most likely cause for this is that random pH errors in the pH pair (6,7; 5,9) have greater relative effects on C_T than in, say, the pH pair (8,3; 4,8).

From this task it was concluded that (1) choosing the pH pairs symmetrical around pK_{ac1} reduces the error in the estimate of C_T due to a systematic error in pH, whatever the cause for such a pH error, and, (2) with the symmetrical pH pairs located closer to pK_{ac1}, random pH errors appear to give rise to increasingly large random errors in C_T.

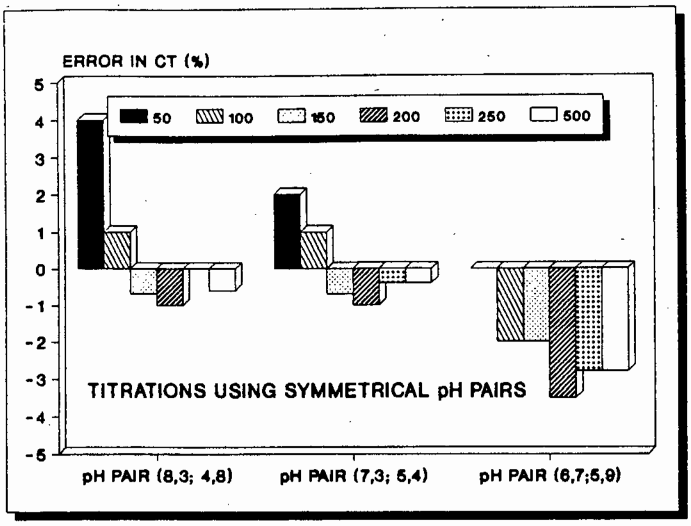

Fig 3.6: Percentage error in calculation of the total carbonate species concentration, C_T, calculated using different pH pairs located symmetrically around pK_{ac1} of carbonate subsystem; the test solutions were made up with $NaHCO_3$ to give C_T concentrations of 50, 100, 150, 200, 250 and 500 mg/ℓ (as $CaCO_3$). The average percentage error in C_T for each solution is plotted for pH pair (8,3; 4,8), for pH pair (7,3; 5,4) and for pH pair (6,7; 5,9).

CO_2 loss during titration

Loss of CO_2 from an aqueous solution containing the carbonate subsystem leads to an increase of the solution pH. It has been stated earlier that if CO_2 is lost during a titration with strong acid from, say, pH_1 to pH_2, then C_T will be overestimated if this measured pH pair is used for its calculation. To investigate the effect of CO_2 loss from solution during titration on the calculation of C_T the following experiment was carried out:

Twelve different Na_2CO_3 solutions were made up to provide a range of expected C_T values from 50 - 1700 mg/ℓ as $CaCO_3$. Each solution was titrated from its initial pH (pH $\simeq$ 11) to pH $\simeq$ 8,3 and then to pH $\simeq$ 4,8. The pH pair (8,3; 4,8) was selected as this eliminates the effect of any systematic pH measurement error on the calculation of C_T (see earlier). It was hypothesized that prolonged stirring at pH $\simeq$ 4,8 would cause loss of CO_2 from the sample and consequently the second pH reading of the pH pair should increase.

Each of the above Na_2CO_3 solutions was tested using the following testing procedure: Stirring for 1 min at initial pH before recording the reading; titrating to pH $\simeq$ 8,3 and recording of pH reading after 1 min of stirring; titrating to pH $\simeq$ 4,8 where pH readings were recorded after 1, 10, 20 and 30 min of stirring. From the recorded pH readings the following pH data pairs were formed: pH–pair$_1$ (8,3; 4,8 with 1 min stirring); pH–pair$_2$ (8,3; 4,8 with 10 min stirring); pH–pair$_3$ (8,3; 4,8 with 20 min stirring) and pH–pair$_4$ (8,3; 4,8 with 30 min stirring). For each pH pair a C_T value was calculated, to give C_{T1} from pH–pair$_1$, C_{T2} from pH–pair$_2$, C_{T3} from pH–pair$_3$ and C_{T4} from pH–pair$_4$ respectively. The titration data and the four C_T values for each solution (three replica tests for each solution were performed) are listed in Appendix F. In Fig 3.7 the measured C_{T1} values (i.e. after 1 min stirring) of the different solutions are plotted against their expected (known) values. The plot indicates that C_{T1} closely equals the known C_T value, i.e. negligible CO_2 loss occurred at all concentrations of C_T with 1 min stirring. Therefore it was concluded that C_{T1} could serve as a basis to assess the effect of CO_2 loss under prolonged stirring conditions: By subtracting C_{T1} from C_{T2}, C_{T3} and C_{T4} three ΔC_T values were obtained which were then plotted in Fig 3.8. From this plot the following conclusions were drawn:

(1) For all the tests, for stirring periods of $\simeq$ 1 min the effect of CO_2 loss on the calculation of C_T is insignificant.

(2) For longer stirring times up to 30 min, loss of CO_2 from solutions with $C_T <$ 500 mg/ℓ (as $CaCO_3$) was negligible; with C_T increasing above 500 mg/ℓ (as $CaCO_3$) CO_2 loss also increased. This introduced an error in the determination of C_T in the original sample.

The above conclusions suggest that a sound titration procedure would be to dilute the sample to a C_T concentration < 500 mg/ℓ as $CaCO_3$ and to complete the titration to the various titration points in less than, say, 10 minutes.

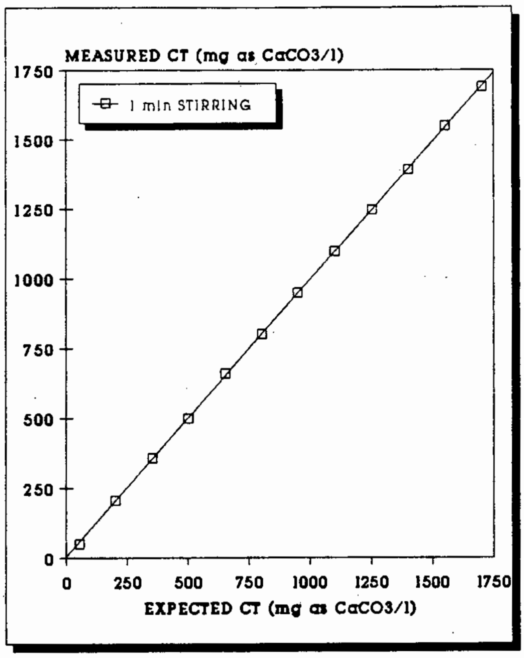

Fig 3.7: Comparison of calculated versus expected (made up) total carbonate species concentrations, C_T, for aqueous Na_2CO_3 solutions; pH pair used for calculation (8,3; 4,8); stirring time of 1 min before taking pH reading at approximately 4,8.

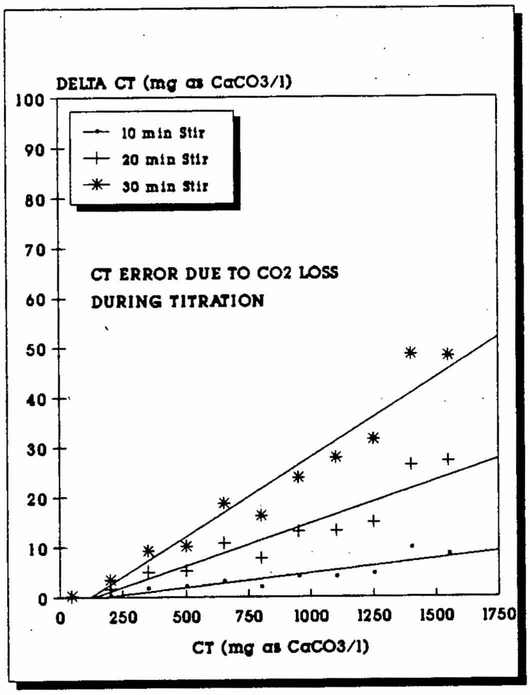

Fig 3.8: Effect of CO_2 loss on calculation of total carbonate species concentration, C_T, due to prolonged stirring periods applied before taking pH reading at the second pH point of pH pair (8,3; 4,8).

The 4 pH point titration method

In the above experiments, C_T and H_2CO_3*alkalinity were determined from titration data between two pH points. It was demonstrated that should there be a systematic error in pH, ΔpH, this can give rise to an error in C_T. However, it was further demonstrated that the error can be largely eliminated by choosing 2 pH points (pH pair) symmetrically located around pK_{ac1}. In this way C_T can be determined accurately without knowing ΔpH. Having C_T and the *initial* pH, the H_2CO_3*alkalinity can be calculated from Eq (3.28). The initial pH, however, is affected by ΔpH and this will lead to in incorrect estimate of the H_2CO_3*alkalinity; this is particularly true if the initial pH is located in a pH region in which the carbonate subsystem has a high buffer index. To eliminate the error in H_2CO_3*alkalinity, an estimate of ΔpH needs to be made.

In a previous section, an iterative procedure to obtain an estimate of ΔpH has been outlined: It involves acid titration from an initial pH (pH_0) to two lower pH points; two pH pairs are made up from three different pH values (pH_0, pH_1) and (pH_0, pH_2); where pH_0 is the initial pH of the titration and pH_1 and pH_2 are two second (lower) pH points. The first pH pair is located symmetrically around pK_{ac1} to enable calculation of an error free $C_{T0,1}$. The second pH pair (pH_0, pH_2) is unsymmetrically located around pK_{ac1}; from this pair $C_{T0,2}$ is calculated. Because of the non–symmetry, $C_{T0,2}$ will be in error and hence will differ from $C_{T0,1}$. The difference between $C_{T0,1}$ and $C_{T0,2}$ forms the basis for the iteration procedure to obtain ΔpH.

In the above procedure, to ensure a significant initial difference between $C_{T0,1}$ and $C_{T0,2}$, pH_1 and pH_2 must be chosen such that $\Delta MAlk_1H_2CO_3*(\Delta pH)$ and $\Delta MAlk_2H_2CO_3*(\Delta pH)$ are significantly different. To achieve this, from experience and by examining the plot in Fig 3.1, the following two conditions should be satisfied: (1) pH_1 and pH_2 should be located in the pH region 4,8 to 5,9, and, (2) pH_1 should be separated from pH_2 by more than 0,6 pH units. These two conditions limit the possible choice of the pH pairs as follows: If pH_2 is selected at the lowest point of the proposed pH range i.e. at 4,8, then pH_1 will be at pH 4,8 + 0,6 = 5,4 which is the lowest possible value for pH_1. Hence in order to establish a pH pair (pH_0; pH_1) equidistant from $pK_{ac1} \simeq 6,3$, pH_0 will be located at approximately 7,3 (see Fig 3.1) which is the highest possible value for pH_0. Alternatively, with the upper limit of pH_1 to pH ≃ 5,9, the corresponding pH_0 is fixed at pH 6,7 and pH_2 should be located below 5,3. Accordingly, the pH range of pH_0 is limited to the range of 6,7 and 7,3. Thus, if the initial pH of the sample is located outside this pH range, the sample needs to be titrated into this range to establish two suitable pH pairs to facilitate an estimate of ΔpH; in this event, if an estimate of ΔpH is required to improve the accuracy of the $H_2CO_3^*$ alkalinity, or, if a check of the condition and calibration of the pH probe is envisaged, 4 pH points (pH_0 and three further pH points pH_1, pH_2 and pH_3) are required in the titration leading to a 4 pH point titration method. In cases where the initial pH falls into the pH region 6,7 to 7,2 the 4 pH point method condenses to a 3 pH point method. If the initial pH (pH_0) of the sample is below 6,7, upward adjustment of pH_0 to pH_1 with strong base is required; the requirement is only an upward adjustment of pH_0, i.e. neither the mass of strong base added nor its normality need to be measured, (for titration procedure see Appendix T).

To test the accuracy and precision of the 4 pH point method, the method was applied to determine C_T (and hence $H_2CO_3^*$alkalinity) at low and high C_T concentrations. The low $C_T/H_2CO_3^*$alkalinity range was specifically separated because the effects of impurities in the distilled water, particularly contamination by CO_2, could become significant – the method determines C_T and from this derives $H_2CO_3^*$alkalinity, so that CO_2 contamination becomes a matter of concern. In contrast, the First Gran Function method determines the $H_2CO_3^*$alkalinity and from this derives C_T and has been shown to give an accurate assessment of $H_2CO_3^*$alkalinity. Accordingly, it was decided to apply both methods in the tests on the low $C_T/H_2CO_3^*$alkalinity solutions before testing the 4 pH point method at high $C_T/H_2CO_3^*$alkalinity values; comparison of results from the two methods would allow evaluation of the 4 pH point titration method.

*Low C_T/H_2CO_3*alkalinity concentration solutions*

A set of $NaHCO_3$ solutions were made up to 10, 20 30, 40 and 50 mg/ℓ C_T, giving the same values for $H_2CO_3^*$alkalinity, both as $CaCO_3$. The solutions were tested using the complete first Gran Function method (Loewenthal *et al.*, 1989), and the 4 pH point method (except for the 50 mg/ℓ C_T solution the initial pH was close to the pH range 7,2 to 6,7 and the 4 pH point method degenerated to a 3 pH point titration method). The results are listed in Appendices G and H. In Figs 3.9a and 3.9b the results for C_T and $H_2CO_3^*$alkalinity obtained from the Gran Function method and 4 pH point titration are plotted against each other; evidently the two methods give values very close to each other. In Fig 3.10a and 3.10b the results for C_T and the $H_2CO_3^*$alkalinity obtained from the Gran Function and 4 pH point

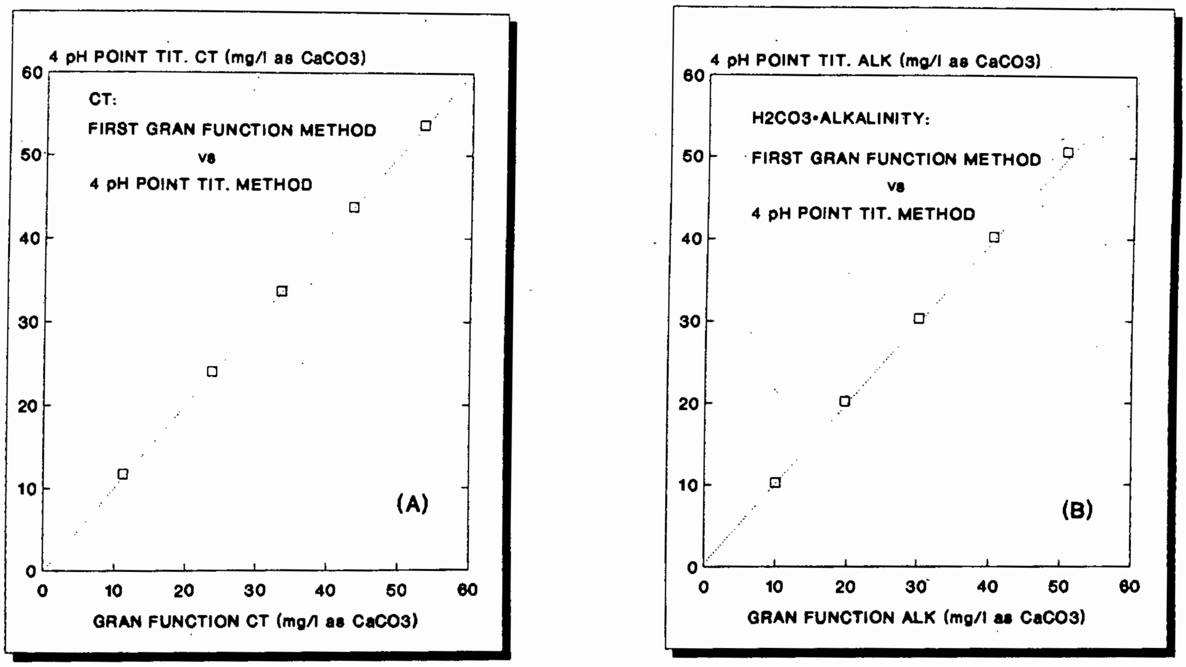

Fig 3.9a,b: Low concentrations of H_2CO_3*alkalinity and total carbonate species concentrations, C_T: Comparison of results obtained from Gran Function method and 4 pH point titration method on aqueous $NaHCO_3$ solutions for: C_T in (3.9a) and H_2CO_3*alkalinity in (3.9b).

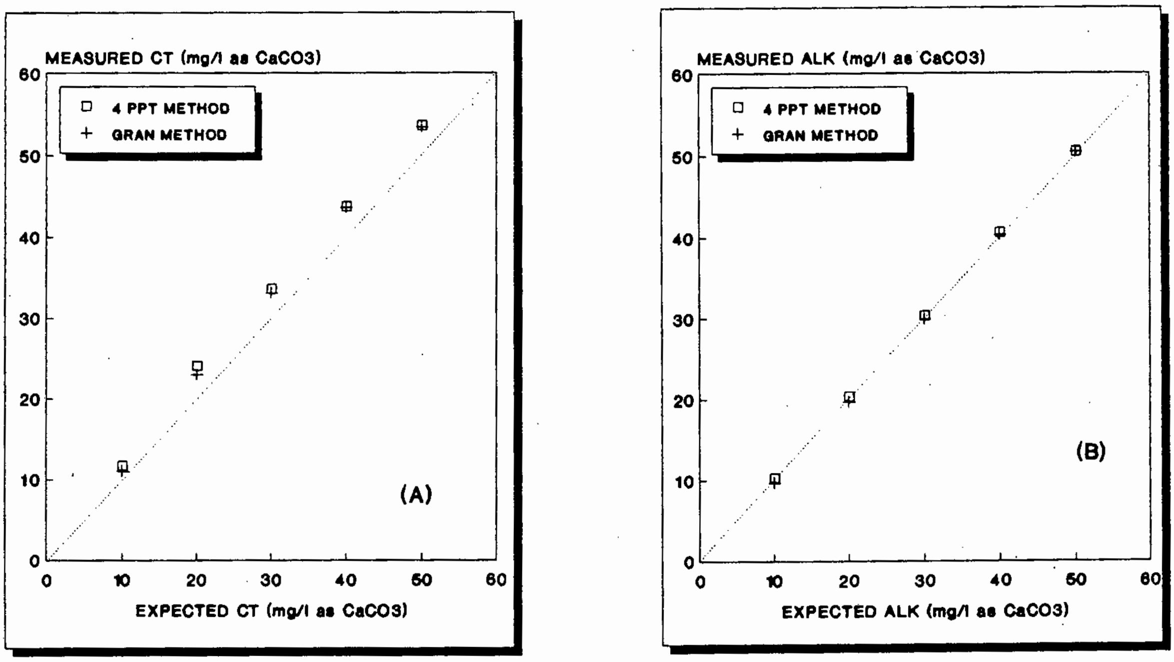

Fig 3.10a,b: Low concentrations of H_2CO_3*alkalinity and total carbonate species concentrations, C_T: Comparison of C_T measured by the Gran Function and 4 pH point titration method in (3.10a), and H_2CO_3*alkalinity measured by the Gran Function and 4 pH point titration method in (3.10b), with their respective expected (made up) values; the various aqueous solutions were made up from $NaHCO_3$ and distilled water.

titration method are plotted versus their respective expected (known) values. Comparing the measured H_2CO_3*alkalinity values with the expected (known) values, the measured values for both 4 pH point titration method and the Gran method show errors below 2 percent of the known values (see Fig 3.10b). With regard to C_T the results from both methods deviate from their respective expected values in that the measured values are consistently higher, by approximately of 3 mg/ℓ as $CaCO_3$ (see Fig 3.10a). Since the error in C_T is virtually the same in both methods, it is likely that C_T additional to the $NaHCO_3$ added was present in the sample possibly through CO_2 contamination or some other effects in the distilled water. That these were present is supported by noting that the initial pH values of the solutions ranged from 7,2 to 7,6 whereas the expected pH value for pure $NaHCO_3$ solutions is about 8,3.

The hypothesis of CO_2 contamination was investigated further by using modified Deffeyes diagrams; these diagrams link the H_2CO_3*alkalinity to the –ve CO_3^{2-}alkalinity (CO_3^{2-}acidity) via pH. In our case the H_2CO_3*alkalinity value is known for the individual solutions; if we assume that the deviation in C_T is due to CO_2 contamination the –ve CO_3^{2-}alkalinity can also be estimated (Loewenthal et al, 1986). Inserting the H_2CO_3*alkalinity and –ve CO_3^{2-}alkalinity values for the individual solutions in the Deffeyes diagram, pH values for these solutions can be obtained. A comparison of the pH values from Deffeyes diagram with the initial measured pH values shows that they are in close agreement. This indicates that the assumption of contamination of CO_2 in the sample is correct.

High C_T/H_2CO_3*alkalinity concentration solutions

A set of $NaHCO_3$ solutions were made up to 100, 200, 300, 400 and 500 mg/ℓ C_T, giving the same values for H_2CO_3*alkalinity, both as $CaCO_3$. C_T and H_2CO_3*alkalinity were estimated using only the 4 pH point method because the low C_T/H_2CO_3*alkalinity investigation had shown that the two methods give virtually identical results. These estimates were compared with their respective expected (known) values; the small errors introduced by CO_2 contamination of the solutions became insignificant because of the high concentrations of C_T and H_2CO_3*alkalinity. The measured results for C_T and H_2CO_3*alkalinity are listed in Appendix I and are plotted for each solution against their respective expected (known) values, in Figs 3.11 and 3.12. In all instances the measured average values of the various solutions, for both C_T and H_2CO_3*alkalinity, deviated by less than 2 percent from their respective expected (known) values.

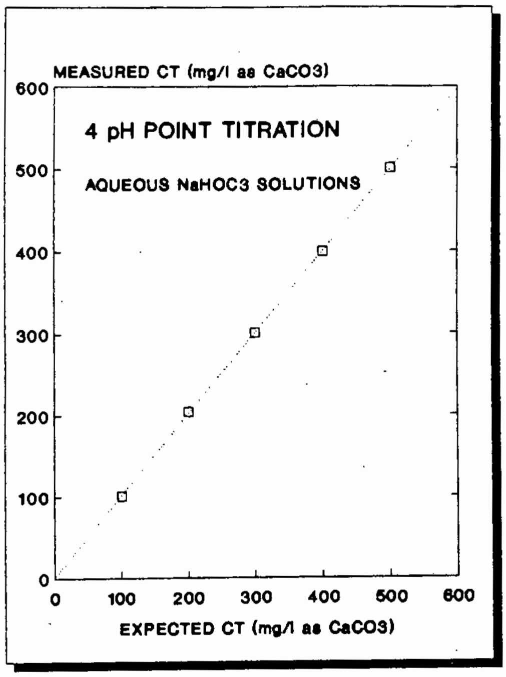

Fig 3.11: High concentrations of total carbonate species concentration, C_T: Results derived from 4 pH point titration method for total carbonate species concentration, C_T, plotted versus their respective expected (made up) values; solutions made up with $NaHCO_3$ and distilled water to give concentrations ranging from 100 – 500 mg/ℓ as $CaCO_3$.

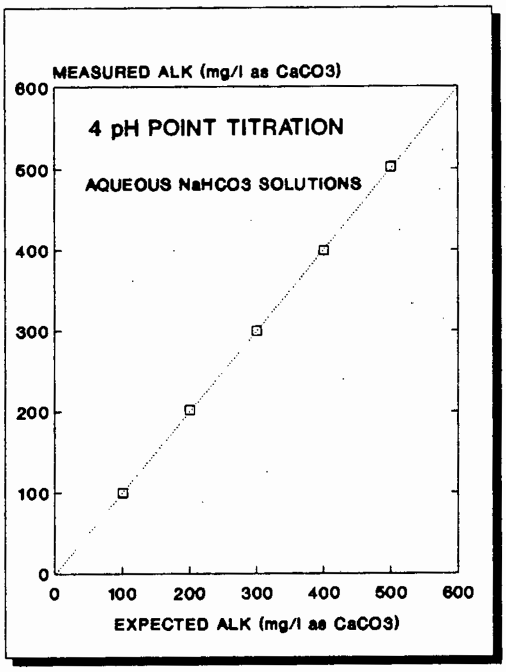

Fig 3.12: High concentrations of H_2CO_3*alkalinity: Results derived from 4 pH point titration method for H_2CO_3*alkalinity plotted versus their respective expected (made up) values; solutions made up with $NaHCO_3$ and distilled water to give concentrations ranging from 100 – 500 mg/ℓ as $CaCO_3$.

3.4 DISCUSSION AND CONCLUSIONS

In this chapter, a 4 pH point titration method was described to determine C_T in solutions containing only the carbonate and water subsystems; from C_T and the initial pH, the H_2CO_3*alkalinity is derived. This method was compared with the First Gran Function method which, contrary to the 4 pH point method, determines H_2CO_3*alkalinity and from this alkalinity and the initial pH, derives C_T. Gran's method has a history of giving very accurate results for the H_2CO_3*alkalinity and therefore constitutes a good base for evaluating the accuracy of the 4 pH point H_2CO_3*alkalinity. The comparison showed close correspondence and the H_2CO_3*alkalinities from the two methods both give estimates close to the expected (known) values. With regard to C_T, close correspondence was found between the measurements of the two methods but in both cases these values deviated from the known values by a constant positive amount (3 mg/ℓ as $CaCO_3$) – very likely due to CO_2 contamination of the distilled water. From these data it appears that for H_2CO_3*alkalinity/C_T > 10 mg/ℓ as $CaCO_3$ the two methods are of closely equal accuracy for determination of both C_T and H_2CO_3*alkalinity.

For the purpose of routine measurement, the First Gran Function method requires a rather complex titration procedure whereas the 4 pH point method requires titration from the initial pH to only 3 further pH points. Furthermore, the 4 pH point method provides, without additional measurements, an estimate of the systematic pH error should this be present. In contrast, the Gran method does not provide for such an estimate and hence the calculation of C_T via the Gran method may contain an error. In the tests reported in this chapter this error was not apparent because the initial pH values were in a region of low buffer capacity and a pH error would have an insignificant effect on the estimate of C_T; this favourable situation will not be present if the initial pH is in a region of high buffer capacity.

With the 4 pH point titration method, because all the measured pH values are corrected for ΔpH, C_T calculated using the first (symmetrical) pH pair (pH_1, pH_2) will attain its true value even if it is only approximately symmetrically located around pK_{ac1}. Hence pH_1 and pH_2 may deviate from their preselected values (by about ± 0,2 pH units) without significantly affecting the accuracy of the determination of C_T, H_2CO_3*alkalinity and ΔpH. Approximately the same measure of flexibility is applicable for the third additional pH point, pH_3. This flexibility in endpoint identification makes the titration procedure more convenient and less time consuming.

The feature of the 4 pH point method, that it provides an estimate of the systematic pH error, ΔpH, serves two purposes, (1) improvement of the accuracy of H_2CO_3*alkalinity estimate, and, (2) assessment of the performance of the pH probe. With regard to (1) even if the probe is poorly calibrated, C_T can be obtained with little error because the method compensates for ΔpH in the calculation of C_T. Knowing C_T and, since an estimate of ΔpH is provided by the method, the H_2CO_3*alkalinity similarly can be derived with little error. Although not reported here the elimination of ΔpH was tested by deliberately calibrating the pH probe with errors of ± 0,1 pH units (see Chapter 6); the calculated ΔpH reflected these imposed pH errors and the results obtained using the faulty calibration differed only slightly from those obtained using a correctly calibrated probe. With regard to (2) if in routine measurements the calculated ΔpH deviates from its usual mean value it would indicate an assignable cause, e.g. a change in the response behaviour of the probe, poor buffer solutions or a poor calibration technique.

The 4 pH point method was tested over a wide range of concentrations from 10 – 500 mg/ℓ C_T, as $CaCO_3$. Overall the measured C_T *and* H_2CO_3*alkalinity values differed from the expected results by less than 2 percent, except for the C_T values in the range of 10 – 50 mg/ℓ as $CaCO_3$ (see above).

The 4 pH point method involves little, if any, extra effort over the conventional H_2CO_3*alkalinity titration methods and is free of any problems encountered with endpoint identification. From a practical point of view the 4 pH point titration could readily replace the conventional methods, with the advantage of higher accuracy and of assessment of systematic pH measurement error.

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CHAPTER 4

A 4 pH POINT TITRATION METHOD FOR DETERMINING THE CARBONATE SUBSYSTEM IN AQUEOUS SOLUTIONS CONTAINING OTHER WEAK ACID/BASES OF KNOWN CONCENTRATIONS

ABSTRACT

In this chapter the 4 pH point titration method is extended to determine the carbonate subsystem in aqueous solutions containing other weak acid/bases of known concentrations: Two typical weak acid/bases are selected, inorganic nitrogen (ammonia/ammonium) with a pK_a far from, and inorganic phosphate with a pK_a near to the 4 pH point titration range of 6,7 to 4,8. The influence of the phosphate and ammonium weak acid/bases on the 4 pH point titration is examined theoretically and experimentally. Knowing the total species concentrations of the ammonium and phosphate weak acid/bases, their respective influences on the determination of the total carbonate species (C_T) and H_2CO_3*alkalinity can be removed. If the total species concentrations of the ammonium and phosphate weak acid/bases are neglected or in error, the error induced in C_T and H_2CO_3*alkalinity by the ammonium is negligible for most practical applications of the 4 pH point titration. However, neglect or incorrect total phosphate species concentrations can have significant effects on the accuracy of C_T and H_2CO_3*alkalinity depending on the relative proportions of total carbonate and total phosphate species present.

4.1 INTRODUCTION

In Chapter 3, a 4 pH point titration procedure was proposed which allows the characterization of the carbonate subsystem in aqueous solution, provided the carbonate subsystem is the only one present. In practice this procedure can be applied only for characterization of terrestrial waters where the carbonate subsystem is the dominating one, to such a degree that other weak acid/base subsystems can be neglected. In anaerobic waste water treatment processes, however, in addition to the carbonate subsystem, the phosphate, sulfide, ammonium and short-chain fatty acids (SCFA) systems may be present in such concentrations that they contribute significantly to the buffering capacity in the pH range covered by the 4 pH point titration method, and hence influence the determination of C_T and H_2CO_3*alkalinity. Consequently these weak acid/base systems no longer can be neglected.

In mixtures of weak acid/bases to obtain the correct C_T and H_2CO_3*alkalinity with the 4 pH point titration method, the influence of the weak acid/bases other than the carbonate system needs to be quantified. With regard to the phosphate, ammonium and sulfide subsystems the total species concentration of each of these subsystems can be readily measured by independent wet chemical techniques; accordingly, it is possible to calculate the buffering capacities each of these subsystems in the pH region covered by the 4 pH point titration method and due account of these can be taken in the calculation of C_T and H_2CO_3*alkalinity. This approach also applies to the SCFA system if separate SCFA determination is available. If, however, a separate SCFA determination is not available, the 4 pH point titration needs to be extended to a 5 pH point titration to obtain estimates of both the SCFA and carbonate subsystem total species concentrations (see Chapter 5).

In this chapter, the 4 pH point method is extended to determine C_T and H_2CO_3*alkalinity in aqueous solutions that contain known concentrations of other weak acid/bases. In this it provides an alternative to the modified Gran Function method (Loewenthal et al., 1989). For simplicity we will examine only the situation where two weak acid/bases, ammonium and phosphate, are present in known concentrations. The method can be readily extended to include a greater number of weak acid/bases.

4.2 THEORY

In the 4 pH point titration proposed in Chapter 3, the sample was titrated from its initial pH (pH_0), to pH_1 and pH_2 [both situated approximately equidistant around the first dissociation constant of the carbonate system (pK_{ac1})], and to a lower pH point (pH_3). From pH_1 and pH_2, C_T was calculated; from pH_3 an estimate of the systematic pH error (ΔpH) was made and an improved value for C_T was obtained; knowing ΔpH the initial pH of the sample could be adjusted which allowed more accurate calculation of the sample H_2CO_3*alkalinity from C_T and the corrected initial pH. The choice of pH_1, pH_2 and pH_3 was governed by the following factors:

- pH_1, pH_2 and pH_3 should be bracketed by the pH buffer solutions used for calibration of the pH probe.

- The difference between pH_2 and pH_3 should be sufficiently large to ensure that any difference in $C_{T1,2}$ and $C_{T1,3}$ (due to ΔpH) is shown up; this difference in C_T is then being used in an iterative calculation to determine ΔpH (see Chapter 3)

- pH_1 and pH_2 must be located approximately symmetrically around pK_{ac1}.

Considering these three conditions, it was shown in Chapter 3 that if the carbonate weak acid/base is the only one present, $pH_1 \simeq 6{,}7$, $pH_2 \simeq 5{,}9$ and $pH_3 \simeq 5{,}0$ are near optimal selections i.e. the titration ranges from pH ≃ 6,7 to ≃ 5,0. In a mixture of weak acid/bases with the total species concentrations of all the weak acid/bases known, except that of the carbonate, the pH values selected above still would apply. If the pK_a value of a weak acid/base is near or within the pH range 6,7 and 5,0 the buffering effect of this weak acid/base can be significant and adversely influence the determination of C_T. Thus, this effect needs to be removed to leave the effect due only to the carbonate weak acid/base. A general approach to achieve this will now be presented for a monoprotic weak acid/base.

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

The basic equations defining a *monoprotic* weak acid/base are as follows:

$$\frac{(H^+)\ [A^-]}{[HA]} = K_a/f_m = K_a' \tag{4.1}$$

$$A_t = [HA] + [A^-] \tag{4.2}$$

where (H^+) = the hydrogen ion activity (mol/ℓ),
$[A^-]$ = concentration of the salt of the weak acid/base (mol/ℓ),
$[HA]$ = concentration of the undissociated weak acid/base (mol/ℓ),
A_t = total species concentration of weak acid/base (mol/ℓ),

K_a, K'_a = the thermodynamic and apparent dissociation constant of the weak acid/base (mol/ℓ).

f_m = monovalent activity coefficient, see Appendix A .

These two equations contain 4 unknowns, hence 2 unknowns need to be measured. Of these A_t and (H^+) are usually measured; $[HA]$ and $[A^-]$ then can be expressed in terms of A_t and (H^+).

A^- as function of A_t and pH:

From Eq (4.2),

$$[HA] \quad = \quad A_t - [A^-] \tag{4.3}$$

Inserting Eq (4.3) in Eq (4.1) and rearranging,

$$[A^-] \quad = \quad \frac{A_t\ K'_a}{(H^+) + K'_a} \tag{4.4}$$

HA as function of A_t and pH:

Inserting Eq (4.4) in Eq (4.2)

$$[HA] \quad = \quad A_t\,(1 - \frac{K'_a}{(H^+) + K'_a}) \tag{4.5}$$

Alkalinity of the weak acid/base as function of A_t and pH

The alkalinity of an aqueous solution containing a mixture of the carbonate and another weak acid/base with respect to their most protonated species $H_2CO_3^*$ and HA, can be written as follows (see Loewenthal et al., 1991):

$$H_2CO_3^*/HA\ alk = [HCO_3^-] + 2\,[CO_3^{2-}] + [A^-] + [OH^-] - [H^+] \tag{4.6}$$

The $H_2CO_3^*$/HA alk can be written as the sum of subsystem alkalinities of each weak acid/base and water:

$$H_2CO_3^*/HA\ alk = Alk\ H_2CO_3^* + Alk\ HA + Alk\ H_2O \tag{4.7}$$

From Eq (4.6, 3.10 and 3.11)

$$\text{Alk HA} = [A^-] \qquad (4.8a)$$

$$\text{Alk } H_2CO_3^* = [HCO_3^-] + 2\,[CO_3^{2-}] \qquad (4.8b)$$

$$\text{Alk } H_2O = [OH^-] - [H^+] \qquad (4.8c)$$

Hence, from Eqs (4.4 and 4.8a) the alkalinity contribution of the HA weak acid/base subsystem can be written as function of A_t and pH:

$$\text{Alk HA} = \frac{A_t\, K'_a}{(H^+) + K'_a} \qquad (4.9)$$

Alkalinity contribution by the HA weak acid/base between two pH points

The mass of titrant required to titrate the HA subsystem from pH_1 to pH_2 can be derived as follows:

The mass of the weak acid/base subsystem alkalinity, MAlk HA, at any pH is,

$$\text{MAlk HA} = V_s\,[A^-]$$

$$= V_s \frac{A_t\, K'_a}{(H^+) + K'_a} \qquad (4.10)$$

where V_s is the sample size.

Considering a titration between two pH values, the mass change in HA subsystem alkalinity from pH_1 to pH_2 can be written as:

$$\Delta \text{MAlk}_{1,2}\text{HA} = \text{MAlk}_1\text{HA} - \text{MAlk}_2\text{HA}$$

$$= V_s\, A_t \frac{K'_a}{(H^+)_1 + K'_a} - (V_s+V_x) \frac{V_s\; A_t}{(V_s+V_x)} \frac{K'_a}{(H^+)_2 + K'_a}$$

$$= V_s A_t \left(\frac{K_a'}{(H^+)_1 + K_a'} - \frac{K_a'}{(H^+)_2 + K_a'}\right)$$

$$= V_s A_t Y_{1,2} \qquad (4.11)$$

where V_x is the mass of titrant added to titrate from pH_1 to pH_2.

Equation (4.11) allows the determination of buffering capacity of any monoprotic weak acid/base subsystem between any two pH points provided its total species concentration is known. In a mixture of weak acid/bases the effect of this additional buffering capacity on the determination of C_T in the 4 pH point titration method needs to be eliminated. In Chapter 3, it has been pointed out that the mass change in alkalinity of the sample solution [mass of titrant added: (Ca V_x)] can be written as the sum of the mass changes in alkalinity of the individual subsystems:

$$\text{Ca } V_x = \Delta MH_2CO_3^*/HA \text{ alk}_{1,2}$$

$$\text{Ca } V_x = \Delta MAlk_{1,2}H_2CO_3^* + \Delta MAlk_{1,2}HA + \Delta MAlk_{1,2}H_2O \qquad (4.12)$$

To determine C_T, $\Delta MAlk_{1,2}H_2CO_3^*$ needs to be written in terms of Ca V_x, $\Delta MAlk_{1,2}HA$ and $\Delta MAlk_{1,2}H_2O$,

$$\Delta MAlk_{1,2}H_2CO_3^* = \text{Ca } V_x - \Delta MAlk_{1,2}HA - \Delta MAlk_{1,2}H_2O \qquad (4.13)$$

In Eq (4.13), (Ca V_x) are known, $\Delta MAlk\ HA$ and $\Delta MAlkH_2O$ calculated from Eqs (4.11 and 3.41), and hence $\Delta MAlkH_2CO_3^*$ can be calculated. Hence, C_T can be calculated from Eq (3.39) in Chapter 3.

This general approach to eliminate the influence of a weak acid/base (other then the carbonate) on the determination of C_T (using the 4 pH point titration), is now investigated further for two types of weak acid/base mixtures in aqueous solutions: (1) carbonate and ammonium subsystems and (2) carbonate and phosphate subsystems.

Determination of C_T in a mixture of the carbonate and ammonium subsystems in aqueous solution

The ammonium subsystem has a pK_a of about 9,2; this value is far outside the titration range of the 4 pH point method (6,7 to 5,0), hence the buffering contribution of the ammonium subsystem will be very small in this titration range and will exert little influence on the determination of C_T.

Substituting the ammonium subsystem for the HA weak acid/base subsystem in Eq (4.7), the solution alkalinity can be written in terms of the subsystem alkalinities as follows:

$$H_2CO_3^*/NH_4^+ \text{ alk} = \text{Alk } H_2CO_3^* + \text{Alk } NH_4^+ + \text{Alk } H_2O \tag{4.14}$$

$$\text{Alk } NH_4^+ = [NH_3] \tag{4.15}$$

Alk $H_2CO_3^*$ and Alk H_2O have been defined in Eqs (4.8b and 4.8c).

From Eq (4.10), the mass of the ammonium subsystem alkalinity, MAlk NH_4^+, at any pH is,

$$\text{MAlk } NH_4^+ = N_T V_s \frac{K'_{an}}{(H^+) + K'_{an}} \tag{4.16}$$

where N_T = the total species concentration of the ammonium subsystem (mol/ℓ), and,

K'_{an} = the apparent dissociation constant of the ammonium subsystem.

Knowing the mass of the ammonium subsystem alkalinity (MAlk NH_4^+) at any pH point, the mass change in this subsystem alkalinity, $\Delta MAlk_{1,2}NH_4^+$, can be calculated as set out in Eq (4.11). Consequently, $\Delta MAlk_{1,2}H_2CO_3^*$ can be determined substituting $\Delta MAlk_{1,2}NH_4^+$ for $\Delta MAlk_{1,2}HA$ in Eq (4.13); $C_{T1,2}$ then is calculated from Eq (3.39).

Assessment of influence of the ammonium subsystem on the determination of C_T

It has been stated earlier that the pK_a value of the ammonium subsystem ($pK_{an} \simeq$ 9,2) is located relatively far from the titration range in the 4 pH point method (e.g pH 7,2 to 5,3). Hence, the buffering contribution of the ammonium subsystem in this pH range is very small and may be neglected except in instances where the total species concentration of the ammonium subsystem is high, and high accuracy in C_T determination is required.

Determination of C_T in a mixture of the carbonate and phosphate subsystems in aqueous solution

The phosphate subsystem is triprotic with $pK_{ap1} \simeq 2{,}1$, $pK_{ap2} \simeq 7{,}2$, $pK_{ap3} \simeq 12{,}0$. However pK_{ap1} and pK_{ap3} are situated far from the 4 pH point titration range and the buffering capacity centered around these two pK_a values can be neglected in the calculation of C_T. This leaves pK_{ap2} as the only one of importance in the 4 pH point titration method. With little error it is possible to deal with the phosphate system as if it was a monoprotic weak acid/base, with pK_{ap2} as the only pK_a value.

Accepting the phosphate system as monoprotic with dissociation species $H_2PO_4^-$ and HPO_4^{2-} ($pK_{ap2} \simeq 7{,}2$), substituting the phosphate subsystem for the HA weak acid/base subsystem in Eq (4.7) the solution alkalinity can be written in terms of the subsystems as follows:

$$H_2CO_3^*/H_2PO_4^- \text{ alk} = \text{Alk } H_2CO_3^* + \text{Alk } H_2PO_4^- + \text{Alk } H_2O \qquad (4.17)$$

$$\text{Alk } H_2PO_4^- = [HPO_4^{2-}] \qquad (4.18)$$

Alk $H_2CO_3^*$ and Alk H_2O have been defined in Eqs (4.8b and 4.8c)

From Eq (4.10), the mass of the ammonium subsystem alkalinity, MAlk $H_2PO_4^-$, at any pH is approximately,

$$\text{MAlk } H_2PO_4^- = P_T\, V_s \frac{K'_{ap2}}{(H^+) + K'_{ap2}} \qquad (4.19)$$

where P_T = the total species concentration of the phosphate subsystem (mol/ℓ), and,
K'_{ap2} = the second apparent dissociation constant of the phosphate subsystem (mol/ℓ).

Knowing the mass of the phosphate subsystem alkalinity (MAlk $H_2PO_4^-$) at any pH point, the mass change in this subsystem alkalinity for a titration between say, pH_1 and pH_2, $\Delta MAlk_{1,2}H_2PO_4^-$, can be calculated as set out in Eq (4.11). Consequently

$\Delta MAlk_{1,2}H_2CO_3^*$ can be determined [by substituting $\Delta MAlk_{1,2}H_2PO_4^-$ for $\Delta MAlk_{1,2}HA$ in Eq (4.13)]; C_T (= $C_{T1,2}$) then is calculated from Eq (3.39).

Assessment of influence of the phosphate subsystem on the determination of C_T

Unlike the pK_a of the ammonium subsystem (pK_{an}), the second pK_a of the phosphate subsystem (pK_{ap2}) is located relatively close to the titration range of the 4 pH point titration method, see Chapter 3. The buffering contribution by the phosphate subsystem in the pH range 7,2 to 4,8 is substantial and needs to be taken into account to eliminate errors in C_T determination, especially at elevated concentrations of P_T relative to C_T.

4.3 EXPERIMENTAL INVESTIGATION

The effect of weak acid/base subsystems on the determination of C_T, and consequently on the $H_2CO_3^*$alkalinity, was investigated experimentally. Two subsystems were selected, (1) ammonium having a pK_{an} = 9,25 (at 25° C) well away from the carbonate subsystem pK_{ac1} = 6,3 (at 25° C), and (2) phosphate having a pK_{ap2} = 7,20 (at 25° C) near pK_{ac1}. The effect of each of these subsystems was investigated separately. For the test solution, the C_T selected was that common in anaerobic systems, i.e. $C_T \simeq$ 1990 mg/ℓ or 2985 mg/ℓ as $CaCO_3$ made up from $NaHCO_3$ so that the alkalinity also was either ≃ 1990 mg/ℓ or 2985 mg/ℓ as $CaCO_3$. Ammonium was selected at concentrations from 100 to 500 mg/ℓ as N, made up from NH_4Cl, and phosphate at concentrations ranging from 16 to 98 mg/ℓ as P, made up from K_2HPO_4. All tests were done at approximately 20° C.

Effect of the ammonium subsystem

A set of solutions was made up with $NaHCO_3$, to give C_T = $H_2CO_3^*$alkalinity ≃ 2985 mg/ℓ as $CaCO_3$, together with addition of NH_4Cl, to give 0, 100, 200, 300, 400 or 500 mgN/ℓ. The solutions were titrated with standardized HCl. Two titration pH pairs were selected approximately symmetrically located around pK_{ac1}: pH pair (8,0; 4,8) and pH pair (7,4; 5,4). For each carbonate/ammonium concentration, 3 replica titrations were performed from pH 8,3 to 7,4 to 5,4 to 4,8, except for the solution containing only the carbonate subsystem where one titration only was done. For these titrations, the pH pair (8,0; 4,8) was selected because is close to the pH pair (8,3; 4,8) which was shown in Chapter 3 to give optimal accuracy in determining C_T in solutions containing only the carbonate subsystem; the second pH pair (7,4; 5,4) was selected to (1) demonstrate the effect of 'moving' the first pH of the pH pair, e.g. 8,3 further away from pK_{an}, and (2) evaluate the effect of the ammonium subsystem on approximately the same pH pair found the most suitable in the 4 pH point titration method to determine C_T and H_2CO_3*alkalinity in aqueous solutions containing only the carbonate weak acid/base, see Chapter 3.

The algorithm employed in deriving the results is as follows:

> The pK_{an} is adjusted for temperature and ionic strength to give pK_{an}'. In Eq (4.11) insert the total ammonium species concentration N_T, the sample volume, V_s, $pK_a' = pK_{an}'$ and $(H^+)_1$ and $(H^+)_2$ from pH_1 and pH_2, and calculate $\Delta MAlk_{1,2}NH_4^+$. Now insert $\Delta MAlk_{1,2}NH_4^+$, together with (Ca V_x) and $\Delta MAlk_{1,2}H_2O$ [from Eq (3.40)], in Eq (4.13) and calculate the mass of H_2CO_3*alkalinity change in the sample for the carbonate subsystem only, i.e. $\Delta MAlk_{1,2}H_2CO_3^*$. In Eq (3.39) insert $\Delta MAlk_{1,2}H_2CO_3^*$, sample volume V_s, $X_{1,2}$ [from Eq (3.38)] and calculate $C_{T1,2}$.

From the measured titration data, two values for C_T were derived, (1) taking into account the presence of the ammonium subsystem giving the "correct" C_T, C_{T1}, and, (2) neglecting the presence of the ammonium subsystem giving an uncorrected C_T, C_{T2}. The results observed and derived for all the tests are listed in Appendix J. To estimate the error introduced by not correcting for the presence of the ammonium subsystem, the tests in which zero ammonium is added (5 tests), are averaged and accepted as the best estimate for C_T in the set of tests. This C_T value is subtracted from the corrected C_{T1} (to give ΔC_{T1}) and from the uncorrected C_{T2} value (to give ΔC_{T2}). In Fig 4.1, ΔC_{T1} and ΔC_{T2} are plotted against the ammonium concentrations for pH pair (8,0; 4,8), and for pH pair (7,4; 5,4) in Fig 4.2. These plots give the following information:

- ΔC_T values uncorrected for presence of the ammonium subsystem are higher for the pH pair (8,0; 4,8) than for pH pair (7,4; 5,4).

- Uncorrected ΔC_T values increase linearly with the increase in ammonium concentrations.

- ΔC_T values corrected for the ammonium subsystem are insignificantly small and virtually independent of the ammonium concentration.

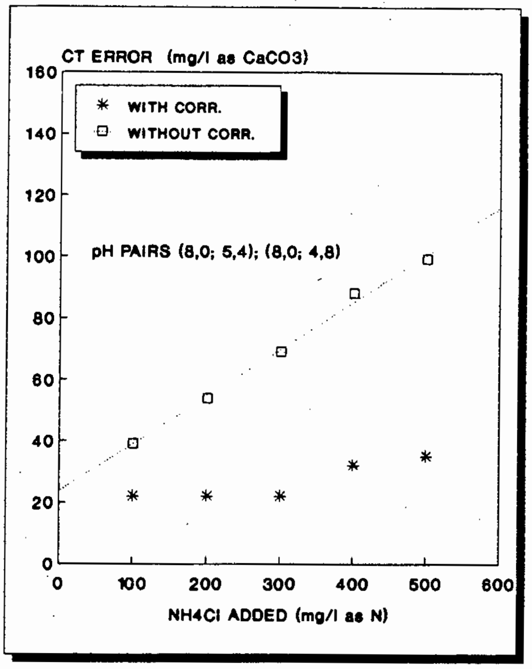

Fig 4.1: Influence of error in total species concentration of ammonium subsystem on determination of C_T by the 4 pH point titration method [using pH pairs (8,0; 4,8) and (8,0; 5,4)]. Test solutions were made up of distilled water, $NaHCO_3$ (2985 mg/ℓ as $CaCO_3$) and various concentrations of NH_4Cl.

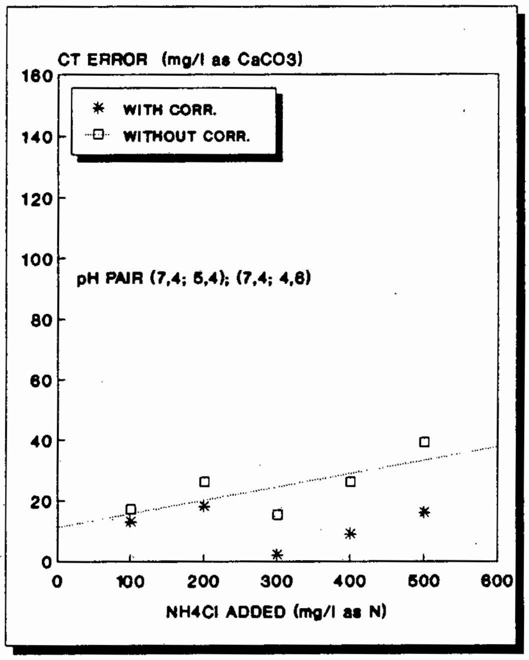

Fig 4.2: Influence of error in total species concentration of ammonium subsystem on determination of C_T by the 4 pH point titration method [using pH pairs (7,4; 5,4) and (7,4; 4,8)]. Test solutions were made up of distilled water, $NaHCO_3$ (2985 mg/ℓ as $CaCO_3$) and various concentrations of NH_4Cl.

From the above, should the symmetrical pH pair be selected even closer around pK_{ac1} than pH pair (7,4; 5,4), the uncorrected ΔC_T values would be even smaller. This would indicate that in a practical situation, if it should not be possible to determine the total ammonium species concentration, the error in C_T induced by the presence of the ammonium subsystem could be minimized by selecting the symmetrical pH pair close to pK_{ac1}. The "normal" pH pair for determining C_T, when the ammonium subsystem is not present, is ≃ (7,4; 5,4), see Chapter 3; this pH pair would give a percentage error in C_T of < 2 percent for 1990 mgC_T/ℓ as $CaCO_3$ and 500 mgN/ℓ should the presence of the ammonium subsystem be neglected.

Effect of the phosphate subsystem

A set of solutions was made up with C_T = H_2CO_3*alkalinity ≃ 2985 mg/ℓ as $CaCO_3$ together with additions of K_2HPO_4 to give 0, 16, 33, 49, 65 or 81 mgP/ℓ. The solutions were titrated with standardized HCl. A titration pH pair was selected approximately symmetrically located around pK_{ac1}, pH pair (7,4; 5,4). For each phosphate concentration, 3 replica titrations were performed together with a single titration on the solution with zero addition of K_2HPO_4. The pH pair (7,4; 5,4) demonstrates the effect of the phosphate subsystem on a pH pair located far from pK_{ac1} (when using the 4 pH point method) for aqueous solutions containing the carbonate and phosphate subsystems. A second set of solutions was prepared as before, except that the C_T/H_2CO_3*alkalinity was selected at ≃ 1990 mg/ℓ as $CaCO_3$. The pH pair was selected closer to pK_{ac1}, i.e. (6,7; 5,9). This pair was to demonstrate the effect of the phosphate subsystem on the 4 pH point titration when the pH pair is located close to pK_{ac1}.

The algorithm employed in deriving the results is similar to that used for the NH_4^+/carbonate subsystem mixture set out above. From the titration data, two values for C_T were derived, (1) taking into account the presence of the phosphate subsystem giving the "correct" C_T, C_{T1}, and, (2) neglecting the presence of the phosphate subsystem giving an uncorrected C_T, C_{T2}. The results observed and derived for all the tests are listed in Appendix K. To estimate the error introduced by not correcting for the presence of the phosphate subsystem, the results for the tests in which zero phosphate is added, are averaged and accepted as the best estimate for C_T in the set of tests. This value is subtracted from the corrected C_{T1} (to give ΔC_{T1}) and from the uncorrected C_{T2} (to give ΔC_{T2}). In Fig 4.3, ΔC_{T1} and ΔC_{T2} are plotted against the phosphate concentrations for pH pair (7,4; 5,4),

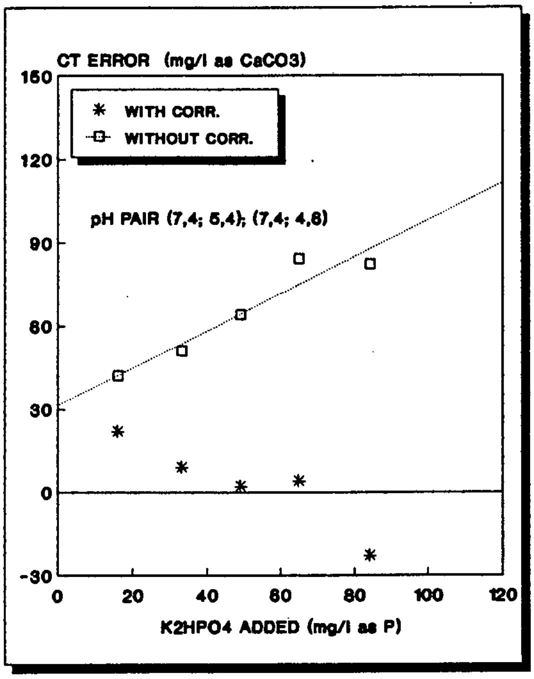

Fig 4.3: Influence of error in total species concentration of phosphate subsystem on determination of C_T by the 4 pH point titration method [using pH pairs (7,4; 5,4) and (7,4; 4,8)]. Test solutions were made up of distilled water, $NaHCO_3$ (2985 mg/ℓ as $CaCO_3$) and various concentrations of K_2HPO_4.

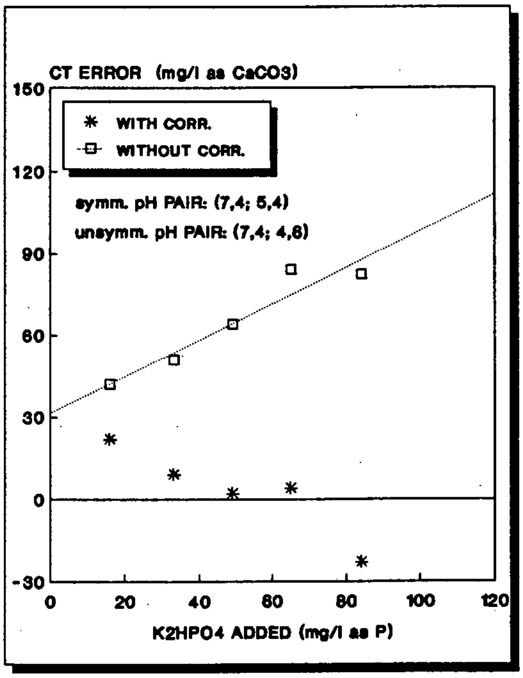

Fig 4.4: Influence of error in total species concentration of phosphate subsystem on determination of C_T by the 4 pH point titration method [using pH pairs (6,7; 5,9) and (6,7; 5,2)]. Test solutions were made up of distilled water, $NaHCO_3$ (1990 mg/ℓ as $CaCO_3$) and various concentrations of K_2HPO_4.

and in Fig 4.4 for pH pair (6,7; 5,9) . From these plots the following information is obtained:

- In a mixture of the carbonate/phosphate subsystems in aqueous solutions, the choice of the set of pH pairs (symmetrical or unsymmetrical) to determine C_T and ΔpH (within the pH range suggested for the 4 pH point method, see Chapter 3), is of little consequence – the errors induced in the determination of C_T using a set of pH pairs closer to pK_{ac1} (e.g. symmetrical 6,7; 5,9; unsymmetrical 6,7; 5,2) is only slightly reduced compared to the pH pairs located further away from pK_{ac1} (e.g. symmetrical 7,4; 5,4; unsymmetrical 7,4; 4,8).

- The presence of the phosphate subsystem has an appreciable effect on the determination of C_T if it is not included in the calculation.

- Knowing the total species concentration of the phosphate subsystem, the 4 point method allows the corrected determination of C_T and H_2CO_3*alkalinity to be virtually error free.

4.4 DISCUSSION

In this Chapter we investigated the effect of weak acid/base subsystems of known concentrations on the determination of C_T, and hence on the H_2CO_3*alkalinity using a 4 pH point titration. The solutions were made up from $NaHCO_3$ and a second weak acid/base and had relatively high concentrations of C_T and H_2CO_3*alkalinity; differences between C_T and H_2CO_3*alkalinity which arise due to CO_2 contamination would become insignificant. Since C_T was virtually identical to the H_2CO_3*alkalinity, the effect of the weak acid/base subsystems on C_T only was reported for the experiments in this chapter. The influence of two weak acid/base subsystems on C_T was investigated separately for the ammonium and for the phosphate subsystems. These two subsystems were chosen because they are common in wastewater treatment and in particular in anaerobic systems.

The ammonium subsystem represents a weak acid/base with a pK_a value located relatively far from the pH titration range recommended for the 4 pH point titration, see Chapter 3. Consequently, the buffering afforded by the ammonium within the suggested pH range is relatively small. It was shown that the choice of the pH range when carrying out a titration significantly affects the influence of the ammonium subsystem on the determination of C_T. From the two pH sets investigated: first set [symmetrical pH pair (8,0; 4,8); unsymmetrical pH pair (8,2; 5,4)] and second set [symmetrical pH pair (7,4; 5,4); unsymmetrical pH pair (7,4; 4,8)] it was shown that the influence of the ammonium subsystem on C_T decreased substantially when the second set of pH pairs was used to determine C_T: For an ammonium concentration of 500 mg/ℓ as N, when this subsystem is not accounted for the induced C_T error for the first pH set is + 104 mg/ℓ as $CaCO_3$ and for the second pH set + 22 mg/ℓ as $CaCO_3$. Hence, if there is uncertainty about the total species concentration of the ammonium subsystem of a particular solution, possible errors in the determination of C_T can be reduced significantly by moving the pH titration range away from the pK_a value of the ammonium system, i.e. pH_1 of the 4 pH point titration is moved close to the lowest possible value of $pH_1 \simeq 6{,}7$, see Chapter 3.

With regard to the phosphate subsystem, representing a weak acid/base with a pK_a value close to that of the carbonate subsystem, the following two pH sets were investigated: the first set [symmetrical pH pair (7,4; 5,4); unsymmetrical pH pair (7,4; 4,8)] and the second set [symmetrical pH pair (6,7; 5,9); unsymmetrical pH pair (6,7; 5,2)] represent the two extreme cases in the pH titration range recommended for the 4 pH point titration method in Chapter 3. The phosphate subsystem influenced the determination of C_T significantly if not corrected for; the error induced when using the two different pH sets differed as follows: For a total species concentration of phosphate of 65 mg/ℓ as P the error in C_T using the first pH set was + 81 mg/ℓ as $CaCO_3$ and for the second set + 62 mg/ℓ as $CaCO_3$. Hence, the C_T error due to the phosphate subsystem, if not corrected for, cannot be reduced by moving the symmetrical pH pair closer to pK_{ac1} to the same extent as in case of the ammonium subsystem. Thus, irrespective of the symmetrical pH pair selected, the determination of C_T will be affected by the phosphate subsystem so that the total species concentration of the phosphate subsystem needs to be determined with fair accuracy in order to correct for its effect on the determination of C_T and the $H_2CO_3^*$alkalinity in the 4 pH point method.

From the effects of the ammonium and phosphate subsystems on C_T, it would appear that if they should be neglected the symmetrical pH pair (6,7; 5,9) has an advantage from two aspects, (1) the the phosphate subsystem induces a lower error in the determination of C_T, and, (2) the ammonium subsystem can be neglected with little error. Furthermore, the initial pH can be as low as 6,7 without requirement for upward adjustment with strong base which is a slight technical inconvenience.

4.5 CLOSURE

For the more practically inclined reader the method set out above may appear too complex for routine use. However, despite the rather elaborate theory the experimental procedure for the 4 pH point titration method (set out step by step in Appendix T) requires little experimental effort and skill; the experimental data are inserted into a computer program (see Appendix U and X) which performs the necessary calculations and makes the results readily available.

4.6 REFERENCES:

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

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CHAPTER 5

A 5 PH POINT TITRATION METHOD FOR DETERMINING THE CARBONATE AND SCFA SUBSYSTEMS IN AN AQUEOUS SOLUTION ALSO CONTAINING KNOWN CONCENTRATIONS OF OTHER WEAK ACID/BASES – THEORETICAL CONSIDERATIONS

ABSTRACT

In this chapter, the theoretical basis for a 5 pH point acid titration method is described that allows the determination of H_2CO_3*alkalinity, total carbonate species concentration (C_T) and total short–chain fatty acid concentration (SCFA) in anaerobic digestor liquids also containing known concentrations of other additional weak acid/bases, e.g. ammonium and phosphate. The known concentrations of the additional weak acid/bases are incorporated in the algorithm employed to calculate the H_2CO_3*alkalinity, C_T and SCFA; in this manner their alkalinity contributions are removed from the alkalinity measurements obtained in the 5 pH point acid titration. The method also provides an estimate of any systematic pH measurement error, provided the carbonate subsystem dominates over the SCFA subsystem, i.e. C_T as $CaCO_3 > 2$ SCFA as acetic acid.

5.1 INTRODUCTION

In Chapter 4, a 4 pH point titration method was described that allows determination of the carbonate subsystem in a mixture of weak acid/bases, provided the total species concentration of the weak acid/bases other than the carbonate subsystem are known. This would apply also if the other weak acid/base in the mixture should be a short chain fatty acid (SCFA). However, measurement of the total species concentration of the SCFA by conventional methods (see Chapter 2) involves considerable analytical skills and expensive equipment. In this Chapter the 4 pH point titration is extended to a 5 pH point titration to eliminate the need for separate determination of the total species concentration of the SCFA. With this modified titration procedure it is possible to obtain estimates of the carbonate system parameters, e.g. C_T, H_2CO_3*alk, and the concentration of the SCFA (expressed as acetic acid).

The theory of the 5 pH point titration method will be considered for two cases: (1) mixture of carbonate and SCFA subsystems only in aqueous solution, (2) mixture of carbonate and SCFA plus phosphate and ammonium subsystems where the last two are known quantitatively by their total species concentrations.

5.2 THEORY

Total species concentrations by titration of the carbonate and SCFA subsystems in aqueous mixtures of these.

Consider a mixture of the carbonate and acetate (representing the SCFA) subsystems in an aqueous medium. The solution alkalinity at any pH relative to the most protonated species, $H_2CO_3^*$ and HAc (Loewenthal *et al.*, 1991), can be written:

$$H_2CO_3^*/HAc\ alk = [HCO_3^-] + 2\,[CO_3^{2-}] + [Ac^-] + [OH^-] - [H^+] \qquad (5.1)$$

Following Loewenthal *et al.* (1991), the $H_2CO_3^*$/HAc alk can be written as the sum of the *subsystem* alkalinities of the weak acid/bases and water:

$$H_2CO_3^*/HAc\ alk = Alk\ H_2CO_3^* + Alk\ HAc + Alk\ H_2O \qquad (5.2)$$

From Eqs (5.1, 3.10 and 3.11)

$$Alk\ HA = [Ac^-] \qquad (5.3a)$$

$$Alk\ H_2CO_3^* = [HCO_3^-] + 2\,[CO_3^{2-}] \qquad (5.3b)$$

$$Alk\ H_2O = [OH^-] - [H^+] \qquad (5.3c)$$

From Eq (5.2), the solution alkalinity at any selected pH_i can be written as

$$H_2CO_3^*/HAc\ alk_i = Alk_iH_2CO_3^* + Alk_iHAc + Alk_iH_2O \qquad (5.4)$$

The mass of solution alkalinity and subsystems alkalinities contained in a sample at pH_1 is:

$$MH_2CO_3^*/HAc\ alk_1 = MAlk_1H_2CO_3^* + MAlk_1HAc + MAlk_1H_2O \qquad (5.5)$$

At a second pH point, pH_2, the solution alkalinity and the subsystem alkalinities will be:

$$H_2CO_3^*/HAc\ alk_2 = Alk_2H_2CO_3^* + Alk_2HAc + Alk_2H_2O \qquad (5.5)$$

Again the mass of solution alkalinity and subsystems alkalinities contained in a sample at pH_2 are:

$$MH_2CO_3^*/HAc\ alk_2 = MAlk_2H_2CO_3^* + MAlk_2HAc + MAlk_2H_2O \qquad (5.6)$$

Subtracting Eq (5.6) from Eq (5.4) gives the mass changes of the solution alkalinity and the subsystem alkalinities in moving from pH_1 to pH_2::

$$\Delta MH_2CO_3^*/HAc\ alk_{1,2} = \Delta MAlk_{1,2}H_2CO_3^* + \Delta MAlk_{1,2}HAc + \Delta MAlk_{1,2}H_2O \qquad (5.7)$$

where

$$\Delta MH_2CO_3^*/HAc\ alk_{1,2} = MH_2CO_3^*/HAc\ alk_1 - MH_2CO_3^*/HAc\ alk_2$$
$$\Delta MAlk_{1,2}H_2CO_3^* = MAlk_1H_2CO_3^* - MAlk_2H_2CO_3^*$$
$$\Delta MAlk_{1,2}HAc = MAlk_1HAc - MAlk_2HAc$$
$$\Delta MAlk_{1,2}H_2O = MAlk_1H_2O - MAlk_2H_2O$$

In Eq (5.7), the term $\Delta MH_2CO_3^*/HAc\ alk_{1,2}$ equals the mass of titrant added to titrate from pH_1 to pH_2, i.e. ($Ca\ V_{x1,\,2}$). The term $\Delta MAlk_{1,2}H_2O$ is calculated from Eq (3.41). This leaves $\Delta MAlk_{1,2}H_2CO_3^*$ and $\Delta MAlk_{1,2}HAc$ as the only two unknowns. In Chapter 3, the $\Delta MAlk_{1,2}H_2CO_3^*$ was expressed in terms of V_s, pH_1, pH_2 and $C_{T1,\,2}$; from Eq (3.39):

$$\Delta MAlk_{1,2}H_2CO_3^* = V_s\ C_{T1,\,2}\ X_{1,2} \qquad (5.8)$$

where V_s = sample size (l), and
$X_{1,2}$ can be calculated from Eq (3.38)

In the same way that $\Delta MAlk_{1,2}H_2CO_3^*$ can be expressed as a function of V_s, pH_1, pH_2 and $C_{T1,2}$ (= C_T), so $\Delta MAlk_{1,2}HAc$ can be expressed as a function of V_s, pH_1, pH_2 and $A_{T1,2}$ (= A_T); from Eq (4.11):

$$\Delta MAlk_{1,2}HAc \qquad = V_s\, A_T\, Y_{1,2} \tag{5.9}$$

where $Y_{1,2}$ is obtained from Eq (4.11).

Substituting ($Ca\ V_{x1,2}$) for $\Delta MH_2CO_3^*/HAc\ alk_{1,2}$, inserting Eqs (5.8 and 5.9) into Eq (5.7) and rearranging:

$$(Ca\ V_{x1,2} - \Delta MAlk_{1,2}H_2O)/V_s = C_T\, X_{1,2} + A_T\, Y_{1,2} \tag{5.10}$$

This equation contains two unknowns (C_T and A_T) and hence cannot be solved – a second set of data needs to be measured by titrating to a further pH point, say pH_3. Analogously to a titration between pH_1 and pH_2, Eq (5.10) is rewritten for a titration between, say, pH_1 and pH_3:

$$(Ca\ V_{x1,3} - \Delta MAlk_{1,3}H_2O)/V_s = C_T\, X_{1,3} + A_T\, Y_{1,3} \tag{5.11}$$

where $V_{x1,3}$ = mass of titrant added from pH_1 to pH_3, and subscript 3 refers to pH_3.

From Eqs (5.10 and 5.11) C_T and A_T can be calculated. Thus by titrating between 3 pH points, from pH_1 to pH_2 and to pH_3, to form the data pairs (pH_1, pH_2) and (pH_1, pH_3), it is possible theoretically to determine C_T and A_T. However, these titrations may not be optimal because of their sensitivity to errors in the pH measurement. It is necessary therefore to establish a titration procedure that will minimize the effect of pH measurement errors on the calculation of C_T and A_T, i.e. improve their accuracy and precision.

Choice of pH points

In Chapter 3 it was stated that pH measurements (using a glass electrode) are prone to a systematic error (ΔpH) resulting, apparently, from the residual liquid junction effect and/or faulty calibration of the pH probe. The effect of such a systematic error on the calculation of MAlk $H_2CO_3^*$ over pH range 3,0 to 8,5 was demonstrated for aqueous solutions containing only the unknown carbonate system and was shown plotted in Fig 3.1. In Chapter 3 it was shown also that with correct choice of the pH pair (pH_1, pH_2) the error in calculation of C_T due to ΔpH can be largely eliminated. Considering a mixture of the carbonate and acetate systems, one may similarly examine the effect of ΔpH on the calculation of C_T and A_T:

From Eq (3.47), the effect of ΔpH on the calculation of MAlk $H_2CO_3{}^*$ is:

$$\text{MAlk } H_2CO_3{}^*(pH_{true}) = \text{MAlk } H_2CO_3{}^*(pH_{obs}) - \Delta\text{MAlk } H_2CO_3{}^*(\Delta pH) \tag{5.12}$$

where ΔMAlk $H_2CO_3{}^*(\Delta pH)$ is the error in MAlk $H_2CO_3{}^*$ (at any selected pH) resulting from ΔpH (pH_{obs} - pH_{true}) and can be calculated from Eq (3.47).

From Eq (3.50) the change in the carbonate subsystem alkalinity between pH_1 and pH_2 is:

$$\begin{aligned}\Delta\text{MAlk}_{1,2}H_2CO_3{}^* &= \text{MAlk}_1H_2CO_3{}^*(pH_{true}) - \text{MAlk}_2H_2CO_3{}^*(pH_{true})\\ &= \text{MAlk}_1H_2CO_3{}^*(pH_{obs}) - \text{MAlk}_2H_2CO_3{}^*(pH_{obs}) -\\ &\quad \Delta\text{MAlk}_1H_2CO_3{}^*(\Delta pH) + \Delta\text{MAlk}_2H_2CO_3{}^*(\Delta pH)\end{aligned} \tag{5.13}$$

Analogous to the carbonate subsystem the effect of ΔpH on the calculation of MAlk HAc can be written as:

$$\text{MAlk HAc } (pH_{true}) = \text{MAlk HAc } (pH_{obs}) - \Delta\text{MAlk HAc } (\Delta pH) \tag{5.14}$$

where MAlk HAc is obtained from Eq (4.10), and, ΔMAlk HAc (ΔpH) is calculated in the same way as ΔMAlk $H_2CO_3{}^*(\Delta pH)$ in Eq (3.47).

The mass change in the acetate subsystem alkalinity between pH_1 and pH_2 is:

$$\begin{aligned}\Delta\text{MAlk}_{1,2}\text{HAc} &= \text{MAlk}_1\text{HAc}(pH_{true}) - \text{MAlk}_2\text{HAc}(pH_{true})\\ &= \text{MAlk}_1\text{HAc}(pH_{obs}) - \text{MAlk}_2\text{HAc}(pH_{obs}) -\\ &\quad \Delta\text{MAlk}_1\text{HAc}(\Delta pH) + \Delta\text{MAlk}_2\text{HAc}(\Delta pH)\end{aligned} \tag{5.15}$$

In Eqs (5.13 and 5.15) the terms $\Delta\text{MAlk}_1H_2CO_3{}^*(\Delta pH)$, $\Delta\text{MAlk}_2H_2CO_3{}^*(\Delta pH)$,

$\Delta MAlk_1HAc(\Delta pH)$ and $\Delta MAlk_2HAc(\Delta pH)$ cannot be calculated because ΔpH is unknown. The magnitudes of the errors in $\Delta MAlk_{1,2}H_2CO_3^*$ and $\Delta MAlk_{1,2}HAc$ caused by ΔpH, changes with ΔpH and pH. To demonstrate the effect of ΔpH on the calculation of $\Delta MAlk\ H_2CO_3^*(\Delta pH)$ and $\Delta MAlk\ HAc(\Delta pH)$, let us assume that $\Delta pH = -0{,}04$ and V_s, C_T and A_T are unity; then $\Delta MAlk\ H_2CO_3^*(\Delta pH)$ and $\Delta MAlk\ HAc\ (\Delta pH)$ can be calculated at any pH by rearranging Eqs (5.12 and 5.14). In Fig 5.1, for $\Delta pH = -0{,}04$, $\Delta MAlk\ H_2CO_3^*(\Delta pH)$ and $\Delta MAlk\ HAc(\Delta pH)$ are shown plotted for pH = 3 to pH = 8,5; in practice, the majority of the pH pairs will lie between pH 3 and 8.

From Fig 5.1 the importance of the correct choice of a pair of pH values in calculating $\Delta MAlk_{1,2}H_2CO_3^*$ and $\Delta MAlk_{1,2}HAc$ becomes apparent: To avoid errors in calculating $\Delta MAlk_{1,2}H_2CO_3$ and $\Delta MAlk_{1,2}HAc$, the pH pair needs to be selected in a way that the influence of the unknown terms $\Delta MAlk_1H_2CO_3^*(\Delta pH)$, $\Delta MAlk_2H_2CO_3^*(\Delta pH)$, $\Delta MAlk_1HAc(\Delta pH)$ and $\Delta MAlk_2HAc(\Delta pH)$ in Eqs (5.13 and 5.15) become minimal. We will now examine three possible choices for these two pH data pairs.

Initial pH of sample plus 2 selected pH points:

It has been stated earlier that two pH pairs are required to solve Eqs (5.10 and 5.11) for C_T and A_T. The most economical choice would be to include the initial pH of the sample (pH_i) and two further pH points to form two pH data pairs,say (pH_i, pH_1) and (pH_1, pH_2). However such a choice of pH points allows very little control over errors in the calculation of C_T and A_T due to ΔpH, and therefore is not recommended.

Initial pH of sample plus 3 selected pH points:

To obtain some measure of control over the effect of ΔpH on C_T and A_T it is necessary to titrate from the initial pH (pH_0) to 3 further pH points. The initial pH is retained to calculate the H_2CO^*alkalinity from C_T, where C_T is obtained from pH_1, pH_2 and pH_3. In selection of the pH points, select pH_2 midway between pK_{ac1} and pK_{aa} (pK values for the carbonate and acetate system respectively) and pH_3 the same distance below pK_{aa} as pH_2 is above it. Now form the pH data pairs (pH_1, pH_2) equidistant from pK_{ac1}, and (pH_2, pH_3) equidistant from pK_{aa} (see Fig 5.2). With the first data pair (pH_1, pH_2) the error due to ΔpH in the carbonate subsystem is eliminated (calculation of $X_{1,2}$ in Eq 5.10), but the error due to ΔpH

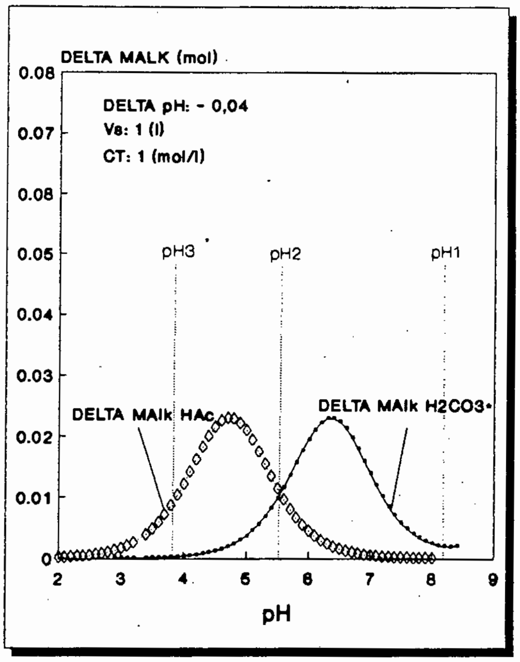

Fig 5.1: Theoretical implications of a systematic pH measurement error, ΔpH, on calculation of subsystem alkalinities: Error in calculation of MAlk H_2CO_3* and MAlk HAc over pH range, pH = 2,0 to pH = 8,5, caused by ΔpH = – 0,04 and V_s and C_T equal to unity. Approximate location of pH points for 3 pH point titration.

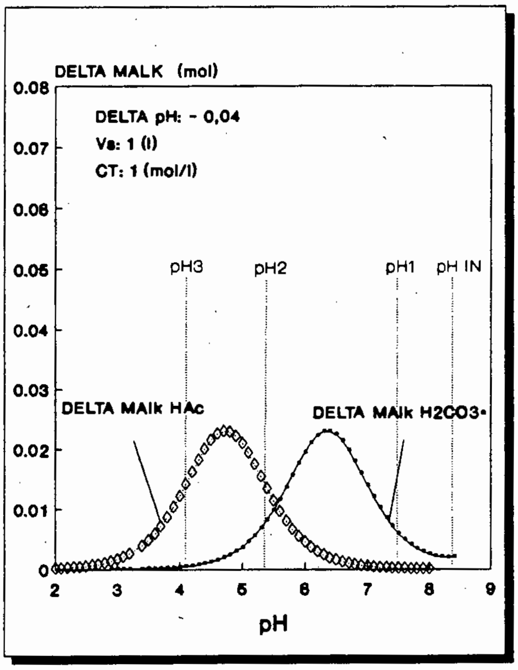

Fig 5.2: Theoretical implications of a systematic pH measurement error, ΔpH, on calculation of subsystem alkalinities: Error in calculation of MAlk H_2CO_3* and MAlk HAc over pH range, pH = 2,0 to pH = 8,5, caused by ΔpH = – 0,04 and V_s and C_T both equal to unity. Approximate location of pH points for 4 pH point titration.

in the acetate subsystem is retained (calculation of $Y_{1,2}$ in Eq 5.10). With the second pH data pair (pH_2, pH_3) the error due to ΔpH in the acetate system is eliminated (calculation of $Y_{2,3}$ in Eq 5.11), but the error in the carbonate system is retained (calculation of $X_{2,3}$ in Eq 5.11). The problem is to minimize these two remaining errors, see below.

Initial pH of sample plus 4 selected pH points:

To minimize the errors induced by the pH pairs selected equidistant from the respective pK_{ac1} and pK_{aa} values (both pairs having in common pH_2), it is necessary to discard the shared pH_2 and select two independent separate pH data pairs (pH_1, pH_2) and (pH_3, pH_4), where pH_1 and pH_2 are selected less than one pH unit apart and equidistant from pK_{ac1}, and pH_3 and pH_4 less than one pH unit apart and equidistant from pK_{aa}. By selecting such a narrow pH range for each pH data pair, the errors in C_T and A_T are reduced as much as practically possible (see Fig 5.3) – the ranges cannot be reduced at will because then random titration errors become significant and the precision of the calculated values for C_T and A_T is reduced. The conditions necessary to obtain reasonably accurate and reproducible results are summarized below:

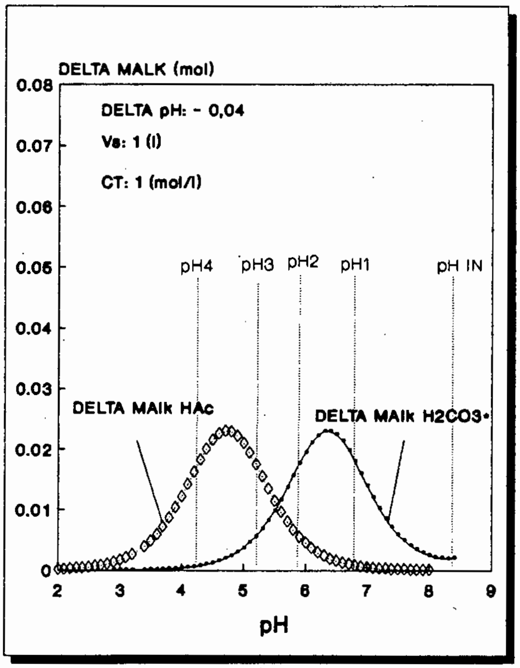

Fig 5.3: Theoretical implications of a systematic pH measurement error, ΔpH, on calculation of subsystem alkalinities: Error in calculation of MAlk $H_2CO_3^*$ and MAlk HAc over pH range, pH = 2,0 to pH = 8,5, caused by ΔpH = - 0,04 and V_S and C_T both equal to unity. Approximate location of pH points for 5 pH point titration.

Optimal choice of pH points for the simultaneous estimate of C_T and A_T by pH titration:

- For optimal pH probe calibration the titration range should be bracketed by the pHs of the buffer solutions, and be kept as narrow as possible.

- The titration must span a pH range in which the buffering capacities of the carbonate and the acetate systems are both appreciable (see Figs 2.1a,e). This requirement would be satisfied for a pH range of pH 6,7 to 4,3.

- The pH pairs (pH_1, pH_2) and (pH_3, pH_4) should be chosen such that the difference in pH for each pair is equal or less than one pH unit, but more than 0,7 pH units.

- To establish Eq (5.10) the first set of data (Ca, V_s, $V_{x1,2}$, pH_1 and pH_2) should be measured with pH_1 and pH_2 located symmetrically around the pK_a value of the carbonate system ($pK_{ac1} \simeq 6,3$): $pH_1 \simeq 6,7$ and $pH_2 \simeq 5,9$.

- To establish Eq (5.11) the second set of data (Ca, V_s, $V_{x3,4}$, pH_3 and pH_4) should be measured with pH_3 and pH_4 located symmetrically around the pK_a value of the acetate system ($pK_{aa} \simeq 4,75$): $pH_3 \simeq 5,2$ and $pH_4 \simeq 4,3$.

Estimate of the systematic pH error (ΔpH) in mixture of the carbonate and acetate systems in an aqueous solution.

In Chapter 3, a method was proposed that allows an estimate of ΔpH when the carbonate system is the only weak acid/base present in an aqueous solution. In a similar fashion one may obtain an estimate of ΔpH in a mixture of the carbonate and acetate systems in an aqueous solution.

Assume a titration from the initial pH (pH_0) to four lower pH points (pH_1 to pH_4) as suggested above. Two sets of C_T and A_T now can be calculated using Eqs (5.10 and 5.11): The first set using the pH data pairs (pH_1, pH_2) and (pH_3, pH_4), to give C_{T1} and A_{T1}; the second set using the pH data pairs (pH_1, pH_4) and (pH_3, pH_4), to give C_{T1} and A_{T2}. In Chapter 3 it was shown that for the carbonate system only in solution with a similar calculation, two C_T values were obtained. Furthermore, it appeared that the difference in the two C_T values very likely was caused by a systematic error in pH; if the pH pairs were adjusted by ΔpH and the values for C_T recalculated then the ΔpH at which the two C_T values became equal, formed an estimate of the systematic error in pH. Similarly in a mixture of the carbonate and acetate subsystems, the difference in (C_{T1}, A_{T1}) and (C_{T2}, A_{T2}) can be linked to ΔpH and an estimate of ΔpH obtained; this however requires the theory to be extended to an aqueous solution containing not only the carbonate subsystem but also the acetate.

To trace the influence of ΔpH on the calculation of (C_{T1}, A_{T1}), (C_{T2}, A_{T2}) let us rewrite Eqs (5.10 and 5.11) for the two sets of pH pairs:

First set: (pH_1, pH_2) and (pH_3, pH_4), giving C_{T1} and A_{T1}

$$(Ca\ V_{x1,2} - \Delta MAlk_{1,2}H_2O)/V_s = C_{T1}\,X_{1,2} + A_{T1}\,Y_{1,2} \qquad (5.16)$$

$$(Ca\ V_{x3,4} - \Delta MAlk_{3,4}H_2O)/V_s = C_{T1}\,X_{3,4} + A_{T1}\,Y_{3,4} \qquad (5.17)$$

where $V_{x1,2}$ = mass of titrant added between pH_1 and pH_2,
$V_{x3,4}$ = mass of titrant added between pH_3 and pH_4.

Second set: (pH_1, pH_4) and (pH_3, pH_4), giving C_{T2} and A_{T2}

$$(Ca\ V_{x1,4} - \Delta MAlk_{1,4}H_2O)/V_s = C_{T2}\,X_{1,4} + A_{T2}\,Y_{1,4} \qquad (5.18)$$

$$(Ca\ V_{x3,4} - \Delta MAlk_{3,4}H_2O)/V_s = C_{T2}\,X_{3,4} + A_{T2}\,Y_{3,4} \qquad (5.19)$$

where $V_{x1,4}$ = mass of titrant added between pH_1 and pH_4.

Comparing Eqs (5.16 and 5.17) with Eqs (5.18 and 5.19) and assuming that the four V_x volumes can be measured without significant error and that the effect of ΔpH on $\Delta MAlk\ H_2O$ is negligible, the difference in the two sets (C_{T1}, A_{T1}) and (C_{T2}, A_{T2}) results from the difference between the terms $X_{1,2}$ and $X_{1,4}$, as well as the difference between $Y_{1,2}$ and $Y_{1,4}$. The difference between $X_{1,2}$ and $X_{1,4}$ and the difference between $Y_{1,2}$ and $Y_{1,4}$ can be linked to ΔpH in the following way:

Difference between $X_{1,2}$ and $X_{1,4}$:

Assuming that V_s and C_T are unity then Eq (5.8) can be written for pH pair (pH_1, pH_2)

$$\Delta MAlk_{1,2}H_2CO_3^* = X_{1,2} \tag{5.20}$$

and for pH pair (pH_1, pH_4)

$$\Delta MAlk_{1,4}H_2CO_3^* = X_{1,4} \tag{5.21}$$

Inserting Eq (5.20) into Eq (5.13) and defining

$$X_{1,2}(pH_{obs}) = MAlk_1H_2CO_3^*(pH_{obs}) - MAlk_2H_2CO_3^*(pH_{obs})$$

gives:

$$X_{1,2}(_{true}) = X_{1,2}(pH_{obs}) - \Delta MAlk_1H_2CO_3(\Delta pH) + \Delta MAlk_2H_2CO_3(\Delta pH) \tag{5.22}$$

Inserting Eq (5.21) into Eq (5.13) and defining:

$$X_{1,4}(pH_{obs}) = MAlk_1H_2CO_3^*(pH_{obs}) - MAlk_4H_2CO_3^*(pH_{obs})$$

gives:

$$X_{1,4}(_{true}) = X_{1,4}(pH_{obs}) - \Delta MAlk_1H_2CO_3(\Delta pH) + \Delta MAlk_4H_2CO_3(\Delta pH) \tag{5.23}$$

In Fig 5.3 for $\Delta pH = -0{,}04$, V_s and C_T equal to unity, $\Delta MAlk\ H_2CO_3(\Delta pH)$ is plotted over a pH range from pH = 3 to pH = 8, including pH_1, pH_2, pH_3 and pH_4. From this plot, $\Delta MAlk_1H_2CO_3^*(\Delta pH)$ and $\Delta MAlk_2H_2CO_3^*(\Delta pH)$ at pH_1 and pH_2 respectively, are closely equal and cancel out in Eq (5.22). Hence, $X_{1,2}$ is largely error free and induces almost no error in the calculation of C_{T1} and A_{T1}. However, $\Delta MAlk_1H_2CO_3^*(\Delta pH)$ and $\Delta MAlk_4H_2CO_3^*(\Delta pH)$ differ considerably and do not cancel out in Eq (5.23). Hence, if there is a ΔpH present in the pH measurements, $X_{1,4}$ will cause an error in the calculation of C_{T2} and A_{T2}.

Difference in C_{T1} and C_{T2} due to $X_{1,2}$ and $X_{1,4}$:

To investigate in what way C_{T1} and C_{T2} differ due to the influence of ΔpH on the carbonate subsystem we need to examine the difference in $X_{1,2}$ and $X_{1,4}$. By choosing pH_1 and pH_2 symmetrical around pK_{ac1}, $X_{1,2}$ close to its true value is obtained (see above), and hence very little error is induced in the calculation of C_{T1}. The error in $X_{1,4}$ ($\Delta X_{1,4}$) due to ΔpH can be written as follows:

Letting

$$\Delta X_{1,4} = \Delta MAlk_4H_2CO_3^*(\Delta pH) - \Delta MAlk_1H_2CO_3^*(\Delta pH)$$

Inserting in Eq (5.23),

$$X_{1,4}(_{obs}) = X_{1,4}(_{true}) - \Delta X_{1,4} \qquad (5.23a)$$

From Fig 5.3, $\Delta X_{1,4}$ will be less than zero. Hence, if not corrected for the influence of ΔpH, $X_{1,4}(_{obs})$ will be greater than its true value and, if $X_{1,4}(_{obs})$ is inserted in Eq (5.18), will decrease C_{T2}. It may be concluded, therefore, that a negative ΔpH (as in Fig 5.3) will lead to $C_{T1} > C_{T2}$, and a positive ΔpH will lead to $C_{T1} < C_{T2}$.

Difference in $Y_{1,2}$ and $Y_{1,4}$:

In a mixture of the carbonate and acetate subsystems the difference in C_{T1} and C_{T2} not only depends on the effect of ΔpH on $X_{1,2}$ and $X_{1,4}$, but also on the effect of ΔpH on $Y_{1,2}$ and $Y_{1,4}$ (see Eqs 5.16 and 5.18). Analogous to $X_{1,2}$ and $X_{1,4}$ the effect of ΔpH on $Y_{1,2}$ and $Y_{1,4}$ can be demonstrated:

Assuming that V_s and C_T are unity then Eq (5.9) can be written for pH pair (pH_1, pH_2)

$$\Delta MAlk_{1,2}HAc = Y_{1,2} \qquad (5.24)$$

and for pH pair (pH_1, pH_4)

$$\Delta MAlk_{1,4}HAc = Y_{1,4} \qquad (5.25)$$

Inserting Eq (5.24) into Eq (5.15) and defining:

$$Y_{1,2}(pH_{obs}) = MAlk_1HAc(pH_{obs}) - MAlk_2HAc(pH_{obs})$$

gives:

$$Y_{1,2}(_{true}) = Y_{1,2}(_{obs}) - \Delta MAlk_1HAc(\Delta pH) + \Delta MAlk_2HAc(\Delta pH) \tag{5.26}$$

Inserting Eq (5.25) into Eq (5.15) and defining:

$$Y_{1,4}(pH_{obs}) = MAlk_1HAc(pH_{obs}) - MAlk_4HAc(pH_{obs})$$

gives:

$$Y_{1,4}(_{true}) = Y_{1,4}(_{obs}) - \Delta MAlk_1HAc(\Delta pH) + \Delta MAlk_4HAc(\Delta pH) \tag{5.26a}$$

From Fig 5.3, the difference between $\Delta MAlk_1HAc(\Delta pH)$ and $\Delta MAlk_2HAc(\Delta pH)$ is relatively small, and, hence has little effect on $Y_{1,2}$. Consequently C_{T1} contains only a small error resulting from $Y_{1,2}$. With regard to the term $Y_{1,4}$, Fig 5.3 indicates a significant difference between $\Delta MAlk_1HAc(\Delta pH)$ and $\Delta MAlk_4HAc(\Delta pH)$, which will induce a substantial error in the calculation of $Y_{1,4}$ and therefore in he calculation of C_{T2} and A_{T2}.

Difference in C_{T1} and C_{T2} due to $Y_{1,2}$ and $Y_{1,4}$:

Because ΔpH causes only a small error in $Y_{1,2}$, C_{T1} is not affected by $Y_{1,2}$ to any significant degree. However, the influence of ΔpH on the calculation of $Y_{1,4}$ may be significant and the implication of this is now further investigated.

Letting:

$$\Delta Y_{1,4} = \Delta MAlk_4HAc(\Delta pH) - \Delta MAlk_1HAc(\Delta pH) \tag{5.27}$$

and rewriting Eq (5.26)

$$Y_{1,4}(_{obs}) = Y_{1,4}(_{true}) - \Delta Y_{1,4} \tag{5.28}$$

From Fig 5.3, $\Delta Y_{1,4}$ is greater than zero; hence, if not corrected for the influence of ΔpH, $Y_{1,4}(_{obs})$ will be less than its true value, and, when inserted in Eq (5.18) will cause an increase in C_{T2}. Hence, in case of a negative ΔpH, $Y_{1,4}$ causes a increase in C_{T2} – in case of a positive ΔpH, $Y_{1,4}$ causes an decrease in C_{T2}.

Influence of errors in $X_{1,4}$ <u>and</u> $Y_{1,4}$ on calculation of C_{T2}:
It was shown above that ΔpH induces an error in both $X_{1,4}$ and $Y_{1,4}$. Both these terms affect the calculation of C_{T2} from Eq (5.18). Assuming a negative ΔpH, from Eq (5.23a), $X_{1,4}$ is greater than its true value and if inserted in Eq (5.18) *decreases* C_{T2}. From Eq (5.28) we note that with a negative ΔpH $Y_{1,4}$ is less than its true value and if inserted in Eq (5.18) *increases* C_{T2}.

Estimation of ΔpH by iteration:
In Chapter 3 it was shown that in an aqueous solution containing only the carbonate subsystem, by choice of appropriate pH pairs, different C_{T1} and C_{T2} values were obtained which allowed an estimate of ΔpH. This was achieved by adjusting pH_{obs} incrementally and recalculating C_{T1} and C_{T2}, pH_{true} could be identified at the point where C_{T1} equaled C_{T2}. From pH_{obs} and pH_{true}, ΔpH could then be calculated. Similarly ΔpH may be estimated in aqueous solutions containing the unknown carbonate and SCFA subsystems. However, the situation is complicated by the fact that $X_{1,4}$ decreases C_{T2} relative to C_{T1} whereas $Y_{1,4}$ increases C_{T2} relative to C_{T1}. This may lead to a situation where C_{T2} is no longer smaller than C_{T1}; this will occur when the carbonate subsystem does not dominate over SCFA subsystem (e.g during anaerobic digestor failure). In this event the iteration procedure to determine ΔpH cannot be applied and no correction for the systematic pH error is possible resulting in loss of accuracy in C_T and A_T. However, this usually will be of little consequence because it will happen only when the system is in failure and there is no advantage in having an accurate value of SCFA, only the fact that SCFA is high and the H_2CO_3*alkalinity is low is of importance. From experience it has been established that in order to form a reliable estimate of ΔpH the sample C_T should be approximately twice A_T (this condition for estimating ΔpH is incorporated in the computer program, i.e. the sample does not need to be assessed with regard to C_T or A_T prior to analysis, the computer program will automatically detect that $C_T < 2\ A_T$ and inform the user).

Influence of the ammonium subsystem on determination of C_T and A_T from 5 pH point titration.

In Chapter 4 a method has been proposed to determine C_T in a mixture of the carbonate plus ammonium subsystems in an aqueous solution. This method will now be incorporated into the situation discussed in this chapter; determination of the carbonate and acetate (representing the SCFA) subsystems in aqueous solutions containing the ammonium subsystem with a known total species concentration. The influence of this additional subsystem on the 5 pH point titration needs to be quantified and eliminated.

To quantify the influence of the ammonium subsystem on the 5 pH point titration, an approach similar to the one used to quantify the influence of the ammonium subsystem on the 4 pH point titration, is adopted.

Following Loewenthal *et al.* (1991) the solution alkalinity of a mixture of the carbonate, acetate and ammonium subsystems in an aqueous solution relative to the reference species $H_2CO_3^*$, HAc and NH_4^+ can be written in terms of the alkalinities of the subsystems in the solution:

$$H_2CO_3^*/HAc/NH_4^+\ alk = Alk\ H_2CO_3^* + Alk\ HAc + Alk\ NH_4^+ + Alk\ H_2O \tag{5.29}$$

The mass of solution alkalinity and subsystem alkalinities contained in the sample at say, pH_1 is:

$$MH_2CO_3^*/HAc/NH_4^+\ alk_1 = MAlk_1H_2CO_3^* + MAlk_1HAc + MAlk_1NH_4^+ + MAlk_1H_2O \tag{5.30}$$

Assume a second pH point, pH_2; at pH_2 the masses of solution and subsystem alkalinities are:

$$MH_2CO_3^*/HAc/NH_4^+\ alk_2 = MAlk_2H_2CO_3^* + MAlk_2HAc + MAlk_2NH_4^+ + MAlk_2H_2O \tag{5.31}$$

Subtracting Eq (5.31) from Eq (5.30) gives the mass change in solution and subsystem alkalinities in moving from pH_1 to pH_2:

$$\Delta MH_2CO_3^*/HAc/NH_4^+ \, alk_{1,2} = \Delta MAlk_{1,2}H_2CO_3^* + \Delta MAlk_{1,2}HAc + \Delta MAlk_{1,2}NH_4^+ + \Delta MAlk_{1,2}H_2O \qquad (5.32)$$

From Eq (4.16), the mass of the ammonium subsystem alkalinity, MAlk NH_4^+ can be calculated at any pH, provided the total species concentration of the ammonium subsystem is known. Hence, the change in the ammonium subsystem alkalinity between pH_1 and pH_2 ($\Delta MAlk_{1,2}NH_4^+$) can be obtained and inserted in Eq (5.32). The change in solution alkalinity between pH_1 and pH_2, $\Delta MH_2CO_3^*/HAc/NH_4^+ \, alk_{1,2}$ can be replaced by the mass of titrant added:

$$(Ca\ V_{x1,\,2} - \Delta MAlk_{1,2}NH_4^+ - \Delta MAlk_{1,2}H_2O)/V_s = C_T\ X_{1,2} + A_T\ Y_{1,2} \qquad (5.33)$$

where Ca = the normality of the titrant,
$V_{x1,\,2}$ = mass of titrant added from pH_1 to pH_2, and
subscript 1 and 2 refer to pH_1 and pH_2.

To solve for the two unknowns (C_T and A_T) a second set of data is measured for a pH pair, say (pH_1, pH_3) and Eq (5.33) can now be rewritten for pH_1 and pH_3:

$$(Ca\ V_{x1,\,3} - \Delta MAlk_{1,3}NH_4^+ - \Delta MAlk_{1,3}H_2O)/V_s = C_T\ X_{1,3} + A_T\ Y_{1,3} \qquad (5.34)$$

where $V_{x1,\,3}$ = mass of titrant added from pH_1 to pH_3 and,
subscript 3 refers to pH_3.

From Eqs (5.34 and 5.33) C_T and A_T can be calculated free from the influence of the ammonium subsystem provided its total species concentration is known.

Influence of the phosphate subsystem on determination of C_T and A_T from 5 pH point titration.

In aqueous solutions containing the carbonate, acetate and phosphate subsystems, the influence of the phosphate subsystem on the determination of C_T and A_T using the 5 pH point method, may be quantified and eliminated in the same way as for the ammonium subsystem above. Accepting the the reference species for the phosphate subsystem as $H_2PO_4^-$ and replacing the term $\Delta MAlk_{1,2}NH_4^+$ in Eq (5.33) with $\Delta MAlk_{1,2}H_2PO_4^-$, and the term $\Delta MAlk_{1,3}NH_4^+$ in Eq (5.34) with $\Delta MAlk_{1,3}H_2PO_4^-$, these two equations can be rewritten for pH pair (pH_1, pH_2) :

$$(Ca\ V_{x1,2} - \Delta MAlk_{1,2}H_2PO_4^- - \Delta MAlk_{1,2}H_2O)/V_s = C_T\ X_{1,2} + A_T\ Y_{1,2} \qquad (5.35)$$

where $\Delta MAlk_{1,2}H_2PO_4^- = MAlk_1H_2PO_4^- - MAlk_2H_2PO_4^-$

and pH pair (pH_1, pH_3):

$$(Ca\ V_{x1,3} - \Delta MAlk_{1,3}H_2PO_4^- - \Delta MAlk_{1,3}H_2O)/V_s = C_T\ X_{1,3} + A_T\ Y_{1,3} \qquad (5.36)$$

where $\Delta MAlk_{1,3}H_2PO_4^- = Alk_1H_2PO_4^- - MAlk_3H_2PO_4^-$

MAlk $H_2PO_4^-$ at pH_1 to pH_4 is calculated from Eq (4.16). Hence analogous to the ammonium subsystem, the influence of the phosphate subsystem on the determination of C_T and A_T can be eliminated provided its total species concentration is known.

In mixtures of the carbonate, acetate and a weak acid/base other than ammonium and phosphate systems, e.g. sulfide, the influence of this weak acid/base on the determination of C_T and A_T may be quantified analogous to the approach taken with the ammonium or phosphate system.

5.3 CONCLUSIONS

In this chapter is developed the theoretical basis for experimental estimation of H_2CO_3*alkalinity and short–chain fatty acid total species concentration (SCFA) in aqueous solutions containing the carbonate and SCFA subsystems of unknown concentrations plus other subsystems of *known* concentrations. The method involves measurement of the initial sample pH (pH_0) and titrating between 4 further pH points, selected in such a way that errors in the estimates of H_2CO_3*alkalinity and SCFA, due to systematic pH errors are minimized. A procedure also is included to estimate the systematic pH measurement error. In the next chapter an experimental study is reported to check the applicability of the theoretical approach and to determine optimal pH points for the titration.

5.4 REFERENCES:

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), pp 107–122.

CHAPTER 6

A 5 PH POINT TITRATION METHOD FOR DETERMINING THE CARBONATE AND SCFA SUBSYSTEMS IN AN AQUEOUS SOLUTION ALSO CONTAINING KNOWN CONCENTRATIONS OF OTHER WEAK ACID/BASES – EXPERIMENTAL INVESTIGATION

ABSTRACT

In this chapter the applicability of the theoretical 5 pH point acid titration method developed in Chapter 5, is experimentally investigated. The guidelines from the theory as to the optimal choice of the pH titration points, to enhance the accuracy of the method, are demonstrated to apply. To test the method aqueous solutions containing $NaHCO_3$ (1990; 2488 mg/ℓ as $CaCO_3$) and acetic acid with concentrations ranging from 100 to 1000 mg/ℓ were titrated using the 5 pH point method; the H_2CO_3*alkalinity and SCFA estimates ranged around the expected values with an average standard deviation (STD) of 5 and 8 percent respectively. Estimates of the SCFA by the 5 pH point acid titration and by Montgomery *et al.*'s wet chemical method on the effluents of UASB reactors treating brewery and wine distillery waste correlated closely (r = 0,98). Other tests demonstrated as predicted, the presence of (1) ammonium has negligible effect on both the H_2CO_3*alkalinity and SCFA estimates, (2) phosphates has significant effect on the H_2CO_3*alkalinity but insignificant effect on the SCFA estimates. The method was demonstrated to be robust in that deliberately imposed pH calibration errors were identified and the error effects on the H_2CO_3*alkalinity and SCFA estimates largely corrected.

6.1 INTRODUCTION

In Chapter 5 the theory of the 5 pH point titration method, to determine the carbonate and SCFA subsystems in aqueous solutions of a mixture of the two subsystems plus known concentrations of the phosphate, ammonium and other weak acid/base subsystems, was set out. In this chapter an experimental enquiry is reported to test the accuracy and precision of the method.

6.2 EXPERIMENTAL INVESTIGATION

Experimentally the following aspects were investigated:

- Determination of the H_2CO_3*alkalinity and SCFA subsystems in made up aqueous solutions of these.

- Effect of the ammonium and phosphate subsystem on the accuracy of determined H_2CO_3*alkalinity and SCFA concentrations.

- Estimation of the systematic pH measurement error, occurring unintentionally, or imposed artificially.

- Determination of H_2CO_3*alkalinity and SCFA in industrial wastes augmented with acetic acid.

- Comparison of SCFA results from the 5 pH point titration method with a conventional wet chemical method.

Solutions containing only the carbonate and SCFA subsystems

It was shown in Chapter 5 that, theoretically, the carbonate and SCFA subsystems, in aqueous solutions can be determined from pH titrations using the 3, 4 or 5 pH titration points, thus leading to 3, 4 or 5 pH point titration methods:

> With the 3 point titration method the second pH point is selected such that the pH pair (initial pH; second pH) will cover a substantial portion of the buffering capacity of the carbonate subsystem and only a small portion of the acetate subsystem, say a pH pair (initial pH; 5,6). The third pH is selected such that the pH pair (initial pH; third pH) will cover virtually the complete buffering capacity of the carbonate subsystem and a substantial portion of the acetate subsystem, say a pH pair (initial pH; 3,9). Two equations, one for each pH pair are set up in terms of C_T and A_T (Eqs 5.10 and 5.11). Inserting the titration data, C_T and A_T can be obtained. However, with this method the systematic pH error, ΔpH, cannot be estimated and causes an error in estimating C_T and A_T. (Note that A_T represents the total species concentration of the SCFA subsystem).

To *reduce* the effect of the systematic pH error, ΔpH, the 3 pH point titration method was extended to a 4 pH point titration method. Here the sample is titrated from its initial pH to 3 fixed pH points: 7,4; 5,4 and 4,1 (with a recommended accuracy of ± 0,1 pH units at each pH point). The fixed pH points are selected as follows: pH_2 is selected approximately midway between pK_{ac1} of the carbonate subsystem and pK_{aa} of the acetate subsystem, at pH $\simeq$ 5,4; pH_1 is selected symmetrical w.r.t. pH_2 around pK_{ac1} and pH_3 is selected symmetrical w.r.t. pH_2 around pK_{aa}, giving two symmetrical pH pairs, symmetrical around pK_{ac1} ($pH_1 \simeq 7,4$; $pH_2 \simeq 5,4$) and symmetrical around pK_{aa} ($pH_2 \simeq 5,4$; $pH_3 \simeq 4,1$). With the first symmetrical pH pair an equation including C_T and A_T is set up, similarly with the second pH pair. Solution of the two equations gives values for C_T and A_T, both affected by ΔpH. However, these C_T and A_T values generally should contain smaller errors than those obtained from the 3 pH point method. The error remaining can be eliminated by extending the 4 pH point titration method to a 5 pH point titration method.

In the 5 pH point titration method, pH_2 is replaced by two pH points between pK_{ac1} and pK_{aa} (pH_2, pH_3); this gives greater freedom to selecting the symmetrical pH pairs around these two pK_a values: The sample is titrated between two pH pairs, (pH_1, pH_2) and (pH_3, pH_4). Two pH pairs are formed to give two simultaneous equations in A_T and C_T, allowing their solution. The first pH pair (pH_1,pH_2) is formed symmetrical around pK_{ac1}; it cannot be selected too close to pK_{ac1} otherwise random errors in the pH measurement and titration become significant (see Chapter 3). Also the pH values must not be selected too far from pK_{ac1}, because pH_1 might be greater than the initial pH in which event the sample pH must first be raised by strong base addition to pH_1 (this addition is not measured and hence not part of the quantitative titration). From experience, the effect of random errors is contained if $pH_1 > 6,65$, thus giving the smallest first symmetrical pH pair around pK_{ac1} as (6,7 ; 5,9). From this pH pair an equation is established containing the error free $X_{1,2}$ but ΔpH being unequal to zero creates a small error in $Y_{1,2}$; a second pH pair (pH_3, pH_4) is formed symmetrical around pK_{aa} (5,2; 4;3). From this pH pair an equation is established containing the error free $Y_{3,4}$ but ΔpH being unequal to zero creates a small error in $X_{3,4}$. From the two equations (Eqs 5.16 and 5.17), C_T and A_T is calculated giving C_{T1} and A_{T1}, which still contain an errors due to errors in the terms $Y_{1,2}$ and $X_{3,4}$. To eliminate the remaining errors in $Y_{1,2}$ and $X_{3,4}$ we need to determine ΔpH: For the purpose of determination of ΔpH the focus is on the carbonate subsystem because it dominates and will be affected by ΔpH to a greater extent than the SCFA subsystem, i.e. attention is focused on C_T. From the measured titration data we form an *unsymmetrical* pH pair (pH_1; pH_4) around pK_{ac1} (6,7; 4,3) and retain the symmetrical pH pair (pH_3; pH_4) around pK_{aa} (5,2; 4,3). With these two pH pairs two equations are formed (Eqs 5.18 and 5.19), the solution of which provides a second value for C_T, C_{T2} (and A_T, A_{T2}) which will be significantly lower than C_{T1} *provided the carbonate subsystem dominates over the SCFA subsystem,* i.e. $C_T \simeq 2\ A_T$ (note that A_T represents the SCFA subsystem), see Chapter 5. If C_T dominates, by trial, the observed pH values then can be adjusted incrementally, and C_{T1} and C_{T2} recalculated using the adjusted pH values; when the adjusted pH values give $C_{T1} = C_{T2}$, the adjusted pH values theoretically equal the error free pH values and the adjustment (ΔpH) gives the associated systematic error in pH. The calculated values of C_T and A_T are now free from the influence of the systematic pH error. In the event that $C_T < 2\ A_T$ no reliable estimate of the systematic pH error can be made, see Chapter 5.

3 pH point titration method (experimental)

Solutions were made up (at different times) with an input $C_T = H_2CO_3$*alkalinity $\simeq$ 2985 mg/ℓ as $CaCO_3$, using $NaHCO_3$, together with additions of HAc to give 100, 200, 300, 400 and 500 mg/ℓ as HAc. The solutions were titrated with standardized HCl. For each concentration 3 replica titrations were performed, from the initial pH to pH 5,6 and 4,2. To determine C_T and A_T, the pH pairs suggested earlier were chosen at approximately: (initial pH; 5,6) and (initial pH; 4,2).

The algorithm employed to derive the results is as follows:

Using the first pH pair, calculate $X_{1,2}$ by inserting the initial pH ($pH_0 = pH_1$) and pH $\simeq$ 5,6 (pH_2) in Eq (3.38), and $Y_{1,2}$ is obtained as shown in Eq (4.11) using the initial pH ($pH_0 = pH_1$) and pH $\simeq$ 5,6 (pH_2); these two terms, together with $\Delta MAlk_{1,2}H_2O$ (from Eq 3.40) are inserted in Eq (5.10) giving an equation which contains C_T and A_T as unknowns. To solve for C_T and A_T a second equation containing C_T and A_T is established from the pH pair (initial pH = pH_3; $pH_4 \simeq$ 4,2): the terms $X_{3,4}$ (analogously to $X_{1,2}$) and $Y_{3,4}$ (analogously to $Y_{1,2}$) are calculated and together with $\Delta MAlk_{3,4}H_2O$ inserted in Eq (5.11). From Eqs (5.10 and 5.11) C_T and A_T are derived. With regard to the carbonate system, knowing C_T and the *initial pH of the solution,* the H_2CO_3*alkalinity can be calculated; H_2CO_3*alkalinity plays a key role in the practical evaluation of the buffering behaviour of an anaerobic digestion liquor (see Chapter 2), whereas C_T is of limited interest from a point of view of pH control in anaerobic digestion. Accordingly we will focus on the H_2CO_3*alkalinity; C_T will be of importance only insofar it influences the accurate determination of H_2CO_3*alkalinity.

For each solution (with 3 replica tests) three experimental H_2CO_3*alkalinity and A_T values were calculated. The expected HAc values were the known (made up) values; the expected H_2CO_3*alkalinity values were determined as follows: Assume that the added HAc acts as a strong acid in the pH range near the initial pH values ($6,6 < pH < 8,1$) of the made up solutions, in which event the input H_2CO_3*alkalinity (2985 mg/ℓ as $CaCO_3$) will be decreased by the concentration of HAc added, i.e. 1 mol of HAc removes 1 mol of H_2CO_3*alkalinity. (This assumption is not strictly correct particularly near $pH = 6,6$; at this pH theoretically approximately 1 percent of the A_T is undissociated). In this fashion, for each solution an expected H_2CO_3*alkalinity value was determined. The measured and derived data are listed in Appendix L.

In Fig 6.1 the measured values for A_T are plotted versus their respective expected values and in Fig 6.2 the expected and measured H_2CO_3*alkalinity values are plotted versus the input HAc concentrations. Figure 6.1 shows that the 3 pH point titration method consistently underestimates the concentrations of HAc by about 45 mg/ℓ as HAc, and Fig 6.2 shows that the H_2CO_3*alkalinity is overestimated consistently by up to approximately 40 mg/ℓ as $CaCO_3$. The magnitude of these errors certainly cannot be accounted for as being due to the assumption above that HAc acts as a strong acid at $pH > 6,6$; very likely the errors are due to the systematic pH error, ΔpH, and the choice of the pH pairs.

4 pH point titration method (experimental)

The experiments undertaken to evaluate the 4 pH point titration method were identical to those of the 3 pH point titration method except that the titration procedure was modified to include, the initial pH (pH_0), $pH_1 \simeq 7,4$, $pH_2 \simeq 5,4$ and $pH_3 \simeq 4,1$. From these pH points two pH pairs were selected, one symmetrical around pK_{ac1} (pH_1, pH_2), and another symmetrical around pK_{aa} (pH_2, pH_3), i.e. pH_2 lies midway between pK_{ac1} and pK_{aa}. The algorithm employed to derive C_T and A_T using these two pH pairs, remained identical to that described for the 3 pH point titration method. Also, the expected H_2CO_3*alkalinity for the made up solutions was

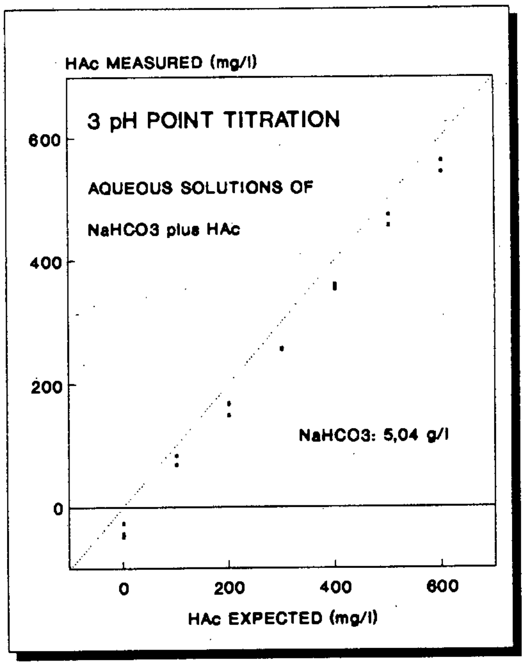

Fig 6.1: Made up aqueous solutions of mixtures of HAc and $NaHCO_3$: varying concentrations of HAc in base solution of 2985 mg$NaHCO_3/\ell$ as $CaCO_3$; measured HAc values were determined using 3 pH point titration method.

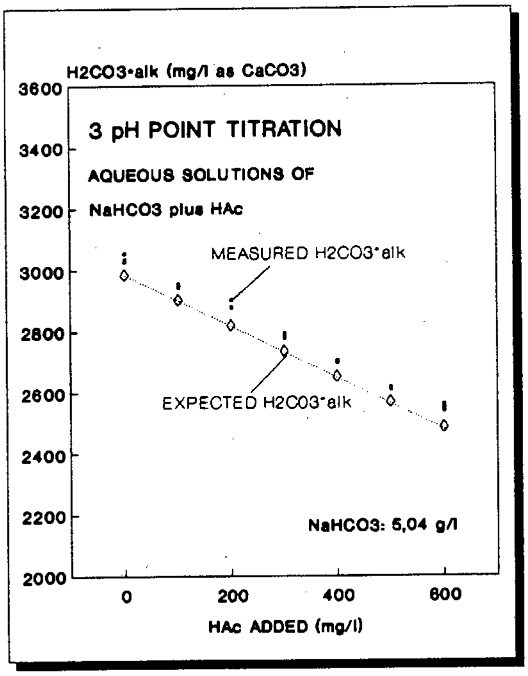

Fig 6.2: Made up aqueous solutions of mixtures of HAc and $NaHCO_3$: varying concentrations of HAc in base solution of 2985 mg$NaHCO_3/\ell$ as $CaCO_3$; measured H_2CO_3*alkalinity values were determined using 3 pH point titration method.

determined as before. The measured and derived data are listed in Appendix M.

In Fig 6.3 the expected HAc concentrations are plotted versus their respective measured values, and in Fig 6.4 the expected and measured H_2CO_3*alkalinities are plotted versus the HAc concentrations of the made up solutions. Comparing the 3 and 4 pH point titration methods, the plot in Fig 6.3 shows an appreciable underestimation of A_T still, of approximately 45 mg/ℓ as HAc; the plot in Fig 6.4 indicates a slight overestimate in H_2CO_3*alkalinity, of approximately 20 mg/ℓ. These remaining consistent errors may be attributed to the fact that the terms $Y_{1,2}$ in Eq 5.10 and $X_{2,3}$ in Eq 5.11 include an error resulting from ΔpH, see section 5.2 in Chapter 5.

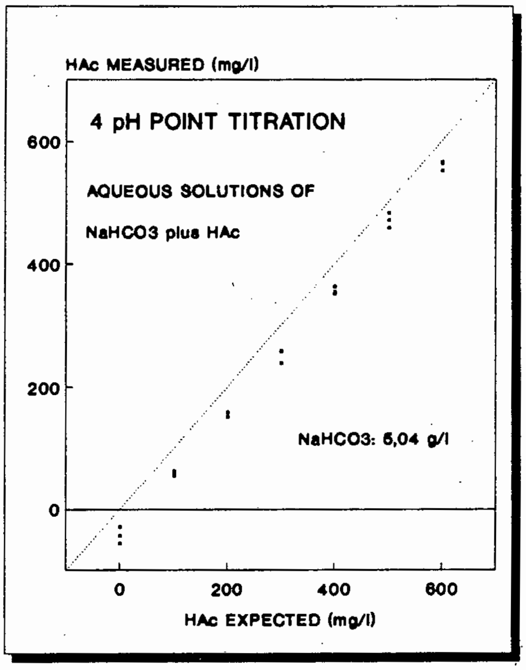

Fig 6.3: Made up aqueous solutions of mixtures of HAc and $NaHCO_3$: varying concentrations of HAc in base solution of 2985 mg$NaHCO_3$/ℓ as $CaCO_3$; measured HAc values were determined using 4 pH point titration method.

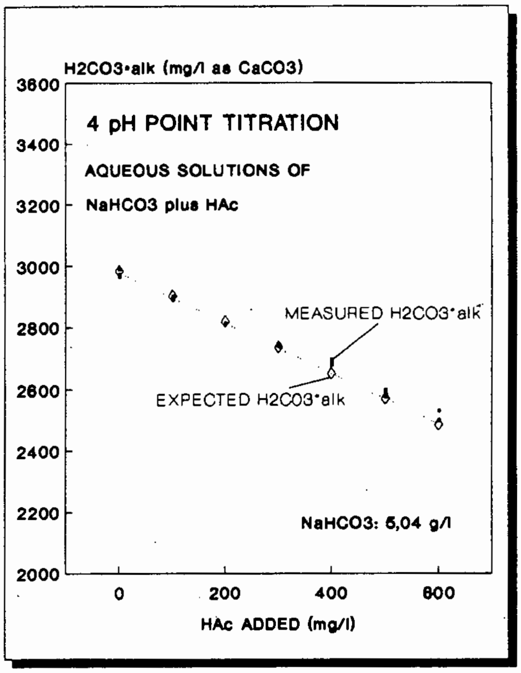

Fig 6.4: Made up aqueous solutions of mixtures of HAc and $NaHCO_3$: varying concentrations of HAc in base solution of 2985 mg$NaHCO_3/\ell$ as $CaCO_3$; measured H_2CO_3*alkalinity values were determined using 4 pH point titration method.

5 pH point titration method (experimental)

Two sets of solutions were made up from $NaHCO_3$ and HAc. The first set had an input $C_T = H_2CO_3$*alkalinity $\simeq$ 1990 mg/ℓ as $CaCO_3$ together with additions of HAc to give 100, 200, 300, 400 and 500 mg/ℓ as HAc. The second set had an input $C_T = H_2CO_3$*alkalinity $\simeq$ 2488 mg/ℓ as $CaCO_3$ together with additions of HAc to give 600, 700, 800, 900 and 1000 mg/ℓ as HAc. The H_2CO_3*alkalinity in the second set was increased to ensure an initial pH greater than 6,6 at the higher HAc concentrations. The solutions were titrated with standardized HCl. For each concentration 5 replica titrations were performed, from its initial pH to $pH_1 \simeq 6{,}7$ to $pH_2 \simeq 5{,}9$ to $pH_3 \simeq 5{,}2$ and $pH_4 \simeq 4{,}3$. With these titration data, C_T, A_T, and ΔpH were determined, using the pH pairs and procedure described earlier. Again from the adjusted initial pH and C_T values, the H_2CO_3*alkalinity was calculated. The results obtained for each solution are listed in Appendix N.

In Fig 6.5 the expected HAc concentrations are plotted versus their respective measured values. This plot shows a good correlation between the two data sets and clearly indicates that the consistent error in HAc observed with the 3 and 4 pH point method was eliminated. Figure 6.6 shows a plot of the measured and expected H_2CO_3*alkalinity values versus HAc concentrations. This plot (and the

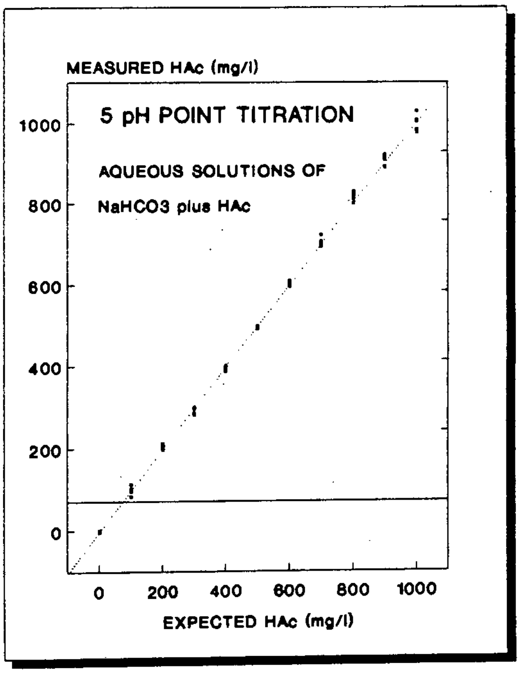

Fig 6.5: Made up aqueous solutions of mixtures of HAc and $NaHCO_3$: varying concentrations of HAc in base solutions of 1990 and 2488 $mgNaHCO_3/\ell$ as $CaCO_3$; measured HAc values were determined using 5 pH point titration method.

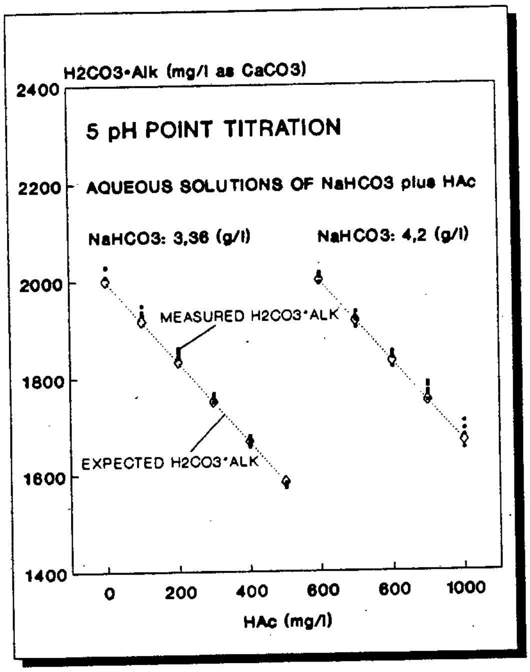

Fig 6.6: Made up aqueous solutions of mixtures of HAc and $NaHCO_3$: varying concentrations of HAc in base solutions of 1990 and 2488 $mgNaHCO_3/\ell$ as $CaCO_3$; measured H_2CO_3*alkalinity values were determined using 5 pH point titration method.

calculated data) indicates little difference between the measured and expected H_2CO_3*alkalinity values, except in the range of high HAc additions (> 700 mg/ℓ) where the measured H_2CO_3*alkalinities exceed their expected values. (A possible reason for this may be that in estimating the expected H_2CO_3*alkalinity the assumption that the added HAc acts as a strong base at the initial pH of the solution no longer is strictly valid - a small fraction of HAc would remain undissociated, i.e. would not supply H^+ ions to the solution, and hence would result in an increase in expected H_2CO_3*alkalinity).

Detection and estimation of ΔpH

The procedure in the 5 pH point titration method provides for the existence of a systematic pH measurement error, ΔpH. This error was estimated and taken into account in the calculation of the SCFA, C_T and H_2CO_3*alkalinity in order to improve the accuracy of the estimates. It is now of interest to enquire whether the method would detect a deliberately faulty pH calibration.

A solution was made up with an input C_T = H_2CO_3*alkalinity ≃ 1990 mg/ℓ as $CaCO_3$ together with 300 mg/ℓ HAc. Five replica titrations (5 pH point titration as described above) using standardized HCl were performed under each of the following conditions:

- Stage 1, the pH probe calibrated with NBS buffer solutions, pH = 7,02 and 4,00 (at 20°C).

- Stage 2, using the same buffer solutions as in stage 1 the calibration set points on the pH meter were deliberately changed by + 0,1 units to give 7,12 (at pH = 7,00 NBS buffer) and 4,1 (with pH = 4,00 NBS buffer).

- Stage 3, again using the same buffer solution as in stage 1 the calibration set points on the pH meter were deliberately changed by – 0,1 units to give 6,92 (at pH = 7,00 NBS buffer) and 3,9 (with pH = 4,00 NBS buffer).

Using the 5 pH point titration methodology, A_T, H_2CO_3*alkalinity and ΔpH were calculated. The titration data and results for the three stages of this experiment are listed in Appendix O. Taking the averaged results for ΔpH for each stage gives ΔpH (stage 1) = – 0,07, ΔpH (stage 2) = – 0,18 and ΔpH (stage 3) = + 0,05. The true pH will be given by Eq 3.46, i.e. $pH_{true} = pH_{observed} + \Delta pH$. To find out if the deliberately introduced pH calibration error is reflected in the calculated ΔpH we compare the ΔpH values from stage 1 to the values obtained from stage 2 and 3. Comparing the ΔpH values calculated at stage 1 and 2 gives a difference of [– 0,07 – (– 0,18)] = + 0,11 pH units. Comparing the ΔpH values calculated at stage 1 and 3 gives a difference of [– 0,07 – (+ 0,05)] = – 0,12 pH units; in both instances the calculated differences in ΔpH (relative to stage 1) correlating closely with the deliberately induced differences of + 0,1 and – 0,1 respectively. This indicates that the calculated ΔpH indeed detects systematic pH measurement errors.

Examining the derived results for A_T and H_2CO_3*alkalinity for stage 1, 2 and 3 shows the following: The averaged A_T values for stage 2 and 3 differ from the averaged results of stage 1 by only + 2 and – 2 percent respectively. The averaged H_2CO_3*alkalinity values for stage 2 and 3 differ from the averaged results of stage 1 by less than + 0,5 percent in both instances. From this it may be concluded that by using the 5 pH point titration method the errors in the derived values of A_T and H_2CO_3*alkalinity due to systematic pH measurement errors are effectively eliminated.

Influence of errors in the ammonium and phosphate subsystems on 5 pH point titration estimates

After evaluating the effect of the systematic pH error, an enquiry into the effects of weak acid/bases (of known concentrations) other than carbonate and acetate, on the determination of A_T and H_2CO_3*alkalinity by means of the 5 pH point titration, was undertaken.

In Chapter 4 it was shown that if the ammonium and phosphate subsystems are included in the algorithm of the 4 pH point titration method for the determination of C_T only, their effects on C_T are eliminated. Similarly, if these two subsystems are incorporated in the algorithm of the 5 pH point titration method to determine C_T and SCFA, these latter two parameter can be obtained free from the influence of the ammonium and phosphate subsystems. To account for the ammonium or phosphate their respective total species concentrations need to be known. It was now of interest to enquire what consequences the neglect or inaccurate determination of these two subsystems would have on the estimates of A_T and C_T when using the 5 pH point titration method. In this enquiry the parameter C_T was preferred to H_2CO_3*alkalinity because C_T is independent of the initial pH of the sample and does not change with the addition of species of other weak acid/bases, e.g. NH_4^+. The effects of each of the two subsystems were investigated separately.

Influence of an error in the ammonium subsystem on 5 pH point titration estimates
From the investigation into the effect of the ammonium subsystem on the determination of C_T in aqueous solutions containing only the carbonate subsystem (Chapter 3), it was concluded that the influence of an error in the total species concentration of the ammonium subsystem (N_T) can be reduced greatly by choosing the symmetrical pH pair (7,4; 5,4) instead of pH pair (8,3; 4,8), i.e. the pH pair located closer to pK_{ac1} and further away from pK_{an} was less susceptible to errors in C_T resulting from the presence of N_T. In the 5 pH point titration the symmetrical pH pairs are located even further away from pK_{an}, first pH pair (6,7; 5,9) and the second pH pair (5,2; 4,3) and consequently the presence of N_T should have even smaller effect on C_T and A_T.

To assess the influence of an error in N_T on the 5 pH point titration, a solution was made up with $NaHCO_3$ giving an input C_T = H_2CO_3*alkalinity ≃ 1990 mg/ℓ as $CaCO_3$ with *zero* addition of HAc. On this solution a 5 pH point titration was performed. From the data, in order to assess the theoretical influence of an error in N_T, the calculation for C_T and A_T was done with zero N_T, and, assuming there was in fact 500 mg/ℓ as N present. To account for the (in this case hypothetical) ammonium the algorithm to calculate C_T and A_T above was applied to include this weak acid/base. This was done as follows: Eqs (5.10 and 5.11) are replaced by Eqs (5.33 and 5.34). From the latter two equations C_T and A_T were obtained with $N_T = 0$, and equal to 500 mg/ℓ as N. The titration data and calculated results are listed in Appendix P. Calculating C_T and A_T for the case of zero N_T addition gave C_T = 2029 mg/ℓ as $CaCO_3$ and A_T = - 2 mg/ℓ as HAc. Calculating C_T and A_T for the case of the assumed N_T addition of 500 mg/ℓ as N gave C_T = 2019 mg/ℓ as $CaCO_3$ and A_T = - 6 mg/ℓ as HAc. From these results it becomes clear that even with large errors of 500 mg/ℓ as N the influence of the error on the determination of C_T (and hence H_2CO_3*alkalinity) and A_T when using the 5 pH point titration method is very small. Hence, errors in N_T are of little consequence in the determination of C_T and A_T.

Influence of an error in the phosphate subsystem on 5 pH point titration estimates
In Chapter 4 it was shown that an error in total species concentration of the phosphate subsystem (P_T) had a significant influence on the value of C_T using the 4 pH point titration in aqueous solutions containing the carbonate and phosphate subsystems irrespective of the choice of the symmetrical pH pairs. It may be expected therefore that an error in P_T - unlike N_T - will substantially influence the value of C_T and, possibly A_T, when using the 5 pH point titration method. To assess this effect on C_T and A_T, the following tests were carried out:

Solutions were made up with an input C_T = H_2CO_3*alkalinity ≃ 1990 mg/ℓ as $CaCO_3$ together with additions of K_2HPO_4 to give 0, 33, 65 and 98 mg/ℓ as P and, *zero* HAc. Using standardized HCl three replica titrations where performed from the initial pH to 6,7 to 5,9 to 5,2 and 4,3 giving a 5 pH point titration.

Using Eqs (5.35 and 5.36), C_T and A_T can be calculated while accounting for the influence of the phosphate subsystem. From the measured titration data, two sets of values for A_T and C_T were derived, (1) taking into account the presence of the phosphate subsystem to give the correct values for A_T and C_T, designated A_{T1} and C_{T1} and, (2) neglecting the presence of the phosphate subsystem (i.e. $P_T = 0$) to give the incorrect set of values for A_T and C_T, designated A_{T2} and C_{T2}. The titration data together with the results are listed in Appendix Q. To estimate the errors induced in A_T and C_T by not correcting for the presence of the phosphate subsystem the tests in which zero phosphate *was added* were averaged and accepted as the best average for A_T and C_T in the set of tests. These values were subtracted from their respective uncorrected A_{T2} and C_{T2} values to give ΔA_{T2} and ΔC_{T2}, and, from their respective corrected A_{T1} and C_{T1} values to give ΔA_{T1} and ΔC_{T1}. In Fig 6.7 ΔA_{T1} and ΔA_{T2} are plotted versus the phosphate concentrations, and in Fig 6.8 ΔC_{T1} and ΔC_{T2} are plotted versus the phosphate concentrations. From these plots it becomes evident that phosphate has very little effect on the determination of HAc using the 5 pH point titration method, i.e. insofar as the determination of HAc is concerned, knowledge of the phosphate concentration is practically unnecessary. However, the effect of phosphate is more noticeable when determining C_T: 100 mg/ℓ (as P) causes an approximate error in C_T of 90 mg/ℓ (as $CaCO_3$). Hence, if accurate determination of C_T or H_2CO_3*alkalinity is required the concentration of P_T needs to be known accurately.

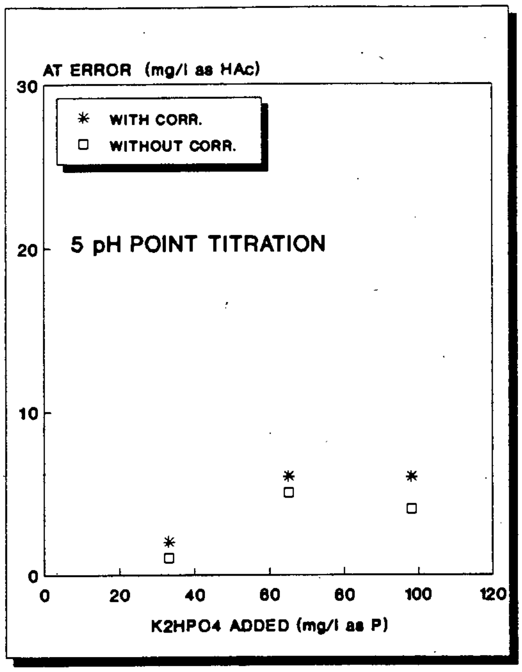

Fig 6.7: Effect of error in total species concentration of phosphate subsystem on determination of A_T by the 5 pH point titration; varying concentrations of K_2HPO_4 in base solution of 1990 mgNaHCO$_3$/ℓ as CaCO$_3$. Two values were determined for A_T: (1) taking into account the phosphate subsystem giving a corrected A_T, and (2) not taking into account the phosphate subsystem giving an uncorrected A_T. Both A_T values were subtracted from a separately determined expected A_T value to give the respective errors.

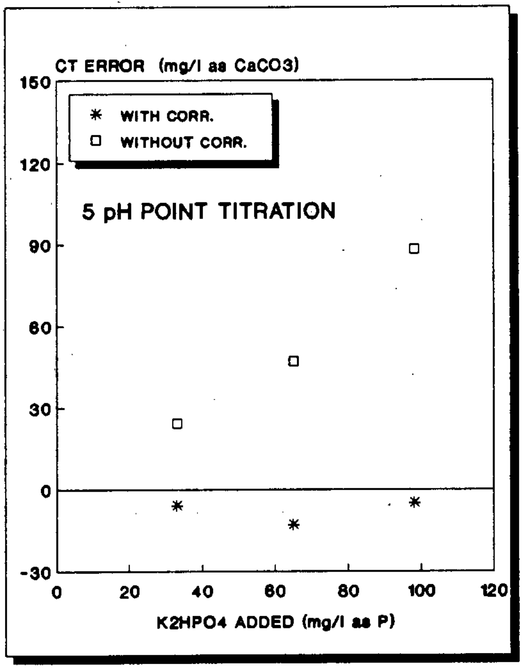

Fig 6.8: Effect of error in total species concentration of phosphate subsystem on determination of C_T by the 5 pH point titration; varying concentrations of K_2HPO_4 in base solution of 1990 mgNaHCO$_3$/ℓ as CaCO$_3$. Two values were determined for C_T: (1) taking into account the phosphate subsystem giving a corrected C_T, and (2) not taking into account the phosphate subsystem giving an uncorrected C_T. Both C_T values were subtracted from a separately determined expected C_T value to give the respective errors.

Industrial wastes augmented with HAc at different concentrations

Having analysed in fair detail the potential errors of the 5 pH point titration method on made up solutions, the method was now applied to real life aqueous wastes. The difficulty here is that the weak acid/bases in the sample are obviously unknown and need to be determined. To evaluate the reliability of the 5 pH point titration method for these solutions one approach would be to augment the solution with a known mass of, say, HAc and check if the derived estimates reflect the increase in HAc. In this fashion the effluents from laboratory scale UASB reactors treating (1) brewery (lauter tun), and (2) wine distillery wastes were tested. In both instances the 5 pH point titration method and a colorimetric test for SCFA (Montgomery *et al.*, 1962) indicated that the effluent as sampled contained low concentrations of SCFA.

The test procedure was as follows: On a filtered sample (filter paper, Schleicher und Schuell 505) taken from the reactor effluent, the ammonium and phosphate concentrations of the sample were determined according to Standard Methods (1989) and included in the algorithm. The ionic strength of the sample was approximated through measurement of the specific conductivity (see Appendix A). One 5 pH point titration was carried out to determine SCFA (as A_T), H_2CO_3*alkalinity and ΔpH. Following this a further five samples were taken, prepared identically to the first sample and augmented with HAc to give, say 100 mg/ℓ as HAc in addition to the SCFA originally present in the sample. For each one a 5 pH point titration was performed to determine SCFA (as A_T), H_2CO_3*alkalinity and ΔpH. This procedure was repeated daily on new batches of effluent: sequentially, the samples were augmented with increasing concentrations of HAc in the following steps: 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mg/ℓ as HAc. In this way, over a period of ten days, ten sets of titration data and results were obtained for the brewery waste. Likewise, over another ten days, ten sets for the wine distillery waste; all these data and calculated results are listed in Appendix R.

To evaluate the measured results of HAc and H_2CO_3*alkalinity, the expected results had to be determined. This was done as follows: For HAc the expected values were found by subtracting the SCFA concentration (given as HAc) of the sample *not* augmented with HAc from the respective sample augmented with HAc. For the H_2CO_3*alkalinity the procedure used above, when testing mixtures of HAc and $NaHCO_3$ solutions, had to be extended to include phosphate (ammonium was not considered because of its insignificant buffering action at and below the initial pH of the sample, see above): again it was assumed that HAc acts as a strong acid in the range of the initial pH values of the samples augmented with HAc. Because of the presence of phosphate in the brewery and wine distillery waste (besides the dominating carbonate subsystem) HAc decreases the alkalinity not only of the carbonate but also the alkalinity of the phosphate subsystem (Loewenthal *et al.*, 1991). To isolate the decrease in the carbonate subsystem alkalinity (due to HAc addition) we need to determine the alkalinity contribution of the phosphate subsystem between the initial pH of the sample (before addition of HAc) and the pH after addition of HAc, see Chapter 4. Subtracting the phosphate subsystem alkalinity contribution from the added HAc, gives the change in carbonate subsystem alkalinity due to the addition of HAc; knowing the change in carbonate subsystem alkalinity the $H_2CO_3^*$alkalinity after HAc addition (expected alkalinity) can be calculated.

In Figs 6.9 and 6.11 the expected HAc concentrations for the brewery and wine distillery wastes respectively are plotted versus the respective measured values. In Figs 6.10 and 6.12 the expected and measured $H_2CO_3^*$alkalinities of the brewery and wine distillery wastes are plotted versus the added HAc concentrations. The plots in Figs 6.9 and 6.11 show close correlation between the measured and expected HAc values indicating that the 5 pH point titration is capable of detecting, quite accurately, accumulation of HAc in the UASB reactor effluent treating the two types of wastes. The plots in Figs 6.10 and 6.12 show that in general the measured alkalinity consistently was higher than the expected; from the numerical data the deviation averaged about 3 percent, with a maximum deviation of 5 percent of the expected value. A possible reason for this deviation may be that weak acid/bases other than the carbonate, ammonium and phosphate were present in the sample thereby also buffering against pH change due to the addition of HAc – this would lead to a higher initial pH of the sample and, consequently, to an increase in measured $H_2CO_3^*$alkalinity.

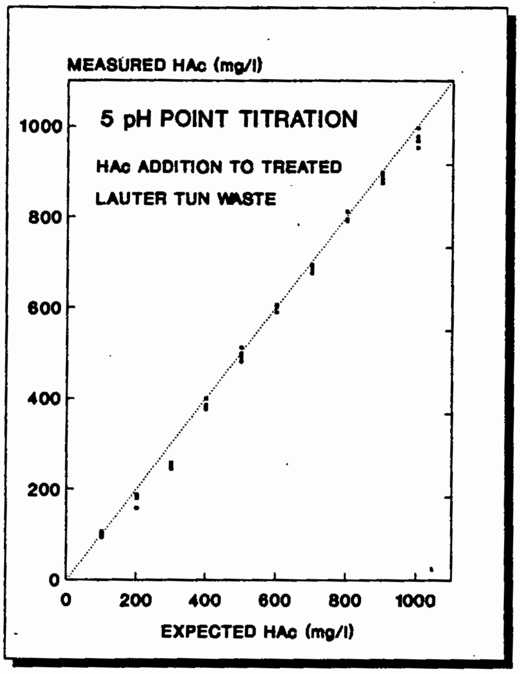

Fig 6.9: Addition of HAc to treated (in laboratory UASB reactor) lauter tun waste and measurement of added (expected) HAc concentrations by the 5 pH point titration method.

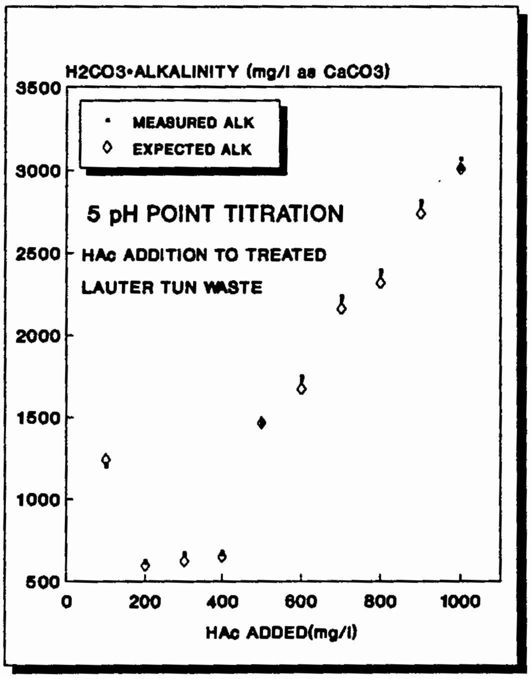

Fig 6.10: Addition of HAc to treated (in laboratory UASB reactor) lauter tun waste and measurement of H_2CO_3*alkalinity after addition of HAc. These results were obtained over a period of time, under different operating conditions, i.e. different H_2CO_3*alkalinity concentrations in the effluent of the UASB reactor.

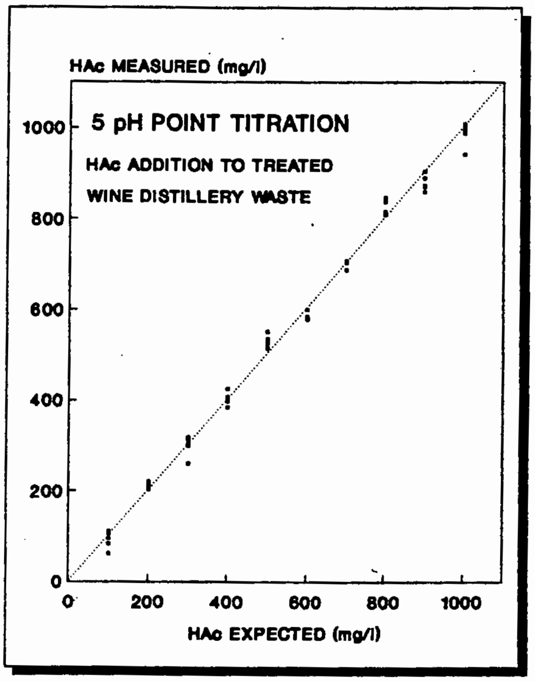

Fig 6.11: Addition of HAc to treated (in laboratory UASB reactor) wine distillery waste and measurement of added (expected) HAc concentrations by the 5 pH point titration method.

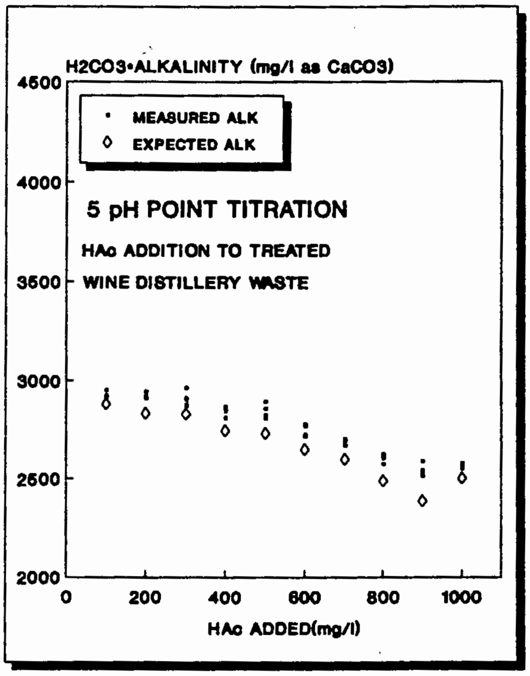

Fig 6.12: Addition of HAc to treated (in laboratory UASB reactor) wine distillery waste and measurement of H_2CO_3*alkalinity after addition of HAc. These results were obtained over a period of time, under different operating conditions, i.e. different H_2CO_3*alkalinity concentrations in the effluent of the UASB reactor.

Conventional chemical versus 5 pH point titration method

In the experiments above, the 5 pH point titration method has been tested for HAc in solutions containing various concentrations of H_2CO_3*alkalinity and in some cases, the phosphate and ammonium subsystems. However, in anaerobic digester liquids besides acetic acid, other SCFA, e.g. propionic and butyric acid, are also found. It has been stated earlier that because the pK_a values of the different SCFA are located closely together, the SCFA subsystem is treated as equivalent acetic acid when determined through the 5 pH point titration method. To enquire if this approach to determine the SCFA was valid, the 5 pH point titration was compared to the conventional chemical method for SCFA developed by Montgomery *et al.* (1962) on samples taken daily from the effluent of laboratory scale UASB systems treating brewery and wine distillery wastes.

In the initial exploratory study samples were filtered through ordinary filter paper (Schleicher und Schuell, 505); subsequently divided and tested for A_T, using the 5 pH point titration method, and using the method of Montgomery *et al.* (1962). Montgomery's method involves spectrophotometry, and the tests showed that his method is very susceptible to residual colour present in the sample. Through comparison with gas chromatography it was found that colour removal prior to testing was necessary to obtain reliable results. Accordingly in subsequent tests the samples were flocculated using aluminium sulphate (8 ml of saturated aluminium sulphate per 100 ml of sample) to remove the colour. Flocculation influenced the alkalinity of the sample but this did not present a problem as the objective was to evaluate the equivalence of the two methods in determining the SCFA. In both methods the sample were diluted into their respective ranges of optimal accuracy; below 600 mg/ℓ of HAc for Montgomery's method and below 500 mg/ℓ as $CaCO_3$ of H_2CO_3*alkalinity for the 5 pH point titration method, see Chapter 3.

Following the above procedure, samples were tested over a period of about 40 days. The results were subdivided into the results obtained from (1) brewery and (2) wine distillery waste; for each waste three typical sets of titration data and results are listed in Appendix S. In Fig 6.13 the results for A_T from 5 pH point titration method are plotted versus those from Montgomery's method for the system treating brewery waste. This system was operated at a low COD loading rate and thus produced very low SCFA (represented by A_T) concentrations. Nevertheless, the plot shows that at very low concentrations of SCFA the two

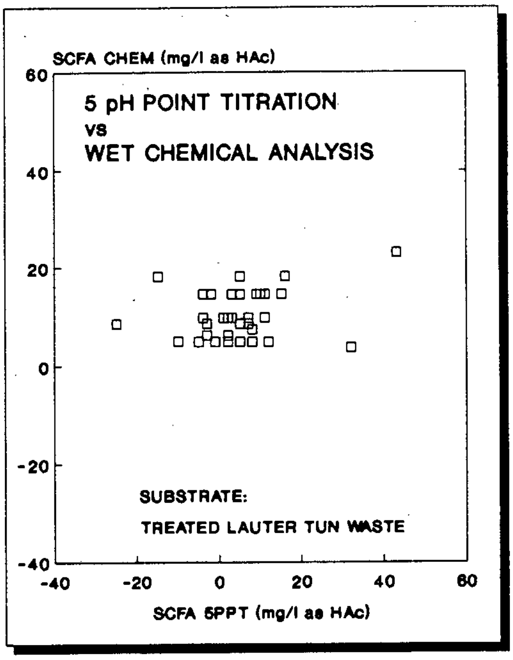

Fig 6.13: Comparison of results for SCFA obtained through wet chemical analysis (Montgomery's method) and 5 pH point titration: samples taken from laboratory scale UASB reactor treating lauter tun waste under low COD loading conditions.

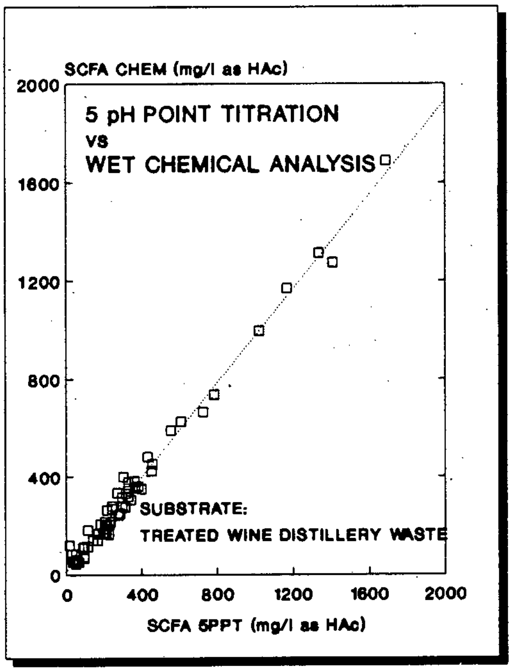

Fig 6.14: Comparison of results for SCFA obtained through wet chemical analysis (Montgomery's method) and 5 pH point titration: samples taken from laboratory scale UASB reactor treating wine distillery waste under low and high COD loading conditions.

methods are in reasonable agreement. In Fig 6.14 the results from the 5 pH point titration method are plotted versus those from Montgomery's method for the UASB system treating wine distillery waste. This plot reflects data over a wide range of concentrations of SCFA, from zero to 1800 mg/ℓ – the two methods are in close correlation; the errors appear to be random and may be due to measurement errors in both methods.

6.3 DISCUSSION AND CONCLUSIONS

In this Chapter it was shown that the 5 pH point titration method has great potential as a testing procedure for the H_2CO_3*alkalinity and SCFA for the purpose of monitoring anaerobic digesters. Compared to other similar titration procedures (see Chapter 2) the method is an improvement with regard to (1) attainable accuracy, (2) testing time required and, (3) simplicity of testing procedure.

The method can be applied to aqueous solutions containing mixtures of the carbonate and SCFA subsystems, both of *unknown* concentrations and other weak acid/bases, e.g. phosphate and ammonium, of *known* concentrations. If the total species concentrations of the additional weak acid/bases are known their influence on the determination of the carbonate and SCFA subsystems can be eliminated. Two prominent weak acid/bases in anaerobic digestion are ammonium and phosphate. Their influences are as follows: In the event that the total species concentration of the ammonium subsystems is unknown and neglected in the calculation, the error induced in the determination of the SCFA and carbonate subsystem is very small and negligible in most cases. With respect to the phosphate subsystem, if its concentration is in error, the incorrect value when incorporated in the algorithm of SCFA and carbonate subsystem determinations has minor consequences for SCFA estimates but substantively affects the estimate of H_2CO_3*alkalinity. Whether this effect is considered significant or not will depend on the type of investigation and the accuracy demanded.

The method can be readily automated if the initial pH of the sample is > 6,7; in this event only a strong acid titration is required to four lower pH points. If however the initial sample pH is < 6,7 the pH needs to be raised to ≃ 6,7 by addition of strong base. The requirement here is only to raise the pH; it is not necessary to standardize the strong base or to measure the strong base added – the amount of titrant from pH_1 (6,7 ± 0,1) to the lower pH values only needs to be monitored because the method *inter alia* basically determines C_T from the pH pairs and C_T is not affected by the titration to pH_1.

The method allows a check on the pH probe and provides an estimate of the systematic pH error where this may be present due to poor calibration or due to the residual liquid junction effect etc..

6.4 CLOSURE

After studying the work reported in these chapters on the 3, 4 and 5 pH point titration method, the reader might form the opinion that this method is complicated, not practical, and unsuitable for routine monitoring. However, the user need only do the rather simple 5 pH point titration in accordance with the guidelines provided (see Appendix V), insert these data in a PC computer, see Appendix W and X) and the results will be available without further effort.

6.5 REFERENCES

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CHAPTER 7

LAUTER TUN (BREWERY) WASTE IN UASB SYSTEMS – FEASIBILITY, ALKALINITY REQUIREMENTS AND pH CONTROL

ABSTRACT

Lauter tun (brewery) waste developed a pelletised sludge bed and was found to be suitable for treatment in a laboratory UASB reactor. Product formation along the line of flow in the bed was similar to that when treating a pure carbohydrate, apple juice substrate. Virtually no H_2CO_3*alkalinity was generated by the process; the H_2CO_3*alkalinity required to buffer the minimum bed pH to > 6,7 had to be supplied from an external source. On a flow through UASB reactor with a base influent COD (COD_b) = 4000 mg/ℓ, the H_2CO_3*alkalinity requirement was 0,9 mg as $CaCO_3$ per mg COD_b. By imposing a recycle from the effluent to the influent, the H_2CO_3*alkalinity required per mg COD_b was reduced substantially. H_2CO_3*alkalinity (in the form of NaOH) was added to the recycle stream, not to the base influent flow; when added to the base influent flow the pH increased to 11 and, apparently, trace elements precipitated leading to partial failure of the process; when added to the recycle stream the pH down stream did not rise above 8,5 and the process operated satisfactorily. In a UASB system with a recycle the H_2CO_3*alkalinity to be supplemented to maintain a near neutral pH was assessed using the effluent H_2CO_3*alkalinity as reference parameter, *not* the influent H_2CO_3*alkalinity, to take into account the internally generated H_2CO_3*alkalinity. For a COD_b = 13 000 mg/ℓ and a practical COD loading rate of 9 kg/(m³ sludge bed.d), a recycle ratio as high as 22:1 reduced COD_b to an effective influent COD of 570 mg/ℓ and did not significantly influence COD reduction (> 90 percent) or effluent SCFA (about 50 mg/ℓ as acetic acid).

7.1 INTRODUCTION

With the 5 pH point titration available to measure the H_2CO_3*alkalinity (see Chapter 5 and 6), we will now investigate the H_2CO_3*alkalinity requirements for different types of substrates (wastes) to control the pH in UASB systems.

Substrates can be divided into two basic categories: (1) substrates that do not generate internal buffer (carbonate subsystem alkalinity) and hence depend completely on buffer from an external source to control the minimum pH in the bed, and (2) substrates that generate internal buffer, say, due to deamination or reduction of sulfate, and hence are partially or completely independent of buffer from an external source for pH control. In this Chapter we will study the behaviour of a waste of the first category, i.e. a waste producing very little internal buffer, lauter tun waste. (In the next chapter the behaviour of a waste in the second category will be studied).

In a brewery plant, there are a number of different waste streams generated from the bottling hall, cleaning of fermentation tanks, filter unit, wort kettle and lauter tun. Some of these waste streams, e.g. the wash water from the bottling hall, may contain substances inhibitory or toxic to anaerobic microorganisms. In the particular brewery from which the waste batches were obtained, all the waste streams discharge to a central holding tank and from there, controlled discharge to a sewer. Of all the waste streams, that from the lauter tun contributed the main mass of COD generated in the brewing process. Lauter tun waste has a high carbohydrate content so that it has potential for treatment in a UASB system. Furthermore, in the particular brewery the lauter tun waste stream could be separated easily from the other waste streams thereby avoiding the risk of interference from potentially inhibitory or toxic chemicals. Accordingly, the lauter tun waste was selected for study.

The study of the lauter tun waste stream, in a laboratory scale UASB reactor, was subdivided into two parts:

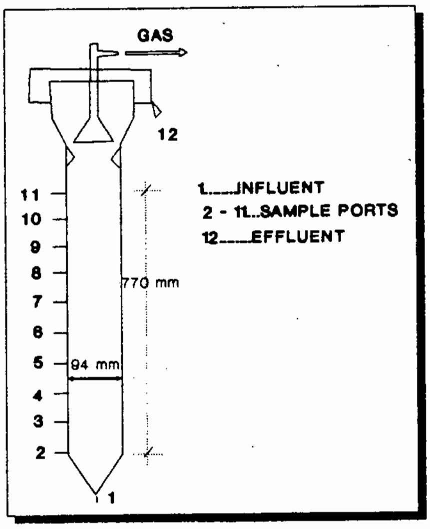
- Feasibility study of the treatment of lauter tun waste in a UASB system, to ascertain formation of a pelletised sludge bed and to study the product formation pattern along the line of flow of the reactor.

- Investigation into the effects of recycling on (1) system performance, and (2) mass of $H_2CO_3^*$alkalinity required to maintain a near neutral minimum pH in the lower part of the sludge bed.

7.2 FEASIBILITY STUDY

<u>Experimental set-up</u>

For the feasibility study, a laboratory scale UASB reactor was constructed from a transparent persepex cylinder of 94 mm diameter, 900 mm high, with a conically shaped inlet at the bottom and a solid/liquid/gas seperator at the top, total reactor volume circa 6,5 ℓ, see Fig 7.1. The substrate was fed by means of a constant speed multi-channel peristaltic pump, the feed rate being controlled by an on/off timer. Gas collection was by means of a hollow inverted cone: Rising gas bubbles are deflected into the cone by a deflector collar around the inside wall of the reactor below the cone; liquid effluent discharges via an annular space between the gas collection cone and and the reactor wall, to enter a small liquid/solid seperator (1000 mℓ); clarified liquid flows over a launder into the collection vessel while solids, which settle out, are returned into the reactor by gravity. Ten sample ports were installed evenly spaced up the reactor wall for sampling along the line of flow. Temperature was maintained at 30° C by a thermostat controlled electrical heating tape wrapped around the reactor.



<u>Fig 7.1:</u> Schematic diagram of laboratory UASB reactor

Waste water characteristics

The influent feed stock (lauter tun waste) was collected from the brewery and stored at 4°C. The waste batches contained different low concentrations of particulate material; in order to eliminate this variable the waste was settled and the supernatant only used as feed to the UASB reactor. The characteristics of the supernatant of the batch used in the feasibility study are shown in Table 7.1. The settled supernatant contained principally carbohydrates; tests for short-chain fatty acids (SCFA) showed that these were present only in minor concentrations, less than 100 mg/ℓ as HAc.

Table 7.1: Characteristics of settled lauter tun waste (batch 0)

Soluble COD fraction	98 %
Soluble COD concentration	12 000 mg/ℓ
inorg-N	near zero
TKN	136 mgN/ℓ
Phosphorus	10 mgP/ℓ
pH	5,2

Each day the feed to the reactor was made up from the settled feed stock by diluting to a COD of 4000 mg/ℓ using tap water. The daily feed was kept refrigerated at 4°C. The feed composition after dilution is given in Table 7.2.

Table 7.2: Characteristics of diluted settled lauter tun waste

Soluble COD concentration	4000 mg/ℓ
inorg-N	near zero
TKN	45 mgN/ℓ
Phosphorus	3 mgP/ℓ
pH	6,0

Assessment of feed for treatment in a UASB system

The feed as shown in Table 7.2 was assessed for suitability as a substrate for the pelletised UASB system, against the prerequisites set out by Sam–Soon *et al.* (1987), ie. (1) high hydrogen partial pressure ($\bar{p}H_2$) environment, (2) cysteine deficiency, (3) excess supply of nitrogen and (4) a near neutral minimum bed pH.

With regard to (1), the high $\bar{p}H_2$ environment, the lauter tun waste contains a high fraction of carbohydrates that should yield hydrogen under high $\bar{p}H_2$ conditions when undergoing acidogenesis in the lower part of the sludge bed.

With regard to (2), cysteine deficiency, no judgment was possible; it was presumed that there would be a cysteine deficiency.

With regard to (3), excess ammonium supply, Sam–Soon *et al.* (1990) suggested a minimum of 0,02 mgN/mg influent COD for optimum pellet production. The settled and diluted lauter tun waste contained virtually no ammonium but contained organic nitrogen of about 45 mgN/ℓ, giving 0,011 mgN/mg influent COD. There was no certainty as to whether the organic nitrogen would be deaminated fast enough to satisfy or partially satisfy the nitrogen requirement for pelletisation in the lower part of the reactor. Besides nitrogen, the other macro nutrient, phosphorus, also appeared to be in short supply, COD:P = 350:0,3, whereas an adequate COD:P ratio should be near to 350:1. To supplement the nutrients in the influent a stock solution containing nitrogen and phosphorus was made up as shown in Table 7.3. Addition of 20 mℓ of this stock solution per litre of diluted lauter tun waste increased the COD:P ratio to 350:1 and the TKN/COD ratio to 0,024 mgN/mgCOD.

With regard to (4), a near neutral bed pH, the influent waste flow had no or virtually no H_2CO_3*alkalinity as indicated by the pH of 6,0, and could generate only a small amount of H_2CO_3*alkalinity from deamination of the organic nitrogen – addition of H_2CO_3*alkalinity would be required. In practice the preferred dosing chemical would be NaOH, mainly for economic reasons and convenience in preparation of the dosing solution. The OH^- ions (of NaOH) react with the CO_2 (H_2CO_3*) generated in the system to form principally HCO_3^- and CO_3 species depending on the pH in the system. From preliminary tests, with NaOH dosing in the influent for an H_2CO_3*alkalinity addition of 1,2 mg/mg influent COD (as suggested by Sam–Soon et al) the pH in the feed rose to > 12.

Table 3: Trace element and nutrient stock solutions

Trace element	Concentration g/ℓ
H_3BO_3	0,05
$FeC\ell_2.{}_2H_2O$	2,00
$ZnC\ell_2$	0,05
$MnSO_4$	0,5
$CuC\ell_2\ 2H_2O$	0,03
$(NH_4)_6\ MO_7\ 0_{24}.4\ H_2O$	0,05
$AlC\ell_3.6H_2O$	0,05
$CoC\ell_2.6H_2O$	2,00
$MnC\ell_2$	0,25
$MgC\ell_2$	1,00
EDTA	0,05
$Ni\ C\ell_2.6H_2O$	0,25
$HC\ell$	1mℓ

Nutrients	Concentration g/ℓ
$NH_4C\ell$	10,00
K_2HPO	4,00

However, there was uncertainty as to what pH level would be established in lower part of the sludge bed with the OH ions as sole alkalinity source because this would depend on the rate at which OH^- ions would react with the CO_2 generated in the system. Accordingly, for the flow through system of the feasibility study, it was decided to use NaOH in combination with $NaHCO_3$ in the following proportion: NaOH = 875 mg/ℓ as $CaCO_3$ and $NaHCO_3$ = 2680 mg/ℓ as $CaCO_3$, giving a total supplementation of H_2CO_3*alkalinity = 3555 mg/ℓ as $CaCO_3$. The pH in the feed after alkalinity supplementation stabilized at 9,1. The ratio of (influent alkalinity concentration)/(influent COD concentration) was now $3555/4000 \simeq 0,9$. This value was lower than the minimum ratio of 1,2 suggested by Sam–Soon *et al.* (1991) to control the minimum bed pH to > 6,6. The reasons for choosing a lower Alk/COD ratio were twofold; (1) in this study a different substrate was investigated i.e not entirely made up from carbohydrates, and (2) the COD loading rate on the sludge bed at the beginning of the feasibility study was low in which event, from the data obtained by Sam–Soon *et al.* (1991), the pH in the lower part of the sludge bed generally did not decline as much as at a higher COD loading rate. If at any stage the alkalinity addition per COD should prove to be inadequate, it could be increased. However, when the COD loading rate was increased substantially the Alk/COD ratio of 0,9 still proved to be adequate.

Trace element solution

To avoid potential deficiencies of trace element supply, a trace element solution (5 $m\ell$ per litre influent), suggested by Zehnder and Wuhrmann (1977) for enrichment cultures of methanogenic bacteria, was added to the feed. Detailed composition of this trace element solution is given in Table 7.3.

Parameters measured

The following analyses and measurements were performed on the system at 1 to 2–day intervals:

- filtered influent and effluent COD,
- filtered influent and effluent TKN and inorg–N,
- pH in settler and sample port 2 and 3, the sample ports likely to have the lowest pH,and,
- substrate flow rate.

In addition to the monitoring program above, profiles of pH, COD, TKN, inorg–N, the SCFA propionic (HPr) and acetic (HAc) were measured along the axis of the reactor at the highest loading rates applied with the system still showing stable response. Samples were taken at each sample port, starting at the top. Samples were filtered using ordinary filter paper, Schleicher und Schuell 595. For the SCFA, samples were refiltered through a 0,45 micronfilter paper (millipore) and the SCFA measured by gas chromatography using a 60/80 Carbo pack C/0,3% Carbo wax packing. COD, TKN and inorg–N were measured in accordance with Standard Methods (1989). For the feasibility study no measurements of alkalinity were undertaken.

Starting up procedure

For the start up and feasibility study the system was operated as a flow through system. From the work of Sam–Soon *et al.* (1987), for such a system if the influent COD concentration was in the range 2500 to 5000 mg/ℓ and the load less than the maximum, the process should exhibit stable response and clearly distinguished product zones. Accordingly, for the lauter tun waste an influent COD concentration of 4000 mg/ℓ was selected.

The reactor was seeded with 4 ℓ of pelletised sludge up to port No 8 from a laboratory scale UASB reactor treating wine distillery waste, to give a bed depth of 580 mm. The sludge bed volume was kept constant to port No 8 by draining excess sludge via sample port 7. The COD concentration was kept constant throughout the starting up period, the COD loading rate being increased by increasing the flow rate. The rate of increase in COD loading was controlled by monitoring the effluent COD (to ensure that the percentage COD removal did not decline substantially when the COD loading rate was increased); the minimum bed pH was monitored to ensure that this did not decline below 6,6. In Fig 7.2 the COD loading rate is plotted versus time, together with the percentage COD removal. From the plots the starting up period can be divided into two periods, (1) an initial period of adaptation of the pelletised sludge to the new substrate with a slow sequential increase in COD loading rate (about 35 days), and (2) a second period of rapid COD loading increase (about 10 days).

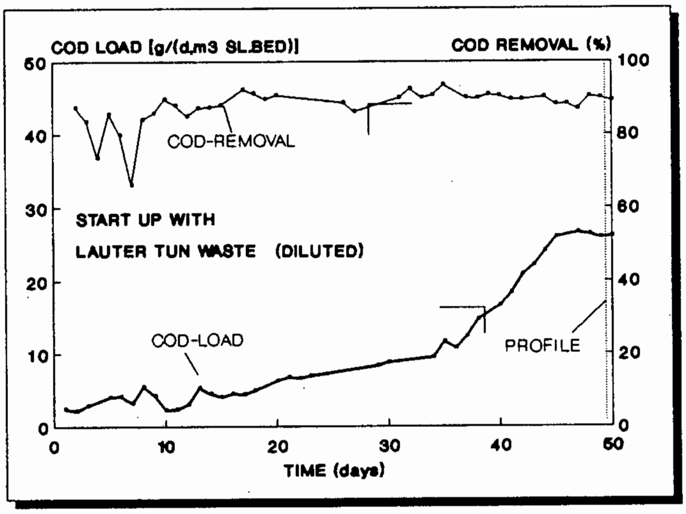


Fig 7.2: Start up period of *flow through* laboratory UASB reactor seeded with 4 ℓ of pelletised sludge from a laboratory scale UASB system treating wine distillery waste. The reactor was fed with diluted lauter tun waste (using tap water); the diluted influent COD (4000 mg/ℓ) was kept constant during the start up period, i.e. the COD loading rate was increased by increasing the flow rate. The term "profile" indicates the time location for measuring various parameters along the line of flow of the reactor (see Fig 7.3).

The plots in Fig 7.2 show that during the initial adaptation period caution had to be exercised in increasing the COD loading rate. At the beginning of the initial adaptation period a COD loading rate of 2 kgCOD/(m^3 sludge bed. d) was applied, which was then gradually increased to about 5 kgCOD/(m^3 sludge bed. d) by the end of the 35 day period. At the beginning of the initial adaptation period, the process was very sensitive to increases in COD loading but adapted well towards the end.

With regard to the second (10 days) period, the rapid increase in COD loading rate from 5 to 25 kgCOD/(m^3 sludge bed. d) was readily accepted by the system, with the COD removal remaining greater than 90 percent, indicating that the sludge bed was well adapted to the new substrate. At the end of the 10 day period the system was operating at steady state with 25 kgCOD/(m^3 sludge bed.d). Further increase in COD loading rate was not envisaged for following reason: On occasion gas collected at random levels in the sludge bed to lift the sludge mass above up to the settler. The pellets appeared to be relatively lighter than those obtained by Sam–Soon *et al.* (1987) when treating apple juice at about the same COD loading rates. These physical factors forced the decision not to consider higher loading rates.

After operating the system, apparently stable, at its maximum imposed loading rate of 25 kg/(m^3 sludge bed.d) for 5 days, profiles of pH, COD, TKN, inorg–N, HAc and HPr were measured.

Product formation

Sam–Soon *et al.* (1987) in their studies of flow through UASB systems suggested measurement of profiles of pH, COD, TKN, inorg–N, HAc and HPr along the line of flow of the reactor, to identify biochemical processes taking place at different levels in the sludge bed. The profiles of the various products, in particular TKN, inorg–N, HAc and HPr provided information from which Sam–Soon *et al.*(1987) developed their hypothesis on pelletisation. In their study of laboratory scale UASB reactors fed with diluted apple juice concentrate they identified different zones of product formation in the bed along the reactor, designated as (1) lower active, (2) upper active, and (3) an upper inactive zones.

The lower active zone was characterised by a significant decrease in pH, an unexpectedly high uptake of inorg–N, accumulation of HAc and HPr and rapid decrease in soluble COD. The upper limit of the lower active zone was taken where the HPr attained its maximum value. In the upper active zone the pH increased, the concentration of HAc and HPr decreased to near zero and the COD decreased further to a stable minimum value. The upper limit of this zone was taken where the rate of change in SCFA concentration decreased to near zero. In the upper inactive zone virtually no changes in product formation took place.

A study of the product formation in these zones led to the following: In the lower active zone the accumulation of HPr indicates a high $\bar{p}H_2$ environment and from the uptake of inorg–N (and information in the literature) they hypothesized that the high $\bar{p}H_2$ induces the production of amino acids in cells of *Methanobrevibacter arboriphilus* but protoplasm formation is limited by the external supply of the amino acid cysteine. The excess amino acids produced are extruded as a biopolymer (polypeptide). This biopolymer forms the basic matrix for pellet formation capturing both *Methanobrevibacter arboriphilus* and other anaerobic microorganisms.

Having obtained profiles on the pelletised bed treating lauter tun waste, these were compared with the profiles observed by Sam–Soon *et al.* (1987), to identify possible similarities in the response. The profiles of pH, COD, HAc, HPr, org–N, inorg–N and TKN are plotted in Fig 7.3.

HAc and HPr profiles: The HAc and HPr concentrations reached their maxima between ports 2 and 3 defining the upper limit of the lower active zone. HPr and HAc thereafter declined rapidly up to port 5 defining the limit of the upper active zone. Above port 5 HAc and HPr remained virtually constant up to the top of the bed at port 8, defining the inactive zone. According to Sam–Soon *et al.* (1987) HPr accumulation would occur only in a high $\bar{p}H_2$ environment. Thus the observed accumulation of HPr indicated that the prerequisite of high $\bar{p}H_2$ was satisfied when treating lauter tun waste. Both the HAc and HPr profiles reached stable minimum values well within the sludge bed indicating that the further increase in COD load was possible.

pH profile: Within the lower active zone the pH declined from 8,6 to about 6,7; thereafter the pH increased to a stable value of 7,2 in the upper active and inactive zones, sludge blanket and settler. The decline in pH coincided with the increases in HAc and HPr. Comparing the pH profile with those reported by Sam–Soon *et al.* (1987), a similar pattern is observed.

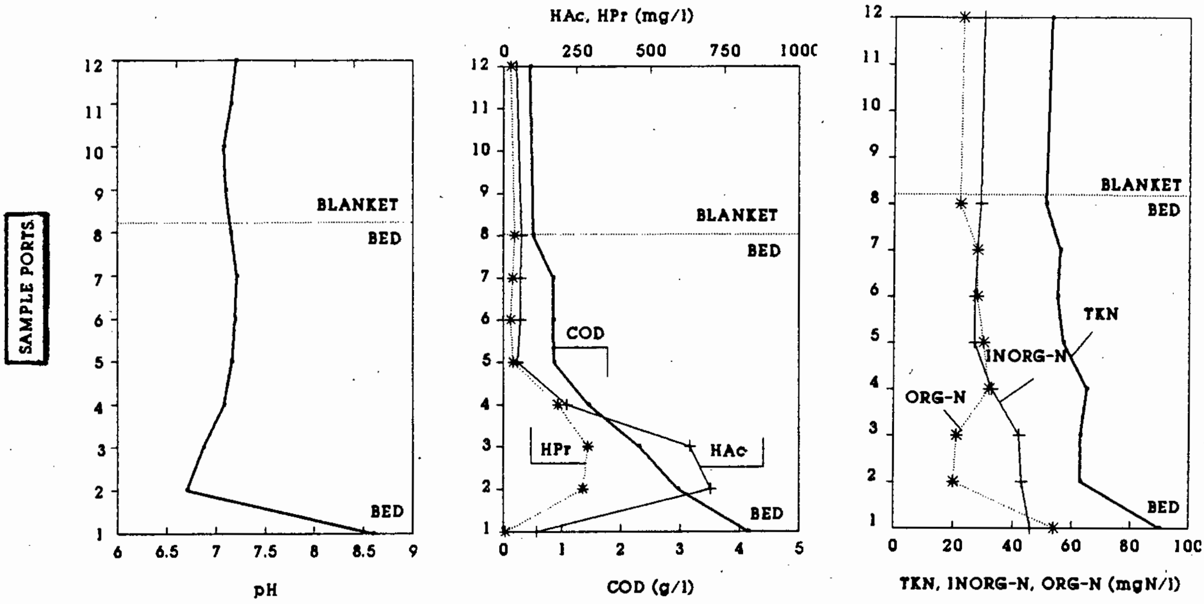


Fig 7.3: *Flow through* laboratory UASB reactor treating *diluted* lauter tun waste: Profiles of pH, COD, HAc, HPr, TKN, inorg–N and org–N along the line of flow. Flow rate: 25 ℓ/d, influent COD concentration: 4000 mg/ℓ, COD loading rate: 25 kgCOD/(m^3 sludge bed. d).

COD profile: The COD decreased at a high rate from 4100 mg/ℓ to 900 mg/ℓ up to sample port 5. Above this level the rate of COD removal was reduced and the COD concentration stabilized at about 400 mg/ℓ at the top of the sludge bed and remained unchanged in the effluent. The more rapid rate of COD removal in the lower part of the sludge bed was similar to that observed by Sam–Soon *et al.* (1987).

TKN, inorg–N and org–N profiles: The org–N profile showed a decline of org–N in the lower part of the sludge bed, due to deamination, followed by a slight increase in the upper part of the sludge bed probably due to pellet breakup. With regard to the inorg–N profile, Sam–Soon *et al.* observed a marked decrease of inorg–N in the lower part of sludge bed. In the diluted lauter tun waste profile, however, inorg–N profile showed little change; this may be attributed to the simultaneous generation of inorg–N (due to deamination of the org–N present in the influent) and uptake of the generated inorg–N due to pelletisation. The uptake of nitrogen is more effectively demonstrated in the TKN profile – a significant decrease of 28 mgN/ℓ (from 90 to 62 mgN/ℓ) occurred below sample port 2. In this part of the sludge bed about 1200 mgCOD/ℓ were removed giving a (N removed)/(COD removed) ratio of 0,02. Under 'normal' anaerobic fermentation conditions, nitrogen requirements would be approximately 0,004 mgN/mgCOD for protoplasm synthesis. Thus the observed nitrogen removal was about 6 times higher than that normally expected, supporting the hypothesis that pellet formation was taking place.

Pellet bed growth: The pelletised sludge bed increased in volume, however, quantitative measurements were not undertaken as the objective in the feasibility study was limited to a qualitative assessment of pelletisation only.

Conclusions

The information gathered during the feasibility study can be summarized as follows:

- The pH, COD, HAc and HPr profiles were similar to those observed by Sam–Soon *et al.* (1987).
- The pelletised bed mass increased.

These observations indicate that lauter tun waste gave rise to a similar pattern of product formation along the line of flow in the bed as that found by Sam–Soon *et al.* (1987) for pure carbohydrate substrate. It was concluded that lauter tun waste was suitable for treatment in a UASB systems.

7.3 RECYCLING AND ALKALINITY REQUIREMENTS

The feasibility study indicated that lauter tun waste in a flow through UASB system (no recycle) would produce a pelletised sludge bed and, at a COD loading rate of 25 kg/(m^3 sludge bed.d), an H_2CO_3*alkalinity/COD ratio in the influent of 0,9 was adequate to sustain a minimum bed pH above 6,7. However addition of H_2CO_3*alkalinity of this magnitude in a full scale UASB plant, would make the treatment of lauter tun waste, or similar wastes, too expensive. Sam–Soon *et al.* (1991) when treating apple juice wastes in a UASB system also found uneconomically high alkalinity requirements of 1,2 to 1,6 mg of alkalinity (as $CaCO_3$) per mg feed influent COD. They introduced a recycle from the effluent to the influent, for two purposes:

(1) To dilute the base influent COD concentration into a range of 2500 to 5000 mg/ℓ for reason that they found the process to respond in a stable fashion within this influent concentration range.

(2) To reduce alkalinity requirements by recovery of the alkalinity from the reactor effluent; with the recycle they found that the base alkalinity requirements (i.e alkalinity requirements without recycle) could be reduced by a factor: influent flow/(influent flow + recycle flow). This factor was established for base influent COD concentrations ranging from 2500 to 8500 mg/ℓ and recycle ratios up to 3:1.

In the present study the influent COD concentrations of the undiluted lauter tun waste ranged from 9000 to 13 000 mg/ℓ, significantly higher than the COD concentrations examined by Sam–Soon *et al.* (1991). With the higher influent COD concentrations it was now of interest to investigate the process response at recycle ratios higher than 3:1 in order to (1) dilute the influent into a COD range that provides stable operation, and (2) to reduce the alkalinity requirements.

With regard to the dilution aspect, an alkalinity requirement that may be economically acceptable may demand a recycle ratio of such magnitude that the influent COD concentration would be reduced below the lower limit of the suggested COD range of 2500 to 5000 mg/ℓ. It was of interest to enquire if stable operation could be achieved with lauter tun waste at diluted influent COD concentrations (by means of a recycle) of less than 2500 mg/ℓ, when treating undiluted influent waste concentrations ranging from 9000 to 13 000 mgCOD/ℓ.

Preliminary remarks

With regard to the H_2CO_3*alkalinity requirements, Sam–Soon *et al.* formulated the reduced alkalinity requirements per litre base influent flow, when imposing a recycle, as follows:

$$\text{Alk}/\ell\,\text{influent} = C \cdot COD_b \cdot \frac{Q}{Q + Q_r} = C \cdot COD_b \cdot \frac{1}{1 + r} \qquad (7.1)$$

where:

Alk/ℓ influent = H_2CO_3*alkalinity required in base influent flow

C = mg H_2CO_3*alkalinity required per mg base influent COD without recycle.

Q = base influent flow, ℓ.

Q_r = recycle flow, ℓ.

r = recycle ratio, Q_r/Q.

COD_b = COD concentration in undiluted influent flow, mg/ℓ.

Within the $[COD_b \cdot 1/(1 + r)]$ range of 2500 to 5000 mg/ℓ, Sam–Soon *et al.* assumed that C would remain substantially constant, independent of the recycle ratio r, C ranging between 1,2 to 1,6. However their data was insufficient to check the validity of this assumption.

In formulating an approach to testing this assumption the following aspects should be considered: In UASB systems operating at their maximum COD loading rates the systems can be expected to give rise to a behaviour deviant from that under lower COD loading rates. This would be pertinent particularly with respect to H_2CO_3*alkalinity requirements. Of greater practical importance would be to study the H_2CO_3*alkalinity requirements under stable operating conditions, i.e. lower COD loading rates. That is, one should direct the enquiry to the H_2CO_3*alkalinity requirements for COD loading rates likely to be applied in practice. From the feasibility study the maximum COD load under which the process did not exhibit overloading conditions explicitly, was 25 kg/(m^3 sludge bed. d); a practical COD loading rate would range between a third or half of the maximum, that is, 9 to 12 kgCOD/(m^3 sludge bed. d). In the feasibility study the lauter tun waste was diluted to 4000 mgCOD/ℓ, with no recycle; in the present study the real life lauter tun COD concentration to be used was 9000 to 13 000 mg/ℓ. Dilution to any selected *effective* influent COD would be achieved by a recycle. The effective influent COD concentration is defined as follows:

$$\text{Effective influent COD } (\text{COD}_e) = \frac{\text{Base infl.COD}}{(1 + r)} \ (\text{mg}/\ell) \qquad (7.2)$$

That is, the effective influent COD is the influent COD after dilution by the recycle *neglecting the COD in the recycle stream.*

In the feasibility study the H_2CO_3*alkalinity requirements were obtained for a minimum pH of 6,7 in the lower part of the sludge bed and the pH buffer was a combination of $NaHCO_3$ and NaOH. From a practical point of view a minimum bed pH higher than 6,7 should be aimed at, to guard against pH changes due to shock loads etc; a minimum sludge bed pH of say 7. Also, the buffer agent most likely to be used in practice would be NaOH.

The study, when instituting a recycle, was divided into two periods, (1) starting up and (2) investigation of alkalinity requirements.

First Start up with recycle

The experimental set–up remained the same as that in the feasibility study, except for the following modifications: (1) a wet gas meter (model No. DM3A, Alexander Wright, London) was installed to measure the volume of carbon dioxide and methane produced in the reactor, (2) the multi channel peristaltic pump, formerly used as feed pump was installed as recycle pump, and, (3) a laboratory positive displacement pump was installed as feed pump. To control the flows both pumps operated on an on/off cycle, switched on and off simultaneously.

For the starting up period a batch of lauter tun waste was collected and stored at 4°C. The waste settled in the storage drum and the supernatant only served as feed to the UASB reactor. The characteristics of the batch is listed in Table 7.4, batch 1.

Table 7.4: Characteristics of settled lauter tun waste (batch 1 and 2)

batch 1:	
Soluble COD fraction	98 %
Soluble COD concentration	9000 mg/ℓ
inorg–N	near zero
TKN	77 mgN/ℓ
Phosphorus	8 mgP/ℓ
pH	5,6
batch 2:	
Soluble COD fraction	98 %
Soluble COD concentration	13 000 mg/ℓ
inorg–N	near zero
TKN	144 mgN/ℓ
Phosphorus	11 mgP/ℓ
pH	5,3

Due to difficulties observed under under high COD loading rates when gas accumulated in the bed, mentioned in the feasibility study, it was decided to reduce the bed volume to 3 ℓ i.e. the sludge bed extended up to sample port 6 giving a bed depth of 400 mm. The reactor was seeded with 3 ℓ of pelletised sludge which had been generated during the feasibility study. The influent feed was from batch 1 (COD = 9000 mg/ℓ). The COD load applied was 12 kgCOD/(m^3 sludge bed.d), about half the maximum COD loading rate applied at the end of the feasibility study. The waste needed to be supplemented with a buffering agent to maintain a near neutral minimum pH in the lower part of the bed. The source of H_2CO_3*alkalinity was changed from ($NaOH$ + $NaHCO_3$) in the feasibility study to NaOH, added to the base influent flow. It was expected that the OH^- would react with CO_2 generated in the reactor to form $NaHCO_3$ (at pH $\simeq$ 7) and via the recycle this $NaHCO_3$ would buffer the combined influent and recycle streams and prevent an unacceptably high pH in the inlet region of the bed. The recycle initially applied was 7:1 to reduce the base influent COD to an effective influent COD of $9000/(1 + 7) = 1125$ mg/ℓ. Alkalinity supplementation was selected at 0,14 mgH_2CO_3*alkalinity (as $CaCO_3$)/(mg base influent COD), added to the feed bucket in the form of NaOH. This supplementation caused the pH in the feed bucket to rise to > 11.

Nutrients and trace elements were added to the feed bucket in approximately the same quantities per mg base influent COD as during the feasibility study, by adding 50 mℓ of the nutrient solution (giving a total of 0,023 mgN/COD) and 10 mℓ trace element solution per litre of undiluted feed.

To check the minimum bed pH, measurements were taken at the sampling ports in the lower part of the sludge bed, using the same method as that developed by Sam–Soon *et al.* (1987).

The system was operated under these conditions for about 45 days. During this period the minimum sludge bed pH did not decline below 6,8. However, the system showed a slow but steady decline in system performance; the gas production steadily declined (Fig 7.4). Pellet synthesis was taking place causing the sludge bed to rise above port 7 and needed to be wasted on occasion to maintain a 3 ℓ bed volume. The settlability of the pellets however appeared to deteriorate progressively; the sludge showed an increased tendency to be lifted to the top of the reactor and some was lost in the effluent. Also, gas tended to become trapped at a point in the bed and lifted the pellet mass above *en bloc* into the settling section. Visually, towards the end of the 45 day period, the pellets were less compact, lighter in colour and surrounded by a gelatinous sheath.

The observations above pointed towards a possible deficiency in trace element supply. Trace elements had been supplied in the same concentration ratios as during the feasibility study, however, the pH in the feed bucket was > 11, substantially higher than that in the feasibility study (pH $\simeq$ 8,6); possibly in the highly alkaline environment the added trace elements precipitated out and settled in the unstirred feed vessel and hence did not reach the sludge bed. Accordingly, it was decided to restart the system, but to apply measures that would enhance the likelihood of stable operation and would eliminate the risk of precipitation of the trace elements.

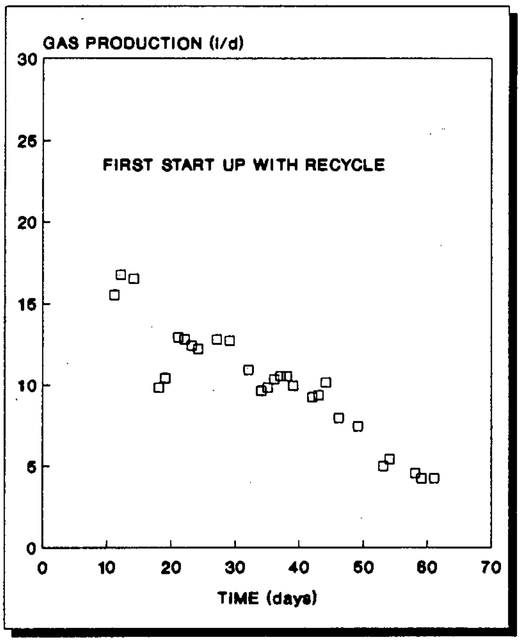


Fig 7.4: First start up period with recycle: The laboratory UASB reactor was fed with *undiluted* lauter tun waste (COD_b = 9000 mg/ℓ) and the reactor effluent recycled to the influent at a recycle ratio of 7:1; COD loading rate: 12 kg/(m^3 sludge bed. d).

Second start up with recycle

To restart the system, with recycle, the following changes were made:

- The sludge bed was drained from the reactor and replaced with 3 ℓ of new pelletised seed sludge obtained from a laboratory UASB system fed with glucose substrate.

- The feed was changed from batch 1 to batch 2, see Table 4. The COD concentration of second batch was 13 000 mg/ℓ, accordingly to restart the system the recycle rate was increased from 7:1 to 15:1 to dilute the base influent COD (COD_b) concentration to an effective influent COD of 13 000/(15 + 1) = 813 mg/ℓ.

- To make quite sure that any possible process decline would not be due to precipitation it was decided that, during the initial part of the experiment, alkalinity addition by NaOH be abandoned and replaced by $NaHCO_3$, added to the undiluted feed, at 1785 mg H_2CO_3*alkalinity (as $CaCO_3$) per litre of base influent. The change to HCO_3^- (as H_2CO_3*alkalinity source) kept the pH in the feed bucket at about 8,3 so that precipitation was unlikely.

- Addition of nutrient and trace element solutions were increased proportionally to the base influent COD: Nutrient stock solution from 50 to 65 mℓ per litre influent, to provide a 0,024 mgN/mg undiluted influent COD and a COD/P ratio of 350:1,6; addition of trace element stock solution from 10 to 15 mℓ per litre influent.

- The point of addition of the trace element solution was changed from the influent stream to the recycle stream

- In order to ensure as far as possible that failure would not be due to a lack of essential nutrients (Speece 1986), two further solutions were made up to enhance the concentrations of Fe^{++}, Ca^{++} and Mg^{++}; one stock solution containing 10 g$FeSO_4 \cdot 7\,H_2O$/ℓ and another containing 10 g$CaCl_2$/ℓ and 10 g$MgCl_2$/ℓ. For these two solutions, 10 mℓ and 20 mℓ per litre undiluted feed respectively were added to the recycle stream.

As the sludge was derived from a UASB system treating glucose the sludge had to be adapted to the lauter tun waste. Accordingly the system was restarted at a low COD loading rate of 3,5 kgCOD/(m^3sludge bed.d). This rate was kept constant for 20 days. Over this period the percentage COD removal increased steadily and stabilized at 95 %. The COD loading rate was then increased incrementally over a period of 45 days to 9 kgCOD/(m^3 sludge bed.d). The COD removal remained above 95 %, gas production increased proportionally with the COD loading rate applied (Fig 7.5), the pelletised sludge became darker and compact with no evidence of gelatinous sheathing. Clearly the process was operating satisfactorily.

From the first and second start up experiments we learn the following:

(1) In the feasibility study the process had operated satisfactorily at higher COD loading rates than in the second start up period, even though some of the trace element supplements present in the second start up were

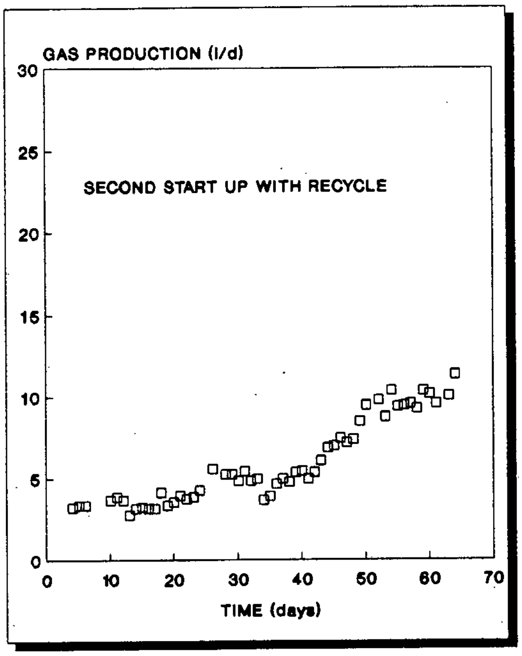


Fig 7.5: Second start up period with recycle: The laboratory UASB reactor was fed with *undiluted* lauter tun waste (COD_b = 13 000 mg/ℓ) and the reactor effluent recycled to the influent at a recycle ratio of 15:1; COD loading rate at the beginning, 3,5 kgCOD/(m^3 sludge bed. d) was increased incrementally to 9 kg/(m^3 sludge bed. d) towards the end of the second start up period.

absent in the feasibility study. It would seem that the failure in the first start up was due to the high pH in the feed causing some of the essential trace elements to become unavailable to the microorganisms, possibly by precipitation.

(2) The UASB process can be started up and operated with a high base influent COD concentration provided the base COD is suitably diluted by a recycle. An effective influent COD of about 800 mg/ℓ (base influent COD 13 000 mg/ℓ with 15:1 recycle ratio) proved to be satisfactory in this study.

(3) In the start up using pelletised sludge from a different source, the initial loading rate should always be low and the minimum bed pH maintained at about 7, to assist adaptation of the sludge to the new substrate.

Point of addition of OH^- as buffer agent

Having identified the apparent cause of failure in the first start up experiment as to be due to precipitation of essential trace elements, consideration was given to means whereby the OH^- could be employed as buffer supplement instead of HCO_3^-. Clearly the NaOH could not be added to the undiluted influent. Instead it was proposed to dose the NaOH into the recycle stream, for the following reasons: (1) the OH^- dosed would react with the dissolved CO_2 to form HCO_3^- and (2) the alkalinity in the recycle stream at the dosing point would limit the rise in pH down stream. Accordingly the H_2CO_3*alkalinity addition to the base influent was withdrawn and the same mass of H_2CO_3*alkalinity in the form of OH^- was fed at a constant rate to the recycle. At the recycle ratio of 15:1, then still in operation, the pH downstream of the point of addition was measured at 8,6. Under such low pH conditions precipitation of trace elements in the recycle was unlikely.

Alkalinity requirements with recycle

Knowing only the minimum bed pH by measurement serves as an indicator as to whether alkalinity dosage needs to be changed. However, on its own the minimum pH is not adequate because it does not permit dosing estimates to be readily made. Thus alternative parameters, related to the minimum bed pH, had to be considered which could serve as basis for dosing estimates.

Sam–Soon *et al.* (1991) selected two principal parameters, the H_2CO_3*alkalinity and the COD in the base influent stream to estimate alkalinity dosage; they argued that a certain mass of H_2CO_3*alkalinity will be required per mass of base influent COD to maintain a minimum bed pH. Hence, they linked the H_2CO_3*alkalinity in the base flow to the base influent COD concentration by,

$$H_2CO_3^*\text{alkalinity}/\ell \text{ influent} = C \cdot COD_b \tag{7.3}$$

When selecting the point in the UASB system at which the H_2CO_3*alkalinity is to be measured, for pH control and dosing estimation, the base influent readily comes to mind, as suggested by Sam–Soon *et al.* (1991). However there are arguments that the H_2CO_3*alkalinity measurement in the *effluent* stream is to be preferred, see below.

*Point of H_2CO_3*alkalinity measurement*

It was stated earlier that under stable operation conditions there is virtually no change in H_2CO_3*alkalinity from the influent to effluent in a UASB system, except if there is internal generation of H_2CO_3*alkalinity. With internal generation of H_2CO_3*alkalinity due to, say, deamination, this reaction appears to take place rapidly in the lower part of the sludge bed and should therefore provide buffer in a similar way as H_2CO_3*alkalinity present in the influent. Another situation is where there are salts of SCFA or other organic acids present in the influent; these when converted to methane and carbon dioxide generate H_2CO_3*alkalinity which will appear in the reactor effluent. If the H_2CO_3*alkalinity is measured in the base feed flow the internally generated alkalinity is not included in the measurement even though it contributes to control of pH in the system, either directly or via the recycle from the effluent to the influent. It is suggested, therefore, that in Eq (7.3) the H_2CO_3*alkalinity in the base influent is replaced by the term H_2CO_3*alkalinity in the effluent, i.e.:

$$H_2CO_3^*\text{alkalinity}/\ell \text{ effluent} = \frac{1}{1 + r} \cdot C \cdot COD_b \qquad (7.4)$$

where

H_2CO_3*alkalinity/ℓ effluent = H_2CO_3*alkalinity in the effluent flow that is associated with a near neutral minimum sludge bed pH.

With these modifications, the intent of the experiment would be to establish the factor C for lauter tun waste.

Experimental procedure

At a COD load of 9 kg/(m^3 sludge bed. d), a base influent COD concentration (COD_b) of 13 000 mg/ℓ, different recycle ratios were tested; with each recycle the mass of NaOH addition was adjusted until the minimum bed pH was ≃ 7. The minimum bed pH was measured daily in the lower part of the sludge bed at sample port 2, and at intervals at all sampling ports located in the bed, to verify that the minimum bed pH was best reflected at sample port 2 and to check the bed pH profile. The H_2CO_3*alkalinity and SCFA concentrations were measured daily in the reactor effluent using the 5 pH point titration method (see Chapter 5), together with the filtered effluent COD. The sludge bed volume was kept constant at sample port 7, by wasting excess sludge, maintaining a sludge bed volume of 3 ℓ. The average sludge bed density was approximately 36 kgVSS/(m^3 sludge bed). No data were collected on sludge production due to pressure of time (an unfortunate omission in retrospect) – reliable estimates require a long period of data accumulation under steady state conditions without disturbance of the bed, by for example, sampling for pH measurement. The study centered on the effect of the recycle ratio on process performance; the period required to adapt and attain stability after change of recycle was 15 to 20 days.

Results and discussion

Recycle and process performance: In Fig 7.6 for each period of operation of a particular recycle ratio, the average filtered effluent COD concentration and the effective influent COD concentration (COD_e) are plotted versus the recycle ratios. Similarly in Fig 7.7 the average effluent SCFA concentrations are plotted versus the recycle ratios. The base influent COD (13 000 mg/ℓ) was diluted by the recycles to an effective COD ranging from 1860 to 580 mg/ℓ under the respective recycle ratios ranging from 6 to 22. Noting the low SCFA and COD concentrations in the effluent throughout the experiment, the magnitude of the recycle ratios had virtually no effect on these effluent values. Thus it would seem that at a COD loading rate of 9 kg/(m^3 sludge bed.d), for the minimum bed pH of ≃ 7 the magnitude of the recycle ratio between 6 and 22:1 had no noticeable adverse effect on the COD removal. For the conditions imposed in the experiment the data indicate that UASB systems can function satisfactorily under high recycle ratios, i.e. for example an effective influent COD as low as about 600 mg/ℓ.

TKN uptake: In their study on nitrogen limitation on pelletisation in a UASB system fed with glucose, Sam–Soon *et al.* (1990) found that an influent TKN/COD ratio of 0,02 (mgN/mgCOD) was adequate for unimpeded pellet formation (cf TKN/COD ≃ 0,004 for anaerobic fermentation systems without pelletisation). In this study the waste contained only 0,011 mgN/mgCOD (144 mgN/ℓ influent, see Table 7.4, batch 2) and hence was supplemented with NH_4Cl to increase this ratio to a total of 0,024 mgN/mgCOD. From the daily TKN measurements in the influent and effluent an average TKN uptake of 190 mgN/ℓ was measured giving a TKN uptake/influent COD of 0,015. Clearly this high TKN/COD demand must be taken into account in assessing the nitrogen requirements for lauter tun waste. From this experiment the minimum nitrogen requirement per litre undiluted influent COD was 0,015 mgN/mgCOD. The TKN/COD uptake in this study was lower than that proposed by Sam–Soon *et al.* (1990); probably because the fraction of carbohydrate in the influent COD of the lauter tun waste was lower than that of glucose substrate.

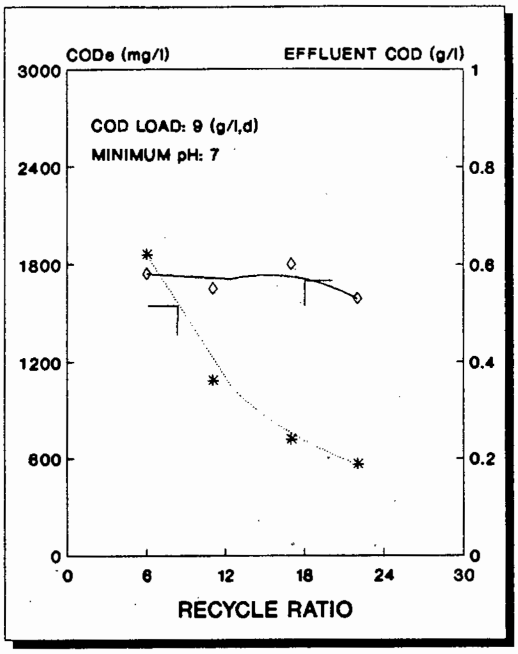


Fig 7.6: Effect of recycle ratio change or, equivalently, effect of change of effective influent COD (COD_e) on the effluent COD concentration. COD loading rate 9 kg/(m^3 sludge bed. d); COD_b = 13 000 mg/ℓ; $COD_e = COD_b \cdot 1/(1+r)$.

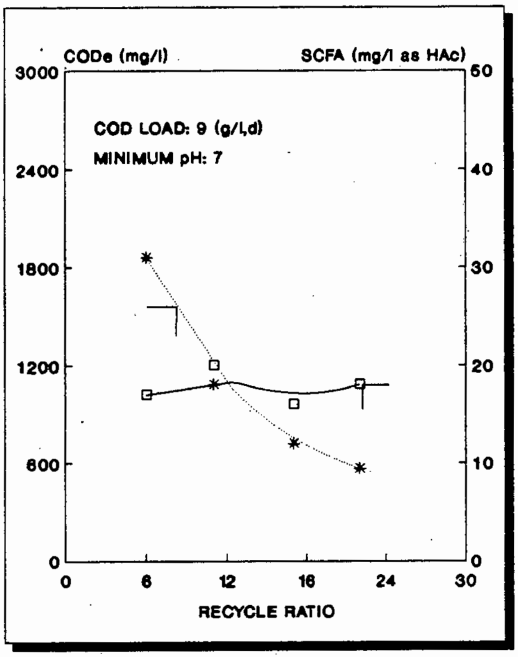


Fig 7.7: Effect of recycle ratio change or, equivalently, effect of effective influent COD (COD_e) on the effluent SCFA concentration. COD loading rate 9 kg/(m^3 sludge bed. d); COD_b = 13 000 mg/ℓ; $COD_e = COD_b \cdot 1/(1+r)$.

Bed pH profile: The minimum recycle ratio employed was 6:1, and the maximum 22:1. In Fig 7.8 the bed pH profiles are shown for these two recycles in operation. At recycle ratio = 6:1 (effective influent COD = 1860 mg/ℓ) the minimum pH was only slightly lower than the pH in upper part of the bed; at a recycle ratio = 22:1 (effective influent COD = 580 mg/ℓ) the pH was virtually constant throughout the bed. Without a detailed evaluation of the bed behaviour it is not possible to give a definite explanation for the equalizing tendency in the pH profile when the recycle ratio increased, i.e. when the effective COD decreased. Very likely this arose from the dynamic situation particularly in the lower part of the sludge bed, through interaction between flow rate, rates of acidogenesis, CO_2 production and uptake (e.g. by hydrogenotrophic methanogens), alkalinity and others.

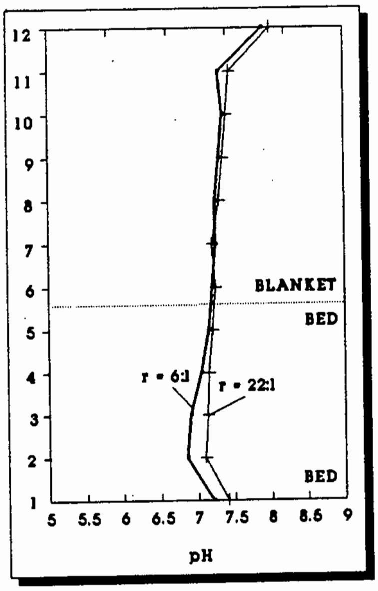


Fig 7.8: pH profiles along the line of flow of the laboratory UASB reactor at two different recycle ratios (6:1 and 22:1); COD_b = 13 000 mg/ℓ and COD loading rate = 9 kg/(m^3 sludge bed. d). Note that the influent pH (at sample port 1) is the pH of the combined base influent and recycle stream.

Behaviour of C: From the measured data, the value of C was derived in Eq 7.1, and, is shown plotted versus the recycle ratio in Fig 7.9 . Evidently C did not remain constant as hypothesized by Sam–Soon *et al.* (1991), but increased with increase in recycle ratio. The value of C at a specific loading rate was influenced by the minimum bed pH selected and therefore can be expected to be higher for a minimum pH $\simeq$ 7 than for one of pH $\simeq$ 6,7. Furthermore from the discussion above the pH established at a certain point in the bed is a function also of the dynamic situation in the bed. From these considerations, a constant C at a specific loading rate for different recycle ratios is likely to be the exception rather than the rule. Consequently, the determination of C from a flow through system using a diluted base flow would be, at best, an approximate estimate.

Despite the fact that C increases with increasing recycle ratios, the recycle ratio has a dominating effect in reducing the $H_2CO_3^*$alkalinity requirements per litre of effluent. This is illustrated in Fig 7.10 showing that the mass of effluent $H_2CO_3^*$alkalinity required per mass of base influent COD is significantly reduced as the recycle increases, i.e. the imposition of a recycle remains an effective means to reduce $H_2CO_3^*$alkalinity requirements in a UASB system.

From the behaviour discussed above it must be concluded that the magnitude of alkalinity supplementation will depend on the minimum bed pH selected, the recycle ratio, the base influent COD, the influent pH, the influent organic acids, the internally generated $H_2CO_3^*$alkalinity and the kinetics of product formation (acidogenesis, etc.) in the bed. At present, no model is available to simulate the effect of these factors on the pH in the bed. It would seem that for the present the $H_2CO_3^*$alkalinity requirements of a UASB system at a specific loading rate, under a range of recycle ratios, can be determined only by experiment.

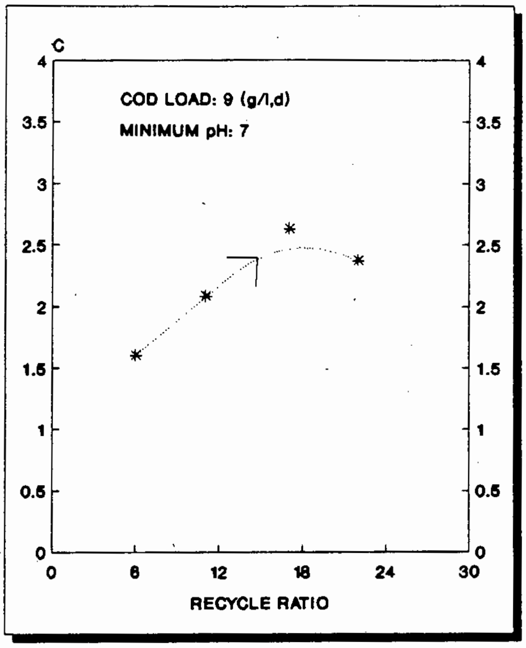


Fig 7.9: H_2CO_3*alkalinity requirements per unit mass of base influent COD to maintain a near neutral minimum bed pH treating undiluted lauter tun waste (COD_b = 13 000 mg/ℓ) when applying different recycle ratios at a constant COD loading rate of 9 kgCOD/(m^3 sludge bed. d): Relationship between recycle ratio and the factor C, see Eq (7.1). (C is expressed in mg H_2CO_3*alkalinity required per mg base influent COD without recycle).

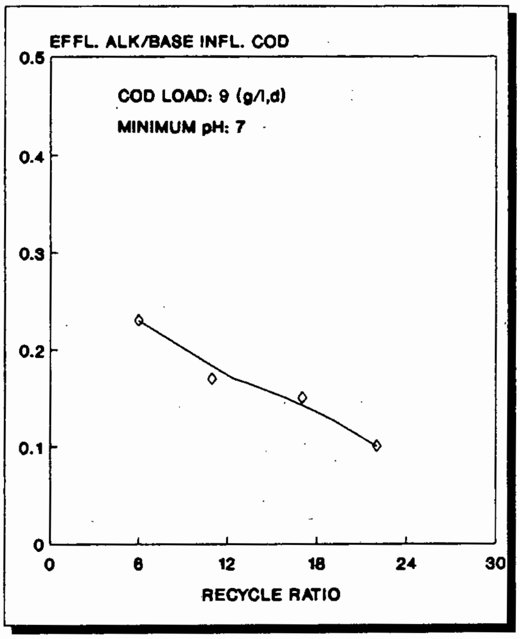
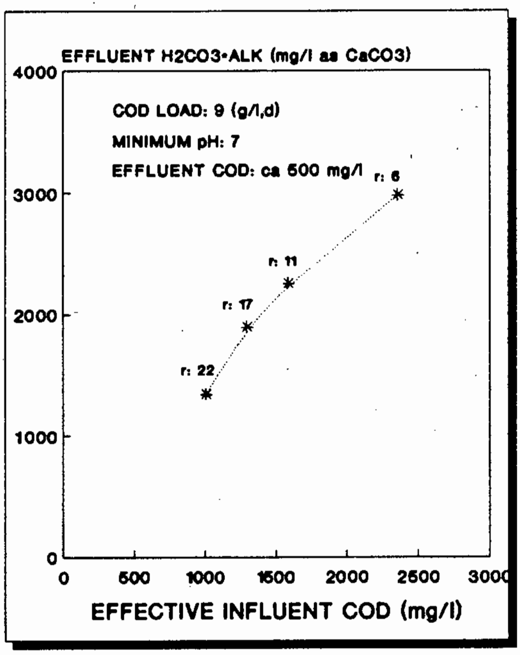


Fig 7.10: Relationship between effluent H_2CO_3*alkalinity requirements per unit mass of base influent COD (to maintain a near neutral minimum bed pH) and recycle ratio; treatment of undiluted lauter tun waste (COD_b = 13 000 mg/ℓ) at a constant COD loading rate of 9 kg/(m^3 sludge bed. d).

*Effective influent COD and effluent H_2CO_3*alkalinity:* Accepting that C does not remain constant over the range of COD concentrations of diluted influent feed (due to recycling), an alternative approach to expressing the H_2CO_3*alkalinity requirements which may have some advantage from a practical point of view is to relate the *effluent* H_2CO_3*alkalinity to the effective influent COD concentration (COD_e). For the COD loading rate of 9 kg/(m^3 sludge bed.d) and a minimum bed pH of 7, the effluent H_2CO_3*alkalinity (as $CaCO_3$) is plotted versus the effective influent COD (COD_e) in Fig 7.11. This plot clearly illustrates the reduced effluent H_2CO_3*alkalinity requirements at lower COD_e resulting from higher recycle ratios. It should be noted that COD_e does not take into account the COD recycled from the reactor effluent; neglecting the recycled COD is acceptable provided the effluent COD is principally unbiodegradable (with respect to the anaerobic process), which usually will be the case if the system operates under stable conditions producing a low effluent COD.



<u>Fig 7.11:</u> Relationship between effective influent COD ($COD_e = COD_b\ 1/(1+r)$ and effluent H_2CO_3*alkalinity requirements (to maintain a near neutral minimum bed pH): treatment of undiluted lauter tun waste (COD_b = 13 000 mg/ℓ) applying different recycle ratios at a constant COD loading rate of 9 kg/(m^3 sludge bed. d).

In treating a specific waste, to make use of COD_e and the effluent H_2CO_3*alkalinity for control to the selected minimum bed pH, the relationship between COD_e and effluent H_2CO_3*alkalinity needs to be investigated experimentally under design conditions. Once this relationship has been established, minimum pH control and pH buffer dosing estimates can be made as follows: COD_e is determined from measurement of COD_b and the recycle ratio. The effluent H_2CO_3*alkalinity (and SCFA) can be measured using the 5 pH point titration method (see Chapter 5). From the experimental relationship between the COD_e and the effluent H_2CO_3*alkalinity, the H_2CO_3*alkalinity required to maintain a near neutral minimum bed pH is determined and compared to the measured H_2CO_3*alkalinity. From the difference between measured and required H_2CO_3*alkalinity the pH buffer dosing requirements can be estimated. Should the loading rate change significantly this procedure will need to be repeated at the new loading rate.

Guide to alkalinity requirements: From this study it became clear that COD_e significantly influences the mass of effluent H_2CO_3*alkalinity required to maintain a near neutral minimum bed pH: At the lowest COD_e (580 mg/ℓ for the recycle ratio = 22:1), the effluent H_2CO_3*alkalinity required was 1360 mg/ℓ (as $CaCO_3$); at the highest COD_e (1860 mg/ℓ at the recycle ratio = 6:1), the effluent H_2CO_3*alkalinity required was 2980 mg/ℓ (as $CaCO_3$). The effluent H_2CO_3*alkalinity requirements for COD_e located between the above two extreme values can be obtained from Fig 7.11. It is evident that the H_2CO_3*alkalinity requirements are reduced substantially at lower COD_e. It should be noted that these findings apply to a COD loading rate of 9 kg/(m^3 sludge bed.d).

pH buffer dosing requirements: It has been stated earlier that lauter tun waste generates little H_2CO_3*alkalinity internally. For this reason virtually all the H_2CO_3*alkalinity measured in the effluent needs to be supplied externally. Hence the mass of pH buffer chemicals, expressed as H_2CO_3*alkalinity, needed for dosing per litre base flow, is virtually equal to the effluent H_2CO_3*alkalinity.

7.5 CONCLUSIONS

(1) The study of lauter tun waste in a laboratory scale UASB system has shown that treatment of this substrate is feasible in a UASB system and that the substrate develops a granular sludge bed. The pattern of product formation along the line of flow of the reactor is very similar to that observed under similar conditions treating a pure carbohydrate type substrate, e.g. glucose or apple juice concentrate.

(2) Lauter tun waste generates no, or only insignificant, internal pH buffer. Buffer needs to be supplied from an external source to control the minimum pH in the reactor to acceptable levels. When supplying H_2CO_3*alkalinity via a strong base (e.g. NaOH) to the base feed flow, the pH may increase to such high levels that some of the trace elements may precipitate and become unavailable to the microorganisms giving rise to partial or complete failure of the process. Hence, the dosing point needs to be selected such that a drastic pH increase at the dosing point is avoided. In this study an appropriate dosing point was found to be the recycle stream; the presence of dissolved CO_2 and H_2CO_3*alkalinity in the recycle stream buffered the pH downstream of the point of strong base addition to a $pH < 8,5$, instead of a pH of > 11 when NaOH was added to the influent flow.

(3) Dilution of the base influent COD from 13 000 to an effective influent COD of 570 mg/ℓ, by applying a recycle ratio of 22:1, appears to have no adverse effect on the process performance. Thus it would seem that the lower limit of the effective influent COD of 2500 mg/ℓ suggested by Sam–Soon *et al.* (1991), can be substantially lowered.

(4) With the target minimum bed pH of $\simeq 7$ the pH profile in the bed exhibited only a slight depression at the minimum value for a recycle ratio of 6:1 (base influent COD diluted by the recycle to 1860 mg/ℓ) and no significant depression at higher recycle ratios. This tendency to smooth out the "dip" in the pH profile when the effective influent COD is reduced, conforms with the observations of Sam–Soon *et al.* (1991).

(5) The alkalinity requirement (mg H_2CO_3*alkalinity/ℓ base influent) to maintain a selected minimum pH in the bed, can be reduced by imposing a

recycle. Sam-Soon *et al.* (1991) formulated the alkalinity requirement/ℓ influent as C · (base influent)/(1 + recycle ratio). This study showed that for a specific COD loading rate C is not constant but increases as the recycle ratio, r, increases, from C = 1,5 (r = 6) to C = 2,4 (r = 22) for the selected COD loading rate of 9 kg/(m^3 sludge bed.d) and the selected minimum pH ≃ 7. Despite this increase, the recycle factor 1/(1 + r) still causes a significant reduction in alkalinity requirements per litre base influent flow.

(6) To maintain a minimum sludge bed pH ≃ 7 at a COD loading rate of 9 kg/(m^3 sludge bed.d), a base influent COD concentration of 13 000 mg/ℓ and a recycle ratio of 22:1, the pH buffer requirements, expressed as H_2CO_3*alkalinity, were 1350 mg/ℓ (as $CaCO_3$) per litre of base influent flow and with the recycle ratio changed to 6:1, 2980 mg/ℓ (as $CaCO_3$). Virtually all of the pH buffer needed to be supplied from an external source.

(7) The TKN/COD ratio of the lauter tun waste was 0,011 mgN/mgCOD; For unimpeded pelletisation when treating glucose in a UASB system Sam-Soon *et al.* (1990) suggested a TKN/COD ratio of 0,02 mgN/mgCOD. In this study the feed was supplemented with NH_4Cl to give a TKN/COD ratio of 0,024; the observed TKN uptake was 0,015 mgN/mg undiluted influent COD. Thus it appears that lauter tun waste needs to be supplied with nitrogen when treated in UASB system to achieve unimpeded pelletisation. The TKN/COD ratio is less than that required for the treatment of glucose substrate probably because the lauter tun has a smaller fraction of carbohydrates per unit influent COD than glucose substrate.

(8) Trace elements were added throughout the investigation, consequently, no pronouncement as to whether the UASB system would operate effectively without trace element supplementation can be made. Care should be taken not to raise the influent pH too high by alkalinity addition via NaOH to the base influent – where this was done in this investigation, even though the pH in the bed remained < 7,6, the system exhibited rapid deterioration apparently due to precipitation of essential trace elements.

(9) In assessing the H_2CO_3*alkalinity supplementation to maintain a selected minimum bed pH, the effluent H_2CO_3*alkalinity must serve as the reference

parameter because this alkalinity includes any $H_2CO_3^*$alkalinity generated in the bed and accordingly takes into account this internal alkalinity source in the estimation of buffer chemical requirements.

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CHAPTER 8

WINE DISTILLERY WASTE IN UASB SYSTEMS – FEASIBILITY, ALKALINITY REQUIREMENTS AND pH CONTROL

ABSTRACT

Wine distillery waste developed a pelletised sludge bed in a UASB system. Product formation along the line of flow in the pelletised bed was similar to that when treating a pure carbohydrate, apple juice waste. Pelletised sludge production was about 0,14 mgVSS/mgCOD removed (as against 0,36 mgVSS/mgCOD removed for apple juice waste), indicating a low influent COD carbohydrate fraction. The pellets were not as compact as with apple juice waste and were smaller ($<$ 2 mm). When recycling the reactor effluent back to the influent the COD removal was greater than 94 percent for COD loading rates up to the maximum of 19 kg/(m^3 sludge bed. d); the maximum COD loading rate was determined by gas lifting pellets in to the settling section, not by process failure. An appreciable amount of $H_2CO_3^*$alkalinity was generated internally due to deamination of proteins and removal of organic salts; at a COD loading rate of about 10 kg/(m^3 sludge bed.d) no external $H_2CO_3^*$alkalinity supplementation was necessary in order to maintain a near neutral minimum bed pH provided the system was operated with a recycle from the effluent to influent at a recycle ratio sufficiently high to dilute the base influent COD concentration to an effective influent COD (COD_e) of $<$ 2000 mg/ℓ. Recycle ratios as high as 33:1, reducing the base influent COD concentration of 27 000 mg/ℓ to a COD_e of 790 mg/ℓ, did not adversely affect COD removal. No nitrogen, phosphate or trace element supplementation was required.

8.1 INTRODUCTION

In Chapter 7 the $H_2CO_3^*$alkalinity requirements to maintain a near neutral minimum sludge bed pH were investigated for brewery waste, a waste type that generates very little internal alkalinity, so that virtually all the pH buffer needs to be supplied from an external source. In this chapter wine distillery waste will be investigated, a waste type that can be expected to generate H_2CO_3*alkalinity during anaerobic digestion due to deamination, and to methane production from organic weak acid/base salts.

Wine distillery waste is the residue left after ethyl alcohol has been distilled from fermented grape juice. It contains organic acids and their salts, soluble proteins and carbohydrates, as well as various inorganic compounds which are normal constituents of wine. In the literature successful treatment of distillery waste (rice wine) in full scale UASB plants has been reported (Cheng *et al.*, 1990). It was of interest, therefore, to investigate the potential of wine distillery waste for treatment in a UASB system.

The study was conducted in a similar manner to that of the brewery waste (see Chapter 6), divided into two parts:

- Feasibility of the treatment of wine distillery waste in a *flow through* UASB system, to ascertain formation of a pelletised sludge bed and to study the product formation pattern along the line of flow of the reactor.

- Investigation into the effects of *recycling* on (1) process performance, and (2) mass of H_2CO_3*alkalinity required to maintain a near neutral minimum pH in the lower part of the sludge bed.

8.2 FEASIBILITY STUDY

Waste water characteristics

Influent feed stock of wine distillery waste was collected from the KWV distillery at Paarl and stored at 4°C. The waste batches contained different low concentrations of particulate material; in order to eliminate this variable the waste was settled and the supernatant only used as feed to the UASB reactor. The average characteristics of the supernatant are shown in Table 8.1.

Table 8.1: Characteristics of settled wine distillery waste in feasibility study (batch 1)

Soluble COD fraction	98 %
Soluble COD concentration	24 000 mg/ℓ
inorg–N	50 mg/ℓ
TKN	360 mgN/ℓ
Phosphorus	110 mgP/ℓ
pH	4,2

Each day the feed to the reactor was made up from the settled feed stock by diluting to a COD of 5500 mg/ℓ using tap water. This influent COD concentration was selected to enable a comparison of the pattern of product formation with that reported by Sam–Soon *et al.* (1987) on treatment of apple juice waste in UASB systems. The daily feed was kept refrigerated at 4°C. The feed composition after dilution is given in Table 8.2.

Table 8.2: Characteristics of diluted settled wine distillery waste in feasibility study

Soluble COD concentration	5500 mg/ℓ
inorg–N	12 mg/ℓ
TKN	83 mgN/ℓ
Phosphorus	26 mgP/ℓ
pH	5,2

Assessment of feed for treatment in a UASB system

The wine distillery waste was assessed for suitability as a substrate for the UASB system against the prerequisites set out by Sam–Soon *et al.* (1987), ie. (1)

development of a high $\bar{p}H_2$ environment, (2) cysteine deficiency, (3) excess supply of nitrogen and (4) a near neutral pH.

With regard to (1), the high $\bar{p}H_2$ environment, a number of analyses of wine distillery waste were obtained from the distillery. These analyses tended to focus either on the potential for recovery of some compounds such as tartaric acid, or, compounds that may cause problems in distillation, for example sugars that may caramelize onto the distillation apparatus. With regard to the presence of carbohydrates in wine distillery waste, the reported data range from about 2000 to 3000 mg/l. Data obtainable in the literature on SCFA average at about 900 mg/l as acetic acid. In Table 8.1 an analysis of a batch of wine distillery waste is given in terms of COD, TKN, inorganic nitrogen and inorganic phosphorus. In this instant, the COD is 24 000 mg/l, a value at the lower end of the usually quoted COD range for wine distillery waste of 20 000 to 40 000 mg/l. From the analysis of organic acids, carbohydrates and SCFA it becomes apparent that these compounds only constitute a fraction (about a third to half) of the COD present in wine distillery waste; no information was available on the nature of the remaining fraction of the COD. With these uncertainties no explicit conclusion was possible as to whether the waste would induce a high $\bar{p}H_2$ in a UASB system or not; the only option was an experimental feasibility study.

With regard to (2), cysteine deficiency, no analysis was available and it was not known whether cysteine was deficient or not.

With regard to (3), excess ammonium supply, Sam–Soon *et al.* (1990) suggested a minimum of 0,02 mgN/mg influent COD for optimum pellet production. The diluted wine distillery waste contained little ammonium (11 mgN/ℓ), but the organic nitrogen was about 72 mgN/ℓ, giving a total nitrogen of 0,015 mgN/mg influent COD i.e. a TKN/COD ratio lower than the recommended value for a carbohydrate substrate. Also, initially there was no certainty as to whether the organic nitrogen would be deaminated sufficiently rapidly to satisfy the nitrogen requirement for pelletisation in the lower part of the reactor. Accordingly, it was decided to supplement the influent feed with 10 mℓ of a nutrient stock solution containing 20 gNH_4Cl/ℓ thus giving a total of 0,025 mgN/mg influent COD, well in excess of that recommended by Sam–Soon *et al.* (1990).

With regard to (4), a near neutral pH, initially it was not known how much alkalinity the substrate would generate internally and how much would need to be added from an external source. To ensure sufficient pH buffer the H_2CO_3*alkalinity requirements were estimated assuming that no alkalinity would be generated internally; a (base influent H_2CO_3*alkalinity)/(base influent COD) ratio of 1,2 was selected as recommended for pure carbohydrate substrate by Sam–Soon *et al.* (1991). The buffer chemicals were 9,4 g$NaHCO_3$ and 0,8 gNaOH per litre base influent; on addition to the waste flow the pH came to about 7,0.

Trace element solution

To avoid potential deficiencies of trace element supply, 5 mℓ/ℓ influent of a trace element solution, suggested by Zehnder and Wuhrmann (1977) for enrichment cultures of methanogenic bacteria, was added to the feed. Detailed composition of this trace element solution is given in Table 7.3, see Chapter 7.

Experimental set–up

For the feasibility study, a laboratory scale UASB reactor similar to that for the lauter tun waste (Chapter 7) was constructed from a transparent persepex cylinder of 94 mm diameter, 1500 mm high, with a conically shaped inlet at the bottom and a solid/liquid/gas seperator at the top, total reactor volume circa 10,5 ℓ, see Fig 8.1. Gas collection was by means of a hollow inverted cone: Rising gas bubbles are deflected into the cone by a deflector collar around the inside wall of the reactor below the cone; liquid effluent discharges via an annular space between the gas collection cone and and the reactor wall, to enter a small liquid/solid seperator (1500 mℓ); clarified liquid flows over a launder into the collection vessel while solids, which settle out, are returned into the reactor by gravity. Twelve evenly spaced sample ports were installed up the reactor wall for sampling along the line of flow. Temperature was maintained at 30° C by a thermostat controlled electrical heating tape wrapped around the reactor.

The UASB system was operated in flow through fashion, i.e. no recycle was employed.

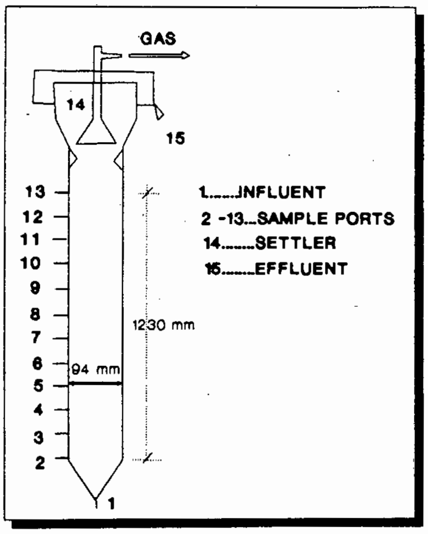

Fig 8.1: Schematic diagram of laboratory UASB reactor

Parameters measured

The following parameters were measured on the system at 1 to 2–day intervals:

- filtered influent and effluent COD,
- filtered influent and effluent TKN and inorg–N,
- pH in settler,and,
- substrate flow rate.

In addition, profiles of pH, COD, TKN, inorg–N, the short–chain fatty acids (SCFA) propionic, HPr, and acetic, HAc, were measured along the axis of the reactor. Samples were taken at each sample port, starting at the top. Samples were filtered using ordinary filter paper, Schleicher und Schuell 595. For the HAc and HPr, samples were refiltered through a 0,45 micronfilter paper (Millipore) and the SCFA measured by gas chromatography using a 60/80 Carbo pack C/0,3% Carbo wax packing. COD, TKN and inorg–N were measured in accordance with Standard Methods (1989). When a profile was measured the $H_2CO_3^*$alkalinity in the reactor effluent was measured using the 5 pH point titration method (see Chapter 5).

Starting up procedure and process performance

The starting up procedure with wine distillery waste differed from that with lauter tun waste (Chapter 7). The flow through reactor was seeded with 4 ℓ of pelletised sludge from a laboratory scale UASB reactor treating glucose substrate at a maximum COD load of 45 kg/(m^3 sludge bed.d); the sludge bed volume was kept constant at 4 ℓ by draining excess sludge from sample port 7. To adapt the seed sludge to the wine distillery waste, initially a mixture of glucose and wine distillery waste (50 : 50 by COD) was fed at a flow rate of 20 ℓ/d and a COD concentration of 5500 mg/ℓ to give a COD loading rate of 27 kg/(m^3 sludge bed.d). Within 17 days from the start, the glucose/wine distillery waste mixture was changed to wine distillery waste only, with an unchanged COD loading rate. At this "high" COD loading rate the system responded with a slight decline in performance (in general when adapting a pellet bed to a new substrate a lower COD loading rate would be recommended). In Fig 8.2 the COD loading rate and the percentage COD removal are shown plotted versus time, with zero time marking the beginning of the start up period. From Fig 8.2 it can be seen that the COD removal declined for some time after the change to pure wine distillery waste but recovered after about 10 days, indicating that the sludge bed had adapted to the new substrate.

Steady state system changes

Once the system appeared to be operating satisfactory at 27 kgCOD/(m^3 sludge bed. d) with 100 percent wine distillery waste as influent, the following studies were undertaken on the flow through system.

Termination of trace element addition: When the percentage COD removal had recovered to 90 percent, by day 35, the addition of trace elements was terminated in order to study if this would have any adverse effects on the COD removal; the percentage COD removal plot in Fig 8.2 did not show any change in trend before and after the termination of addition of trace elements and it was concluded that no additional trace elements were required.

Termination of nitrogen augmentation: The daily measurements of TKN and inorg-N in the effluent, of about 90 and 75 mg/ℓ respectively, indicated an oversupply of nitrogen and that the addition of NH_4Cl solution possibly could be terminated. To test this hypothesis addition of NH_4Cl solution was terminated at day 40. The percentage COD removal continued to increase after termination of

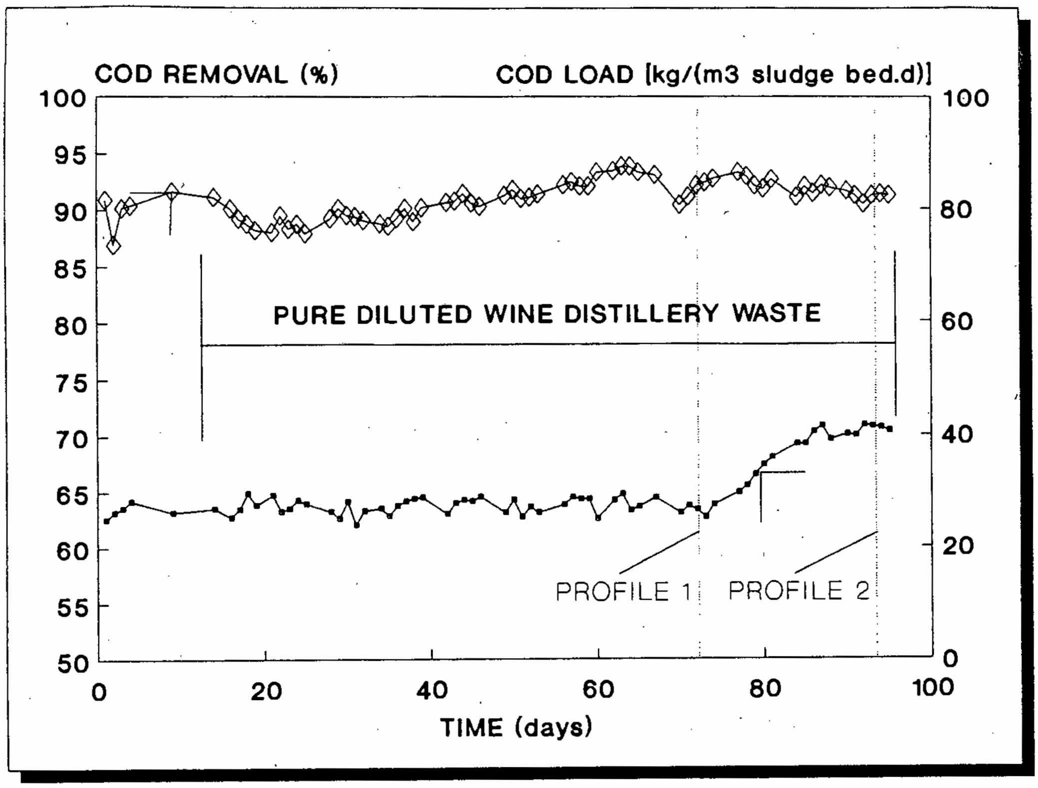

Fig 8.2: Start up period of *flow through* laboratory UASB reactor seeded with 4 ℓ of pelletised sludge from a laboratory scale UASB system treating glucose substrate. Feed substrate: initially, mixture of wine distillery waste and glucose (50:50 in COD) diluted with tap water to give an influent COD of 5500 mg/ℓ; after 17 days the feed was changed to diluted wine distillery waste only (COD = 5500 mg/ℓ). The COD loading rate was increased by increasing the flow rate. The terms "profile" 1 and "profile" 2 indicate the time locations for measuring various parameters along the line of flow of the reactor (see Figs 8.3 and 8.4).

NH_4Cl addition (see Fig 8.2), that is, this change did not adversely affect COD removal. Without nitrogen supplementation the influent TKN was 83 mgN/ℓ and the effluent TKN 45 mg/ℓ (effluent inorg-N = 30 mg/ℓ), that is, there still was an excess supply of nitrogen in the feed.

Alkalinity addition: It was stated earlier that to ensure that the minimum bed pH did not decline below 6,6, the influent was augmented with 9,4 $gNaHCO_3$ and 0,8 gNaOH per litre base influent to give an H_2CO_3*alkalinity/COD ratio of 1,2 (mg as $CaCO_3$/mg). With 100 percent wine distillery waste this gave rise to a minimum bed pH of 7,4 indicating an excess of H_2CO_3*alkalinity. Accordingly, over the period day 45 to 55, the mass of $NaHCO_3$ addition was reduced gradually to 2,0 g/ℓ with NaOH constant at 0,8 g/ℓ; this established a minimum bed pH of 6,6 (suggested as the lower limit by Sam–Soon *et al.*, 1987). With this addition, the H_2CO_3*alkalinity supplied externally amounted to 2190 mg/ℓ (as $CaCO_3$). The H_2CO_3*alkalinity in the effluent was measured at 2560 mg/ℓ (as $CaCO_3$) indicating the internal generation of H_2CO_3*alkalinity of 370 mg/ℓ (as $CaCO_3$). The ratio of effluent H_2CO_3*alkalinity/influent COD to maintain a minimum bed pH of 6,6 therefore was 2560/5500 = 0,5, significantly lower than that found by Sam–Soon *et al.* (1991) for apple juice waste.

Steady state product formation

With the minimum profile pH ≃ 6,6 and a COD loading rate of 27 kg/(m^3 sludge bed.d) the system was run from day 55 to day 74 to ensure complete steady state conditions. On day 74 a set of profiles of pH, COD, HAc, HPr, TKN, inorg–N and org–N (profile set 1) was measured which is shown plotted in Fig 8.3.

Following the measurement of the this set of profiles two changes were made: (1) The COD loading rate was increased from 27 to 41 kg/(m^3 sludge bed.d) by maintaining the influent COD concentration at 5500 mg/ℓ but increasing the influent flow rate from 20 to 30 ℓ/d. (2) H_2CO_3*alkalinity supplementation was increased approximately in the same ratio as the COD loading rate to 3980 mg/ℓ influent as $CaCO_3$, (5 g$NaHCO_3$ and 0,8 gNaOH per litre of influent). After the system had reached steady state under the higher loading rate the effluent H_2CO_3*alkalinity was about 4400 mg/ℓ as $CaCO_3$ giving an effluent H_2CO_3*alkalinity/COD ratio of 4400/5500 = 0,8. The minimum bed pH increased from 6,6 to 6,8. After the system had been allowed sufficient time to ensure steady state behaviour, a further set of profiles (profile set 2) of the products of interest was measured on day 95, shown plotted in Fig 8.4.

pH: pH profile 1 (see Fig 8.3) measured on day 74 and pH profile 2 (see Fig 8.4) measured on day 95, were similar in that both showed a considerable pH decline in the lower part of the sludge bed. In profile 1 the minimum pH declined to as low as pH ≃ 6,5 indicating that the influent Alk/COD ratio of 0,5 was not sufficient. In profile 2 the minimum pH declined to pH ≃ 6,8 indicating that the

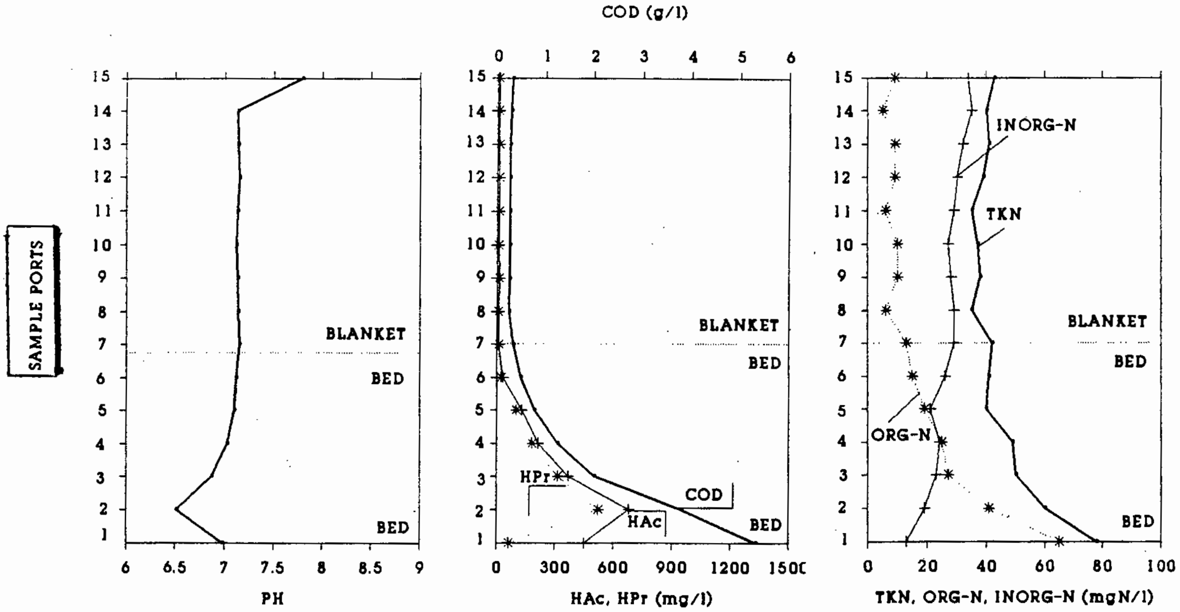

Fig 8.3: *Flow through* laboratory UASB reactor treating *diluted* wine distillery waste: Profiles of pH, COD, HAc, HPr, TKN, inorg–N and org–N along the line of flow. Flow rate: 20 ℓ/d, influent COD concentration: 5500 mg/ℓ, COD loading rate: 27 kgCOD/(m³ sludge bed.d).

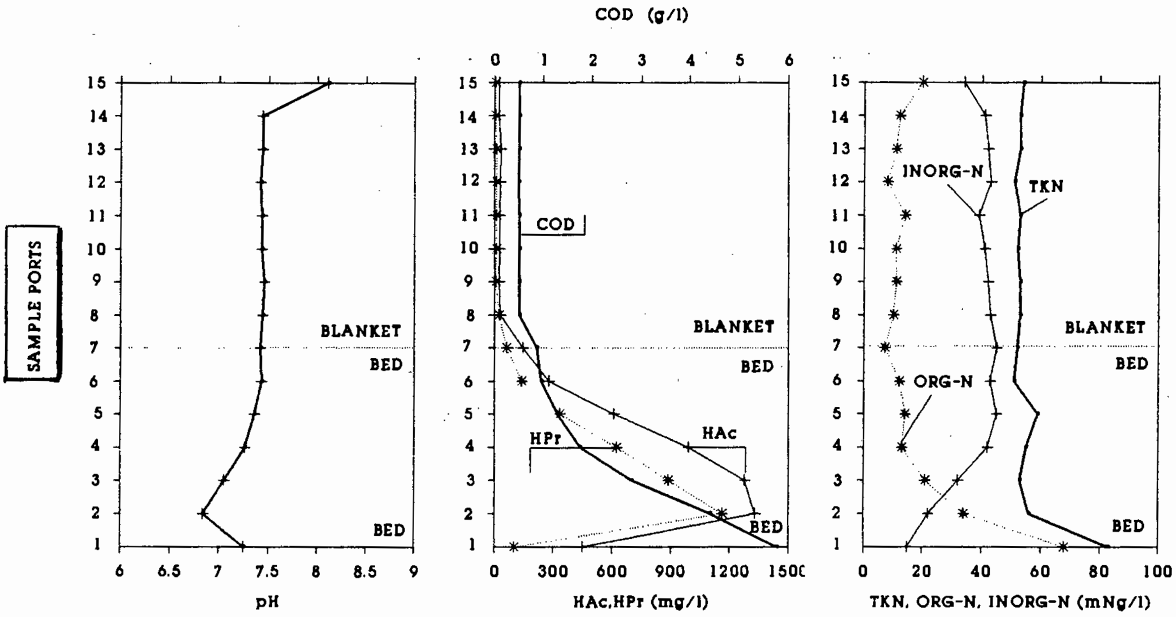

Fig 8.4: *Flow through* laboratory UASB reactor treating *diluted* wine distillery waste: Profiles of pH, COD, HAc, HPr, TKN, inorg–N and org–N along the line of flow. Flow rate: 30 ℓ/d, influent COD concentration: 5500 mg/ℓ, COD loading rate: 41 kgCOD/(m³ sludge bed.d).

effluent Alk/COD ratio of 0,8 was sufficient to buffer the minimum pH above the minimum value of 6,6 as suggested by Sam–Soon *et al.* (1987). In the pH profile the decline in pH in the lower part of the sludge bed coincided with the increase in HAc and HPr. Comparing both pH profiles with those reported by Sam–Soon *et al.* (1987), the behaviour patterns are similar.

COD profiles: The COD profile 1 (see Fig 8.3) and COD profile 2 (see Fig 8.4), both showed a rapid decrease in the lower part of the sludge bed. COD profile 1 reached its minimum value (≃ 400 mg/ℓ) well within the sludge bed whereas COD profile 2 reached its minimum (700 mg/ℓ) only at or near the top of the bed, and the minimum value was higher than that of COD profile 1. This very likely was due to the higher COD loading rate in profile 2. The rapid rate of COD removal in the lower part of the sludge bed, observed in both COD profiles, again is similar to that observed by Sam–Soon *et al.* (1987).

HAc: The HAc profile 1 (Fig 8.3) and HAc profile 2 (Fig 8.4) reached their respective maxima of 680 and 1310 mg/ℓ in the lower part of the sludge bed, and thereafter decreased to near zero in the upper part of the sludge bed. The two profiles differ in two aspects, (1) maximum HAc concentration in profile 2 was considerably higher than that in profile 1,and, (2) the minimum HAc concentration in profile 1 was attained well within the bed, whereas that in profile 2 reached its minimum only near the top of the bed. Both of these observations reflect the increased COD loading rate and the second indicates that *the reactor was being loaded to near or at its maximum capacity.*

HPr: Similar to the HAc profiles, the HPr profile 1 (Fig 8.3) and HPr profile 2 (Fig 8.4) measured on day 74 and 95 respectively, reached their respective maxima 530 and 1190 mg/ℓ in the lower part of the sludge bed and thereafter decreased to near zero in the upper part of the bed. According to Sam–Soon *et al.* (1987) HPr accumulation would occur only in a high $\bar{p}H_2$ environment. Thus the observed accumulation of HPr indicated that the prerequisite of high $\bar{p}H_2$ was being satisfied.

TKN, inorg–N and org–N: The respective TKN, inorg–N and org–N profiles measured on day 74 and 95 (see Fig 8.3 and 8.4) exhibited similar patterns.: The two org–N concentration profiles decreased rapidly in the lower part of the sludge bed, due to deamination, reaching a minimum value in the upper part of the sludge bed. The inorg–N profiles however *increased* in the lower part of the bed and stabilized to their maximum values in the upper part. In contrast, Sam–Soon *et al.* (1987) observed a marked *decrease* of inorg–N in the lower part of sludge bed. The increase observed in the wine distillery waste profiles may be attributed to rapid rate of generation of inorg–N (due to deamination of org–N present in the influent), more rapid than the rate of uptake of inorg–N due to pelletisation. The net uptake of nitrogen is demonstrated in the TKN profiles – a significant decrease of about 25 mgN/ℓ (from 80 to 55 mgN/ℓ) in both TKN profiles below sample port 3. In this part of the sludge bed on average about 3000 mgCOD/ℓ were removed. Under 'normal' anaerobic fermentation conditions nitrogen requirements would be approximately 0,004 mgN/mgCOD for protoplasm synthesis, i.e. the expected TKN removal under 'normal' conditions below sample port 3, would have been 12 mgN/ℓ. The observed nitrogen removal of 25 mgN/ℓ was about double that normally expected thereby supporting the hypothesis that pellet formation was taking place.

Pellet growth:

Sam–Soon *et al.* (1987) showed that pellet generation takes place in the high $\bar{p}H_2$ zone and observed pellet break up in the upper part of the sludge bed. The HPr profiles in Fig 8.4 indicated that the high $\bar{p}H_2$ zone extended up to about sample port 3 (volume ≃ 1,1 ℓ). To measure the pellet yield under high $\bar{p}H_2$ conditions the system was operated under the same operating conditions as at day 95 of the feasibility study, i.e. flow rate 30 ℓ/d and influent COD concentration 5500 mg/ℓ. The sludge bed was drained above sample port 3 so that only the sludge in the high $\bar{p}H_2$ zone remained in the bed. Over a period of 20 days the following measurements were taken on a daily basis:

- the sludge bed was drained to the level of sample port 3 into a measuring cylinder and from the drained sludge volume the mass of VSS produced per day was determined.

- filtered and unfiltered influent and effluent COD concentrations.

- influent flow rate.

The pellet growth yield was determined as follows: The filtered effluent COD was subtracted from the filtered influent COD concentration and the difference multiplied by the daily flow rate to give the mass of soluble COD removed per day. The specific pellet yield (Y) was calculated as:

$$Y = \frac{\text{mass of VSS generated/d}}{\text{mass of COD removed/d}} \tag{8.1}$$

The average specific pellet yield measured over the 20 day period was 0,14 mgVSS/mgCOD. Comparing this yield value with the pellet yield value reported by Sam–Soon *et al.* (1987) of 0,36 mgVSS/mgCOD the following comments are pertinent:

> The pellet yield was obtained only from the mass of pelletised *sludge* wasted from the reactor every day; this did not necessarily reflect the *total sludge* production which would also include the pellet debris discharged from the sludge bed into the sludge blanket and reactor effluent. However, to take this into account would have required a much more elaborate experimental procedure including drainage of the total volume above the bed (the blanket) and measurement of the total particulate matter in the effluent. There is a further complication that the influent itself contained approximately 2 percent of the COD as particulate matter; thus it was not clear whether the particulate matter in the blanket and in the effluent originated from the pellet debris or from the influent particulate matter. Hence, the value of the specific yield of solids generated, reported here, must be taken as a net *pellet* specific yield.
>
> The cause for the lower pellet yield most likely was that the influent COD of the wine distillery waste contained a lower fraction of carbohydrates than the apple juice waste.

Conclusions

The information gathered during the feasibility study on wine distillery waste in a flow through UASB reactor can be summarized as follows:

- The pH, COD, HAc and HPr profiles were similar to those observed when treating a carbohydrate waste (apple juice waste); the COD reduction was > 85 percent at a COD loading rate as high as 41 kg/(m^3 sludge bed. d).

- A pelletised sludge was produced, but at a reduced rate compared with a pure carbohydrate substrate.

These observations indicate that wine distillery waste gave rise to a product formation in a UASB system similar to that found by Sam–Soon *et al.* (1987) for pure carbohydrate substrate albeit with reduced pelletisation. It is concluded that wine distillery waste is suitable for treatment in a UASB systems.

8.3 RECYCLING, ALKALINITY AND pH

In Chapter 7 the effects of recycling on process performance and H_2CO_3*alkalinity requirements for lauter tun waste in a UASB system was investigated. With an influent COD concentration of 13 000 mg/ℓ, a COD loading rate of 9 kg/(m^3 sludge bed.d) and recycle ratios ranging between 6 to 22:1 to give an *effective influent* COD (i.e. base influent COD/(1 + recycle ratio) ranging from 1800 to 570 mg/ℓ, no adverse effects on COD removal was found. The concentration of H_2CO_3*alkalinity required per litre of influent was found to change with the effective influent COD or equivalently with the recycle ratio. In this chapter we will examine the relationship between the parameters, effective influent COD concentration, recycle ratio, effluent H_2CO_3*alkalinity, alkalinity supplementation and minimum bed pH, when treating wine distillery waste in a UASB system at a COD loading rate likely to be used in practice.

The investigation with undiluted wine distillery waste as base influent was divided into the following tasks:

(1) Recycling and system performance,

(2) Self sufficiency in H_2CO_3*alkalinity requirements,

(3) Relationship between effective influent COD, effluent H_2CO_3*alkalinity and minimum bed pH, and,

(4) Permissible COD loading rate.

Recycling and system performance

In this task the objective was to establish if recycling of the reactor effluent, to dilute the base influent substrate into the COD range of 2500 to 5000 mg/ℓ (suggested by Sam-Soon *et al.*, 1991), would not affect the process performance adversely, provided the minimum pH remained above 6,7.

The experimental set-up remained the same as that in the feasibility study, except for the following modifications: (1) a wet gas meter (model No. DM3A, Alexander Wright, London) was installed to measure the volume of carbon dioxide and methane produced in the reactor, (2) the gas composition was analysed for methane and carbon dioxide using gas chromatography (Gow-Mac 502) with helium as carrier gas, (3) the peristaltic pump, previously used as feed pump, was installed as recycle pump, and, (4) a laboratory positive displacement pump was installed as feed pump. To control the flows both pumps operated on an on/off cycle, switched on and off simultaneously. The characteristics of the wine distillery waste batch are shown in Table 8.3.

Table 8.3: Characteristics of settled wine distillery waste (batch 2)

Soluble COD fraction	98 %
Soluble COD concentration	23 000 mg/ℓ
inorg-N	34 mgN/ℓ
TKN	200 mgN/ℓ
Phosphorus	105 mgP/ℓ
pH	4,5

Measurement of the individual SCFA in the *influent* by means of a gas chromatograph was not successful as the waste poisoned the particular packing used. The reactor was seeded with 3 ℓ of pelletised sludge (sludge bed height ≃ 43 cm) which had been generated during the feasibility study. This sludge bed volume was maintained throughout the investigation. A COD loading rate of 15 kgCOD/(m^3 sludge bed.d) was applied - about a third of the maximum COD loading rate applied at the end of the feasibility study. From the profiles in the feasibility study, this mass of sludge was adequate for the fermentation reactions to reach completion. A 7:1 recycle ratio was employed; with the base influent COD concentration of 23 000 mg/ℓ this gave an effective influent COD concentration (COD_e) of 23 000/(1+7) = 2880 mg/ℓ.

Alkalinity supplementation: At the beginning of the experiment it was not known how much internal alkalinity the new waste batch would generate. In the feasibility study the mass of H_2CO_3*alkalinity (mg as $CaCO_3$) generated per mg influent COD came to 370/5500 = 0,0673. Comparing the COD strength of the undiluted batch in the present study (23 000 mg/ℓ) with that in the feasibility study (24 000 mg/ℓ), the two batches appeared to be of a similar constitution and it was assumed that they would generate the same mass of H_2CO_3*alkalinity per mass of influent COD. In the present task this implied generation of H_2CO_3*alkalinity of 0,0673·23 000 = 1550 mg/(ℓ effluent). With a recycle of 7:1 (COD_e = 2880 mg/ℓ) the mass of H_2CO_3*alkalinity generated per mass of *effective* influent COD was estimated at 1550/2880 = 0,54 mgH_2CO_3*alkalinity/mgCOD. There was no information available if an H_2CO_3*alkalinity of this magnitude would be sufficient to maintain a near neutral minimum pH in the bed. Because of these uncertainties it was decided to add 1,5 gNaOH/(ℓ base influent), i.e. 1875 mgH_2CO_3*alkalinity/(ℓ base influent) as $CaCO_3$, to give an estimated total 3500 mgH_2CO_3*alkalinity/(ℓ effluent) i.e. 3500/2880 = 1,2 mgH_2CO_3*alkalinity per mg effective influent COD, a value close to the Alk/COD ratio proposed by Sam–Soon *et al.* (1991). The NaOH was added directly to the influent; the pH in the feed remaining below below 7. This low pH value after dosing was due to the very low pH of the wine distillery waste (pH ≃ 4,5 for batch 2), due to the presence of SCFA and other organic acids. No trace element or nutrient solutions were added because it had been established during the feasibility study that omission of these solutions from the feed had no noticeable consequences on the COD removal.

The parameters measured were minimum bed pH, filtered effluent COD concentration, filtered influent and effluent TKN, gas production rate and composition; in addition, the effluent SCFA and H_2CO_3*alkalinity were measured with the 5 pH point titration method (see Chapter 5). Individual SCFA were not measured.

Results and discussion

The system was operated without any changes under the above conditions for 59 days. The following results were obtained for the various parameters:

COD and SCFA: The effluent COD concentrations measured at 2 to 3 day intervals are shown plotted versus time in Fig 8.5 . The plot shows a steady improvement in performance, the effluent COD concentration decreased from 1600 mg/ℓ at the start of the testing period, stabilizing at about 600 mg/ℓ to give a steady state percentage COD removal was 97 percent. This high percentage COD removal indicates that the 7:1 recycle ratio did not adversely affect COD removal. The effluent SCFA concentrations measured at 2 to 3 days intervals are also shown plotted in Fig 8.5. The values remained low throughout, at about 50 mg/ℓ as HAc.

TKN: The nitrogen uptake of the system was obtained by measuring the TKN in the base influent and effluent. The average TKN was 241 mgN/ℓ in the influent and 32 mgN/ℓ in the effluent, giving a TKN uptake of 209 mgN/ℓ influent. When relating the TKN uptake to the COD removal a N/COD ratio of 209/(23 000 − 600) = 0,009 was obtained which agreed with the value obtained in the feasibility study. This ratio is substantially higher than that for anaerobic processes without pellet formation (N/COD ≃ 0,004) indicating that part of the nitrogen possibly was used for pellet generation. However, the N/COD ratio was significantly lower than the ratio obtained for lauter tun waste (N/COD = 0,016 see Chapter 7) and with glucose substrate (N/COD = 0,02) by Sam–Soon *et al.* (1990). The low N/COD value for wine distillery waste implies that the mass production of pellets per mass of influent COD also would be low, as found in the feasibility study. From an analysis provided by the distillery (see Table 8.4) an appreciable fraction of COD is in the form of organic acids which probably did not induce a high hydrogen partial pressure ($\bar{p}H_2$) to the same extent as the carbohydrates as contained in apple juice waste.

Table 8.4: Analysis of wine distillery waste with respect to organic acids

Tartaric acid	1,7 g/ℓ
Malic acid	0,5 g/ℓ
Lactic acid	1,8 g/ℓ
Succinic acid	1,6 g/ℓ
Acetic acid	0,6 g/ℓ

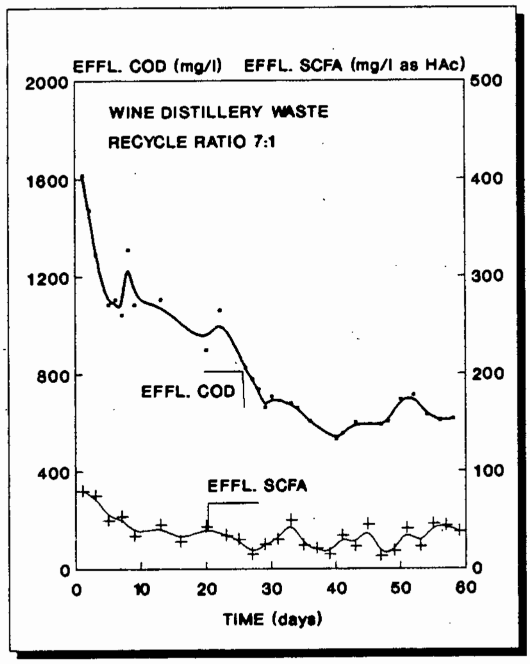

Fig 8.5: Effluent COD and SCFA concentrations a of laboratory UASB reactor treating *undiluted* wine distillery waste operated with a 7:1 recycle; Base influent COD concentration: 23 000 mg/ℓ; effective influent COD: 2880 mg/ℓ; COD loading rate: 9 kg/(m^3 sludge bed.d).

Gas production and composition: Gas production of the reactor stabilized after 10 days at about 19 ℓ/d with a carbon dioxide fraction of 28 percent, the remaining fraction being methane. The stable gas production and composition provided further evidence that using a 7:1 recycle did not impair process performance.

pH: To establish the point of minimum pH in the bed, at intervals pH profiles were measured. These indicated that the pH was at its minimum at port 2 with pH = 6,9, increased to pH ≃ 7,0 at port 3 and remained virtually constant at ≃ 7,0 in the region above port 3. The pH pattern remained unchanged throughout the experiment. Thus, the estimated H_2CO_3*alkalinity requirements appeared to be adequate to maintain a near neutral minimum bed pH. The actual total H_2CO_3*alkalinity in the effluent, measured towards the end of this experiment, was circa 3400 mg/ℓ as $CaCO_3$. Knowing the effluent H_2CO_3*alkalinity, the H_2CO_3*alkalinity/effective influent COD ratio came to 3400/2880 = 1,2. Subtracting the mass of H_2CO_3*alkalinity contributed by the 1,5 gNaOH/ℓ influent i.e 1875 mgH_2CO_3*alkalinity/ℓ influent, from that measured in the effluent, the internally generated H_2CO_3*alkalinity was: 3400 – 1875 = 1525 mgH_2CO_3*alkalinity/ℓ influent, a value very near the estimated one, 1550 mgH_2CO_3*alkalinity/ℓ, see "Alkalinity supplementation" above.

Self sufficiency in H_2CO_3*alkalinity requirements

In the task above, via H_2CO_3*alkalinity measurements in the effluent, it was shown that a fair quantity of H_2CO_3*alkalinity was generated internally. In this task the objective was to enquire, by applying high recycle ratios, if the internally generated H_2CO_3*alkalinity might be sufficient to enable operation of the system without addition of H_2CO_3*alkalinity from an external source. In the above task the ratio of effluent H_2CO_3*alkalinity/COD_e of 1,2 to maintain a near neutral pH was established by increasing the effluent H_2CO_3*alkalinity by adding NaOH to the base influent, i.e. H_2CO_3*alkalinity was added to the internally generated H_2CO_3*alkalinity. In this task, instead of adding H_2CO_3*alkalinity COD_e would be reduced by increasing the recycle ratio to achieve an effluent H_2CO_3*alkalinity/COD_e ratio close to 1,2 from the internally generated effluent H_2CO_3*alkalinity. In this way a near neutral minimum bed pH would be established without NaOH addition.

The experimental set-up remained the same as that in the previous experiment. The characteristics of the waste batch is shown in Table 8.5, in particular, note that the influent COD was 31 000 mg/ℓ.

Table 8.5: Characteristics for settled wine distillery waste (batch 3)

Soluble COD fraction	98 %
Soluble COD concentration	31 000 mg/ℓ
inorg-N	90 mgN/ℓ
TKN	400 mgN/ℓ
Phosphorus	155 mgP/ℓ
pH	4,2

The sludge bed which had been adapted to recycling conditions (as described in the precious task) was used as seed sludge for this experiment. The sludge bed volume was kept constant at 3 ℓ by draining excess sludge at weekly intervals. A COD loading rate of 9 kg/(m^3 sludge bed.d) was selected which was equal to that applied for the lauter tun waste (see Chapter 7). In this way a comparison of the two waste types with regard to $H_2CO_3^*$alkalinity requirements would be possible.

Recycle ratio and NaOH addition: The recycle ratio was increased from 7:1 (in the above task) to 18:1 in this task. With an influent COD of 31 000 mg/ℓ, with this recycle ratio, the effective influent COD = 31 000/(18+1) = 1630 mg/ℓ. The effective influent COD concentration was lower than in the previous task where the effective influent COD concentration was 2880 mg/ℓ. At the beginning of the experiment no reliable information was available how much $H_2CO_3^*$alkalinity would be generated by the new feed batch. The previous task had shown that about 0,065 mg$H_2CO_3^*$alkalinity per mg base influent COD were generated internally. Using this ratio to assess the potential alkalinity generation in the new feed batch, an approximate internally generated $H_2CO_3^*$alkalinity was calculated as 0,065·31 000 = 2015 mg/ℓ. This would lead to an $H_2CO_3^*$alkalinity/COD_e ratio of 2015/1630 = 1,2 which had been found to be sufficient to maintain a near neutral minimum bed pH in the previous experiment. However, because there was still some uncertainty as to the mass of the internally generated H_2CO_3*alkalinity it was decided to supplement the feed with 1,0 gNaOH/ℓ influent giving a conservative H_2CO_3*alkalinity/COD_e ratio of (2015+1250)/1630 = 2.

No nutrients or trace elements were added. Process monitoring remained the same as in the previous task.

Results and discussion:

COD and SCFA: The effluent COD concentrations measured at 2 to 3 day intervals are shown plotted versus time in Fig 8.6. This plot shows that the effluent COD increased at the beginning and then stabilized at about 1000 mg/ℓ. A fraction of this increase may be accounted for by the increase in base influent COD from 23 000 (which gave an effluent COD ≃ 600 mg/ℓ) to 31 000 mg/ℓ (to give proportionally an expected effluent COD of 800 mg/ℓ). This leaves an increase of 200 mg/ℓ unaccounted for – probably the unbiodegradable fraction of the two batches differed. The effluent SCFA concentrations are also shown plotted versus time in Fig 8.6. The plot shows that the effluent SCFA concentrations remained constant at about 50 mg/ℓ (as HAc) indicating stable operation conditions during the experiment.

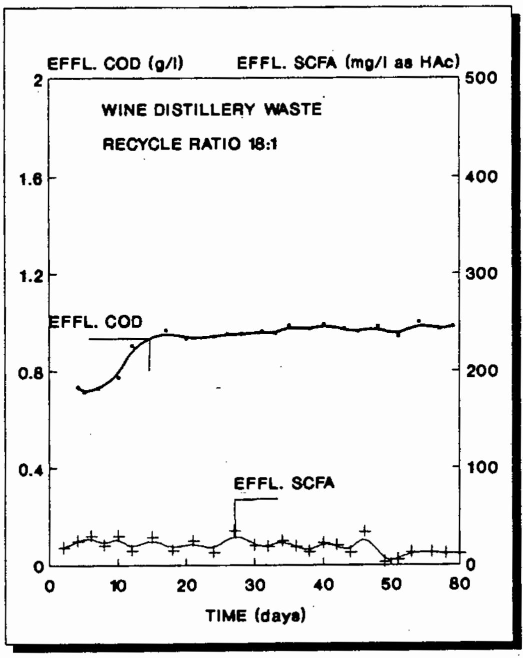

Fig 8.6: Effluent COD and SCFA concentrations of laboratory UASB reactor treating *undiluted* wine distillery waste operated with a 18:1 recycle: Base influent COD concentration: 31 000 mg/ℓ; effective influent COD: 1630 mg/ℓ; COD loading rate: 9 kg/(m^3 sludge bed.d).

Gas production and composition: Gas production was very stable over the period and averaged at 10 ℓ/d with a constant carbon dioxide fraction of about 24 percent i.e. 76 percent methane.

*Effluent H_2CO_3*alkalinity and pH:* The effluent H_2CO_3*alkalinity measured at 2 to 3 day intervals is plotted versus time in Fig 8.7 . The plot shows that while the feed was supplemented with 1gNaOH/ℓ base influent a gradual but significant increase in effluent H_2CO_3*alkalinity took place. The minimum bed pH concomitantly increased from 7,1 to 7,4 by day 23, when supplementation of NaOH was terminated because the pH was approaching the upper limit (pH ≃ 7,4) for anaerobic digestion. The gradual increase in effluent H_2CO_3*alkalinity and pH was due to the fact that with the high influent COD concentration the volume of feed per day for the applied COD loading rate was only 0,9 ℓ; the liquid volume of the system was about 10,5 ℓ, so that the "washout" period before stable conditions developed would extend to about 20 days. After NaOH addition was

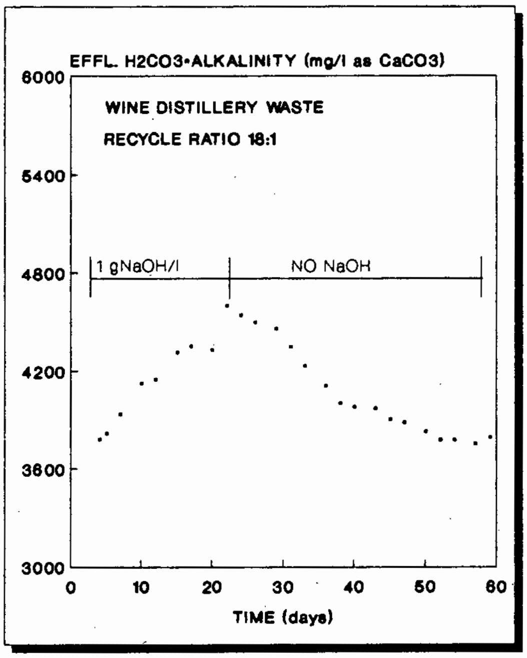

Fig 8.7: Investigation into self sufficiency in H_2CO_3*alkalinity: Change of effluent H_2CO_3*alkalinity with addition of 1 gNaOH/(ℓ base influent) and zero NaOH addition.

terminated the measured effluent H_2CO_3*alkalinity gradually declined until stability was attained again via washout, after approximately 20 days. The minimum bed pH stabilized at pH 7,2 and the effluent H_2CO_3*alkalinity stabilized at 3700 mg/ℓ; this H_2CO_3*alkalinity was generated completely internally, giving an effluent H_2CO_3*alkalinity/COD_e ratio of 3700/1630 = 2,3. This ratio was considerably higher than that in the task above and would be the main reason why the minimum bed pH increased from 6,9 (in the previous task) to 7,2 in this one, in both instances with no H_2CO_3*alkalinity supplementation.

From this task it was concluded that with wine distillery waste (that generates H_2CO_3*alkalinity internally) it is possible to attain H_2CO_3*alkalinity self sufficiency (i.e. to ensure a near neutral minimum bed pH) by applying an appropriate recycle, in the case considered a recycle ratio of 18:1.

Relationship between effective influent COD, effluent H_2CO_3*alkalinity and minimum bed pH

In the task above it was shown that for that particular batch of wine distillery waste no addition of H_2CO_3*alkalinity was required to maintain a near neutral minimum bed pH if an appropriate recycle was applied. In fact the minimum bed pH was above the envisaged neutral pH, at pH $\simeq$ 7,2. The minimum bed pH could have been lowered to pH $\simeq$ 7, in two ways: (1) by increasing the COD_e, i.e. reducing the recycle ratio or (2) by decreasing the effluent H_2CO_3*alkalinity by adding strong acid to the influent. In both events the effluent H_2CO_3*alkalinity/(COD_e) ratio will be decreased which will lead to a lower minimum bed pH. We shall now test the two options in two separate experiments.

*Option 1: COD loading rate, base influent COD and effluent H_2CO_3*alkalinity constant, effective influent COD changing*

The experimental set-up remained the same as that in the previous two experiments. The characteristics of the waste batch are shown in Table 8.6.

Table 8.6: Characteristics for settled wine distillery waste (batch 4)

Soluble COD fraction	98 %
Soluble COD concentration	27 000 mg/ℓ
inorg-N	80 mgN/ℓ
TKN	410 mgN/ℓ
Phosphorus	140 mgP/ℓ
pH	4,3

The sludge bed which had developed in the previous task served as seed sludge for this experiment. The sludge bed volume was kept constant at 3 ℓ by draining excess sludge at weekly intervals. A COD loading rate of 9 kg/(m^3 sludge bed.d) was selected which was equal to that applied in the previous task. The average sludge bed density was approximately 42 kgVSS/(m^3 sludge bed). To ensure a significant change in minimum bed pH three widely differing recycle ratios were selected to dilute the influent COD to three respective effective influent COD concentrations: The experiment was started on day zero with a recycle ratio of 33:1, on day 20 this ratio was changed to 20:1, and finally on day 40 the ratio was changed to 7:1 and the system operated for a further 20 days. Because this task was started with a recycle ratio greater than that found to give H_2CO_3*alkalinity self sufficiency in the previous task (r = 18:1), no H_2CO_3*alkalinity was added to the influent. No nutrients or trace elements were added. Process monitoring remained the same as in the previous studies.

Results and discussion:

With the change in recycle ratios the monitored parameters changed significantly: For each of the three periods, when different respective recycle ratios were applied, the averaged values for the individual monitoring parameters are listed in Table 8.7.

Table 8.7: Monitored parameters for recycle experiment with constant COD loading rate (9 kg/(m^3 sludge bed.d), constant base influent COD (COD_b = 27 000 mg/ℓ), constant effluent H_2CO_3*alkalinity (3700 mg/ℓ as $CaCO_3$) and *changing* effective influent COD (COD_e) or, equivalently, *changing* recycle.

RECYCLE RATIO	EFFECTIVE INFLUENT COD (mg/l)	MINIMUM BED pH	EFFLUENT COD (mg/l)	EFFLUENT SCFA (mg/l) as HAc	pCO_2 (%)	TOTAL GAS PRODUCTION (l/d) STP	METHANE PRODUCTION (l/d) STP
33:1	790	7,5	1560	30	17	12	8,8
20:1	1290	7,3	1610	50	22	13	8,9
7:1	3375	6,8	1580	35	31	15	9,1

COD *and SCFA*: The effluent COD averaged at 1600 mg/ℓ (standard deviation $\simeq$ 80 mg/ℓ) irrespective of the recycle ratio, giving a COD removal rate of about 94 percent. The effluent SCFA averaged at 45 mg/ℓ (standard deviation $\simeq$ 20 mg/ℓ) irrespective of the recycle ratio, indicating stable operation conditions throughout the experiment.

TKN: The nitrogen uptake by the system measured in terms of TKN exhibited no significant change during the experiment. On average 260 mgN/(ℓ influent) were removed, giving a TKN/COD ratio of 260/(27000–1600) = 0,010 mgN/mgCOD; this ratio was close to those found in the previous experiments indicating that pellet generation was not influenced by the recycle ratio provided the minimum bed pH $\simeq$ 7.

*H_2CO_3*alkalinity and pH:* The effluent H_2CO_3*alkalinity remained nearly unchanged during this task at about 3700 mg/ℓ as $CaCO_3$. This is to be expected

because in the same batch (with constant COD) the H_2CO_3*alkalinity generated per litre of base influent would remain constant. Hence any change in minimum bed pH would be due to the change in effective influent COD (at the constant COD loading rate applied). The minimum bed pH decreased from 7,5 at the 33:1 recycle ratio ($COD_e = 790$ mg/ℓ), to 7,2 at the recycle ratio 20:1 ($COD_e = 1290$ mg/ℓ), to 6,8 at the 7:1 recycle ratio ($COD_e = 3375$ mg/ℓ).

Gas production and composition: As the minimum bed pH *decreased* so the gas production rate *increased* with the total mass of methane produced per day remaining approximately constant. The increase in gas production rate coincided with an increase in the carbon dioxide fraction in the gas. This behaviour can be explained as follows (Loewenthal *et al.*, 1986): For a *constant* total carbonate species concentration as the pH decreases the $H_2CO_3^*$ concentration (and hence the CO_2 concentration) increases raising the partial pressure of CO_2 in the liquid, which increases the CO_2 transfer to the gas phase. This causes that the increase in gas production rate was approximately proportional to the increase in the fraction of carbon dioxide. Thus the change in gas production rate did not arise from a change in biochemical behaviour but due to physical laws of gas/liquid interactions under a change in pH.

These observations merit two conclusions: At a constant COD loading rate, constant base influent COD concentration and constant effluent H_2CO_3*alkalinity, (1) the recycle ratio (or equivalently the COD_e) could be used as a means to change the minimum bed pH and (2) a relatively large change in the recycle ratio (or COD_e) was required to induce a significant change in minimum bed pH.

*Option 2: COD loading rate, base influent COD concentration and effective influent COD constant, effluent H_2CO_3*alkalinity changing*

In this option experiments were performed at two fixed COD_e by imposing two recycle ratios of 22:1 and 12:1. For each recycle ratio a range of effluent H_2CO_3*alkalinity values were examined. The change in effluent H_2CO_3*alkalinity was affected by addition of HCl to the base influent. The experimental set-up remained the same as that in option 1. The characteristics of the wine distillery batch is shown in Table 8.8.

Table 8.8: Characteristics for settled wine distillery waste (batch 5)

Soluble COD fraction	98 %
Soluble COD concentration	27 000 mg/ℓ
inorg-N	90 mgN/ℓ
TKN	400 mgN/ℓ
Phosphorus	150 mgP/ℓ
pH	4,2

The sludge bed which had developed in option 1 was used as seed sludge for this experiment. The sludge bed volume was kept constant at 3 ℓ by draining excess sludge at weekly intervals. A COD loading rate of 9 kg/(m^3 sludge bed.d) was selected which was equal to that applied in option 1. The average sludge bed density was 40 kgVSS/(m^3 sludge bed). No nutrients or trace elements were added. Process monitoring remained the same as in option 1. The base influent COD was 27 000 mg/ℓ and the base flow 1 litre per day.

The first recycle ratio of 22:1 was instituted to give a COD_e of 1170 mg/ℓ. The system was operated for 30 days. During this period 50 mmol of HCl were added per litre of base influent which combined with the "washout effect" of H_2CO_3*alkalinity caused the H_2CO_3*alkalinity in the effluent to drop gradually from about 3500 to 1500 mg/ℓ (as $CaCO_3$); concomitantly the minimum bed pH declined from 7,4 to 6,6 over a period of 30 days. When the minimum bed pH declined to 6,6, HCl addition was terminated because the lower pH would have adversely affected the methanogens. After the HCl addition was terminated the recycle ratio was changed from 22:1 to 12:1, changing the effective influent COD to 2080 mg/ℓ. A gradual increase in H_2CO_3*alkalinity commenced to take place, again through "washout". Thus by utilizing the large retention time, via the the washout effect, HCl addition or omission and different recycles, the change in minimum bed pH with changing H_2CO_3*alkalinity could be studied at two different effective influent CODs.

Results and discussion:

COD and *SCFA:* The effluent COD and effluent SCFA concentrations during both recycle ratio periods are shown plotted in Fig 8.8. The effluent COD plot shows an increase at the beginning of this experiment but a steady decrease thereafter with a COD removal of about 95 % at the end of both recycle periods. The initial increase might have been due to the change to a different batch of wine distillery waste, i.e. the system requiring a short period of adaptation. The effluent SCFA concentrations remained low throughout the the recycle periods (below 60 mg/ℓ as HAc), indicating that the system was not affected significantly by the different recycle ratios (or COD_e) for minimum bed pH > 6,7.

Gas production and composition: The rate of gas production and the percentage of CO_2 in the gas are shown plotted in Fig 8.9. The rates of gas production and percentage CO_2 in the gas increased as the minimum bed pH decreased. When the minimum bed pH increased (after termination of HCl addition on day 35) the rate of gas production and the percentage of CO_2 in the gas decreased. An explanation for this increase in gas production and in the percentage CO_2 in the gas, with decreasing minimum bed pH, has been given earlier.

*H_2CO_3*alkalinity and minimum bed pH:* For the period during which a 22:1 recycle was employed (effective influent COD = 1170 mg/ℓ) the minimum bed pHs and the effluent H_2CO_3*alkalinities are shown plotted against each other in Fig 8.10. From Figs 8.10, (1) the minimum bed pH remained within the acceptable limits (pH = 7,4 and 6,8) even though the effluent H_2CO_3*alkalinities changed from about 3500 to 1800 mg/ℓ as $CaCO_3$, (2) to maintain a minimum bed pH of 7 at an effective influent COD of 1170 mg/ℓ, an effluent H_2CO_3*alkalinity of 2200 mg/ℓ as $CaCO_3$ was required. For the period during which a 12:1 recycle was employed (effective influent COD = 2080 mg/ℓ) the minimum bed pHs and the effluent H_2CO_3*alkalinities are shown plotted against each other in Fig 8.11. From Figs 8.11, (1) the minimum bed pH remained within the acceptable limits (pH = 6,8 and 7,2) even though the effluent H_2CO_3*alkalinities changed from about 2000 to 3000 mg/ℓ as $CaCO_3$, (2) to maintain a minimum bed pH of 7 at an effective influent COD of 1170 mg/ℓ an effluent H_2CO_3*alkalinity of 2800 mg/ℓ as $CaCO_3$ was required.

From option 2 it was concluded that for the same influent COD and the selected loading rate, (1) as the H_2CO_3*alkalinity in the effluent decreased the minimum bed pH concomitantly decreased, (2) for the same effluent H_2CO_3*alkalinity the higher recycle ratio, i.e. the lower COD_e, the higher the minimum bed pH.

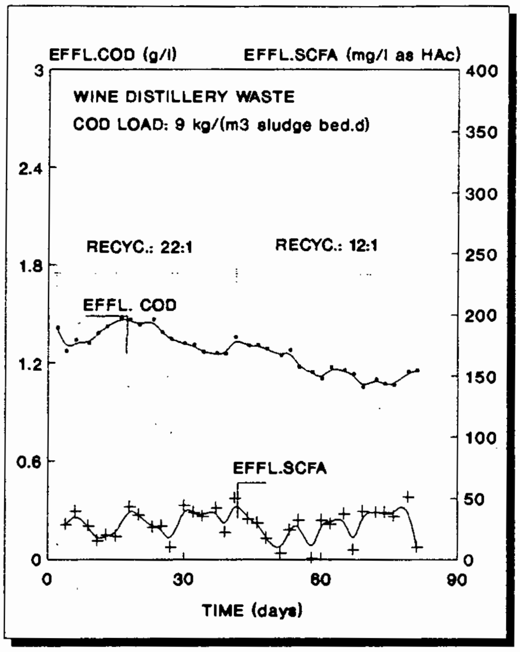

Fig 8.8: Effluent COD and SCFA concentrations of laboratory UASB reactor treating *undiluted* wine distillery waste operated with a 22:1 and 12:1 recycle respectively: Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 1170 mg/ℓ and 2080 mg/ℓ respectively; COD loading rate: 9 kg/(m³ sludge bed. d).

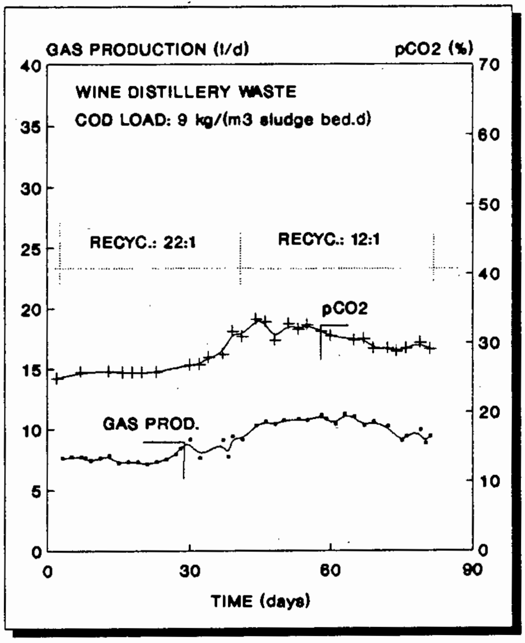

Fig 8.9: Total gas production per day and fraction of carbon dioxide in the gas of laboratory UASB reactor treating *undiluted* wine distillery waste operated with a 22:1 and 12:1 recycle respectively: Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 1170 mg/ℓ and 2080 mg/ℓ respectively; COD loading rate: 9 kg/(m³ sludge bed. d).

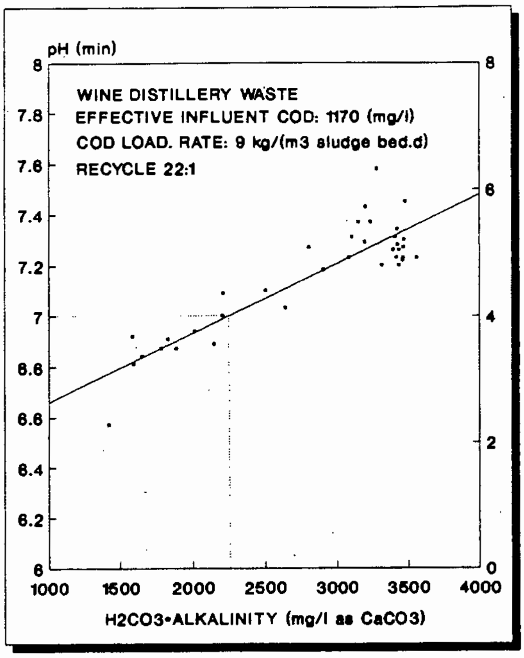

Fig 8.10: Relationship between H_2CO_3*alkalinity and minimum bed pH for laboratory UASB system treating undiluted wine distillery waste at a 22:1 recycle: Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 1170 mg/ℓ; COD loading rate: 9 kg/(m³ sludge bed. d).

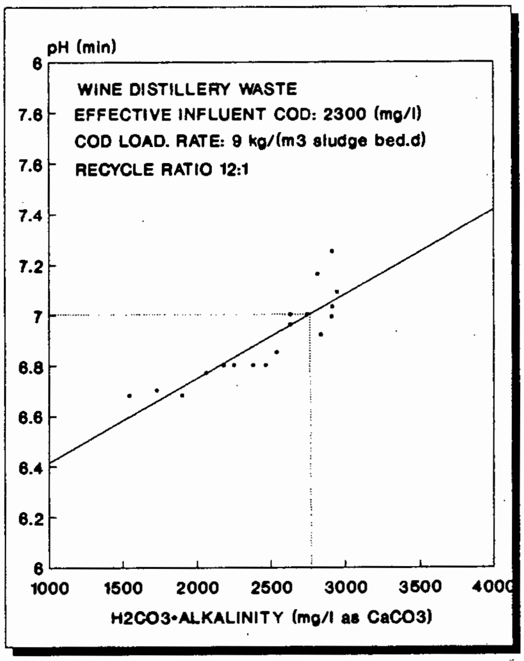

Fig 8.11: Relationship between H_2CO_3*alkalinity and minimum bed pH for laboratory UASB system treating undiluted wine distillery waste at a 12:1 recycle: Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 2080 mg/ℓ; COD loading rate: 9 kg/(m³ sludge bed. d).

Relationship between COD loading rate and minimum bed pH

In the experiments above the relationship between the minimum bed pH, the effective influent COD (or recycle ratio) and the effluent H_2CO_3*alkalinity had been investigated. All these tests were done at a constant COD loading rate of 9 kg/(m^3 sludge bed. d). The average sludge bed density was 39 kgVSS/(m^3 sludge bed). It was of interest to establish to what extent the minimum bed pH would change at different COD loading rates with the COD_e and effluent H_2CO_3*alkalinity remaining constant. In order to keep the effluent H_2CO_3*alkalinity constant the base influent COD was kept constant and the COD loading rate was changed by changing the base influent flow rate. To keep the effective influent COD constant the recycle ratio had to remain the same; this meant that when the base influent flow was increased, to increase the COD loading rate, the recycle flow rate had to be increased proportionally in order to keep r = recycle flow/base flow constant, i.e. keep COD_e constant.

Experimental set–up: In all experiments in which a recycle was employed (also to a lesser degree in the flow through reactor), at higher COD loading rates, i.e. higher than 9 kg/(m^3 sludge bed.d), in these small diameter reactors at times gas collected at random levels in the sludge bed and tended to lift the sludge above to the top of the reactor. Because COD loading rates much higher than 9 kg/(m^3 sludge bed.d) were envisaged in this experiment, it was decided to change the reactor set–up to minimize chances of sludge uplift. The change aimed at reducing the flow of gas in the upper part of the sludge bed. This could be achieved by constructing a baffled UASB system with two in–series compartments placed next to each other, where the second compartment receives the effluent of the first compartment, both compartments operating as upflow reactors, see Fig 8.12. The sludge bed was divided between the two reactors, i.e. the first reactor operated at a sludge bed level of 250 mm (2 ℓ of pelletised sludge) and the second at a sludge bed level of 125 mm (1 ℓ of pelletised sludge). In each compartment (cross sectional area: 90 · 90 mm) a settling section was installed and provision made for gas collection. Other than the change in reactor configuration, the experimental set–up remained the same as that in the previous experiments.

The characteristics of the wine distillery batch are shown in Table 8.9. No nutrients or trace elements were added.

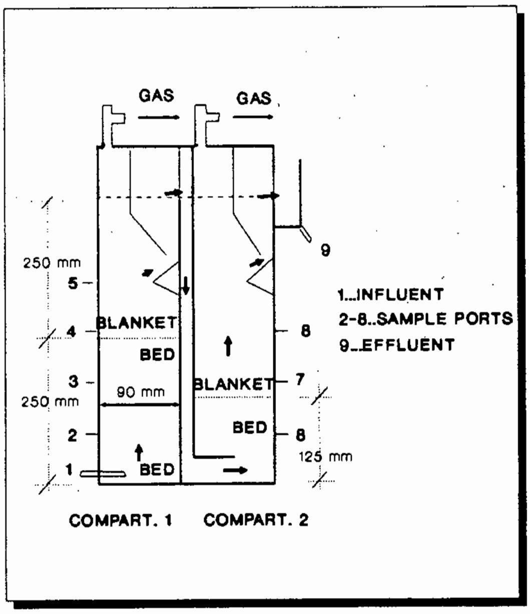

Fig 8.12: Schematic diagram for baffled laboratory UASB reactor with two in–series compartments.

Table 8.9: Waste characteristics for settled wine distillery waste (batch 6)

Soluble COD fraction	98 %
Soluble COD concentration	29 000 mg/ℓ
inorg–N	90 mgN/ℓ
TKN	430 mgN/ℓ
Phosphorus	160 mgP/ℓ
pH	4,1

The sludge bed which had developed in the previous experiment was used as seed sludge for this experiment. The sludge bed volume was kept constant at 2 ℓ in the first compartment, and at 1 ℓ in the second compartment by draining excess sludge at weekly intervals. An initial COD loading rate of 7 kg/[m^3 sludge bed (compartment 1+2).d] was selected to investigate process behaviour in the lower range of possible COD loading rates.

Recycle ratio: From the experiments on the relationships between effective influent COD, effluent H_2CO_3*alkalinity and minimum bed pH reported in the previous sections, using wine distillery waste with similar characteristics it was concluded that an effective influent COD of about 2200 mg/ℓ should result in a near neutral minimum bed pH. Accordingly a recycle ratio of 12:1 was maintained throughout the experiment under different COD loading rates, giving a COD_e of 29 000/(12+1) = 2230 mg/ℓ.

Process monitoring remained the same as in the previous task.

Results and discussion:

COD loading rates: In Fig 8.13 the COD loading rates applied during the this experiment are shown plotted versus time. The COD loading rate was increased incrementally from 7 to 19 kg/(m^3 sludge bed.d) within a period of 38 days. Towards the end of this period, despite the reduced sludge bed level in compartment 1, gas lifted individual pellets to the settling section and, gas collecting at bed levels below 100 mm (measured from the bottom) lifted the sludge *en mass* into the settling section. In all the tests using wine distillery waste the pellets did not appear as compact, or settle as readily as, for example, the pellets formed with glucose substrate. Lifting of the individual pellets probably was related to a reduced pellet density and a slight filamentous surface texture of the pellets; the tendency to accumulate gas in the bed probably was partly due to small reactor cross-section and partly due to the surface texture and density of the pellets. Compared to the feasibility study, when COD loading rates up to 45 kg/(m^3 sludge bed. d) were employed the tendency of sludge pellets being lifted to the top of the reactor was more pronounced in this experiment than in the feasibility experiment. For these reasons COD loading rates higher than 19 kg/(m^3 sludge bed.d) were not attempted. It may be noticed that during the feasibility study on a flow through UASB reactor fed with diluted wine distillery waste higher COD loading rates of up to 41 kg/(m^3 sludge bed.d) were possible. However, those "high" loading rates were only applied for a relatively short period of time; it is not clear whether a COD loading rate of 41 kg/(m^3 sludge bed.d) would have been possible over a longer period of time.

Effluent COD concentrations: The effluent COD concentrations were monitored in compartment 1 (samples taken from the settling section) and compartment 2, i.e.

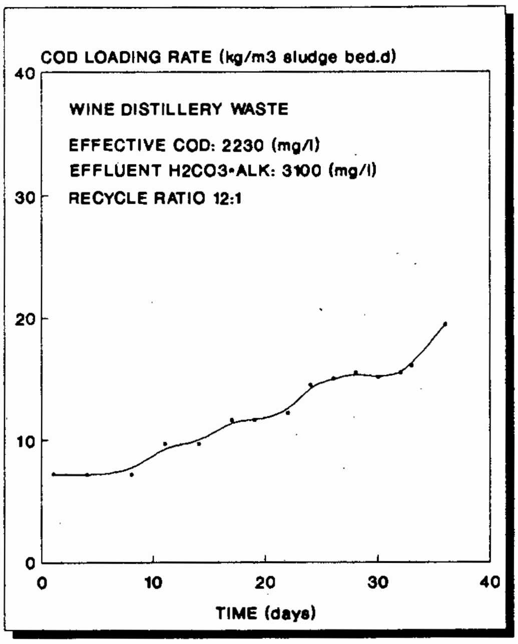

Fig 8.13: COD loading rate increase with time in baffled laboratory UASB system treating undiluted wine distillery waste: Base influent COD: 29 000 mg/ℓ; recycle ratio: 12:1; effective influent COD: 2230 mg/ℓ; effluent H_2CO_3*alkalinity: 3100 (mg/ℓ as $CaCO_3$).

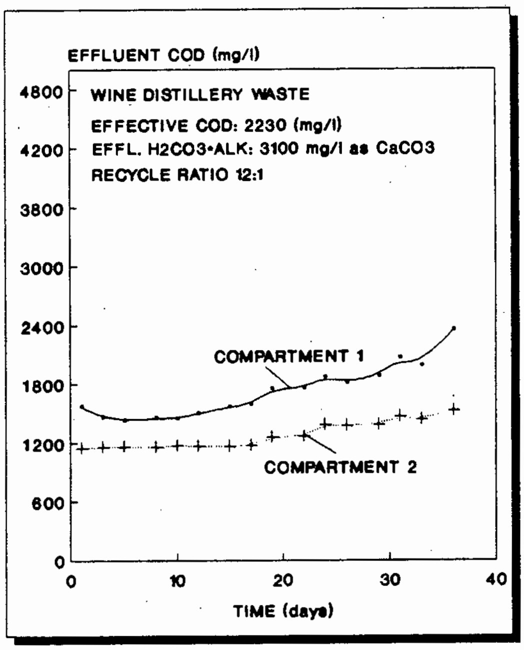

Fig 8.14: Effluent COD concentrations from compartment 1 and 2 in baffled laboratory UASB reactor treating *undiluted* wine distillery waste with a 12:1 recycle and changing COD loading rate (see Fig 8.13): Base influent COD concentration: 29 000 mg/ℓ; effective influent COD: 2230 mg/ℓ.

reactor effluent, and are shown plotted in Fig 8.14. Both plots show an increase of the effluent COD concentration when higher COD loading rates were applied.

SCFA concentrations: SCFA were monitored in the effluent from compartments 1 and 2 (reactor effluent) and are shown plotted in Fig 8.15. The plot of the SCFA from the first reactor compartment follows the same trend as that of the COD from this compartment, both increased with increasing COD loading rates. However, for the second compartment the effluent SCFA remained below 60 mg/ℓ throughout the experiment, with only an insignificant increase at higher COD loading rates, indicating that the in-series system was not overloaded.

Gas production: The gas production rates were measured in compartment 1 and 2 and are shown plotted in Fig 8.16. Both plots show an approximately proportional increase in gas production rates with increase in COD loading rate. The COD loading rate possibly could have been increased further but lifting of the pellets in the first compartment became evident at the COD loading rate of 19 kg/(m^3 sludge bed. d).

Gas composition: The gas produced in compartment 1 was analysed for methane and carbon dioxide; in Fig 8.17 the fraction of carbon dioxide is shown plotted versus time. This plot shows a slight increase in the fraction of carbon dioxide from 30 percent at the beginning of the experiment to 33 percent towards the end of the experiment. This increase is associated with a decrease in the pH in the sludge bed. This observation is in agreement with the expectation that the carbon dioxide fraction increases as the bed pH falls, as explained earlier.

COD loading rate and minimum bed pH: In Fig 8.18 the different COD loading rates (at constant COD_e and $H_2CO_3^*$alkalinity) are plotted versus the measured minimum bed pH. The plot indicates that an approximately threefold increase in COD loading rate changed the minimum bed pH from 7,1 to 6,8. Hence, at the an effective influent COD of 2230 mg/ℓ and an effluent $H_2CO_3^*$alkalinity of 3100 mg/ℓ as $CaCO_3$ the minimum bed pH remained within the pH limits for anaerobic fermentation (6,8 to 7,4) even though significant changes in COD loading rate took place.

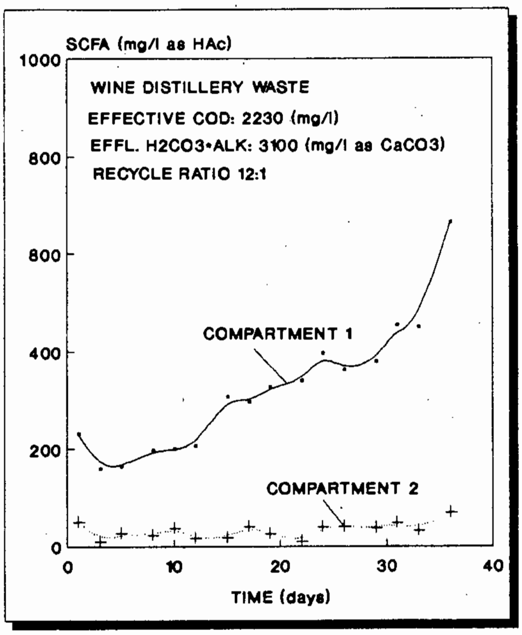

Fig 8.15: Effluent SCFA concentrations from compartment 1 and 2 in baffled laboratory UASB reactor treating *undiluted* wine distillery waste with a 12:1 recycle and changing COD loading rate (see Fig 8.13): Base influent COD concentration: 29 000 mg/ℓ; effective influent COD: 2230 mg/ℓ.

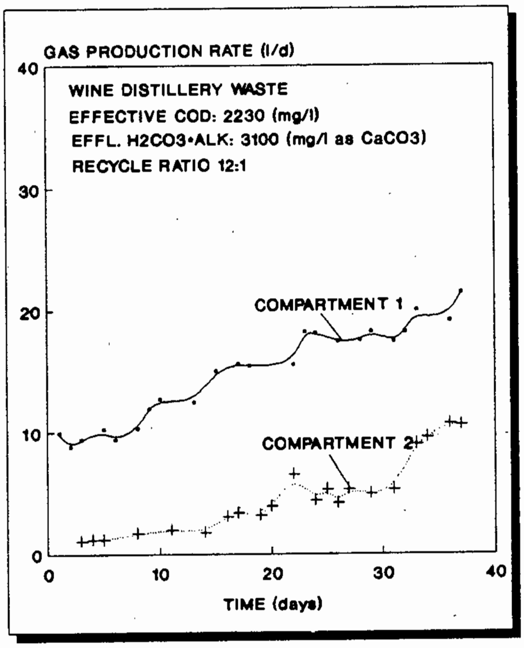

Fig 8.16: Total gas production per day in compartment 1 and 2 in baffled laboratory UASB reactor treating *undiluted* wine distillery waste with a 12:1 recycle and changing COD loading rate (see Fig 8.13): Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 2230 mg/ℓ.

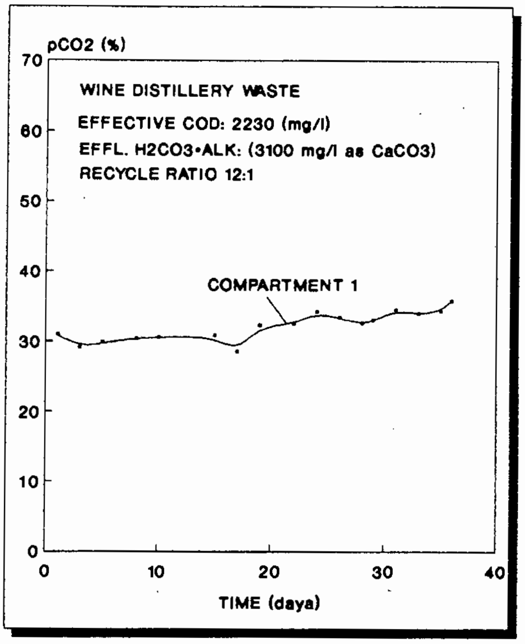

Fig 8.17: Fraction of carbon dioxide in total gas production in compartment 1 in baffled laboratory UASB reactor treating *undiluted* wine distillery waste with a 12:1 recycle and changing COD loading rate (see Fig 8.13): Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 2230 mg/ℓ.

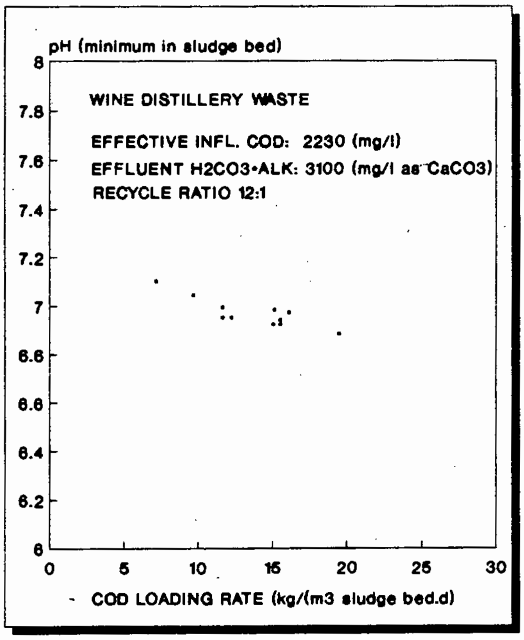

Fig 8.18: Relationship between minimum bed pH and COD loading rate in compartment 1 in baffled laboratory UASB reactor treating *undiluted* wine distillery waste with a 12:1 recycle and changing COD loading rate (see Fig 8.13): Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 2230 mg/ℓ.

From this task it can be concluded that for a constant base influent COD, a fixed recycle ratio (i.e. fixed COD_e) and constant H_2CO_3*alkalinity the minimum bed pH is relatively insensitive to the COD loading rate.

8.4 CONCLUSIONS

(1) The study of wine distillery waste in a laboratory scale UASB system showed that treatment of this substrate is feasible in a UASB system, and that the substrate develops a pelletised sludge bed. The pattern of product formation along the line of flow of the reactor is very similar to that observed under similar conditions treating a pure carbohydrate type substrate, e.g. glucose or apple juice concentrate.

(2) The TKN/COD ratio of the wine distillery waste was about 0,014 mgN/mgCOD; for unimpeded pelletisation when treating glucose in a UASB system Sam-Soon *et al.* (1990) suggested a TKN/COD ratio of 0,02 mgN/mgCOD. However, in this study the average mass of TKN uptake per mass of COD for wine distillery waste was 0,01 mgN/mgCOD. This reduced TKN uptake may be ascribed to the nature of the waste, i.e. part of the COD (short chain fatty acids and other organic acids) did not induce high hydrogen partial pressure conditions and hence, reduced biopolymer production took place. From the measured TKN uptake of about 0,01 mgN/mgCOD it would appear that in most cases wine distillery waste requires no addition of nitrogen, or only a little.

(3) Pellet production in the high hydrogen partial pressure region of the reactor was 0,14 mgVSS/(mgCOD removed). This pellet yield is significantly lower than that reported by Sam-Soon *et al.* (1987), 0,36 mgVSS/(mgCOD removed), when treating apple juicing wastes. This observation is in agreement with the reduced TKN uptake due to reduced pellet formation.

(4) The pellets produced were smaller, less compact than with glucose substrate as influent and appeared to have a sightly filamentous surface texture. This contributed to the pellets being lifted by the escaping gas to the gas seperator and the settler when the COD loading rate exceeded about 15 kg/(m^3 sludge bed.d) and in this manner set the upper limit for the COD

loading rate. (This applies to the part of the study in which undiluted wine distillery waste was fed to the UASB reactor using various recycle ratios to control the minimum bed pH to near neutral. With a flow through UASB system which was fed with diluted wine distillery waste, COD loading rates up to 41 kg/(m^3 sludge bed.d) were achieved without signs of system failure).

(5) When pH buffer was added in the form of NaOH to the undiluted feed, with addition of 1 gNaOH per litre feed the pH did not increase above 8,0 because the waste pH was very low (pH $\simeq$ 3) due to the presence of short chain fatty acids and other organic acids and their salts. Wine distillery waste generated significant internal buffer, i.e. H_2CO_3*alkalinity. This alkalinity was generated due to the removal of H^+ ions during deamination of proteins and the conversion of organic weak acid/base salts. The mass of H_2CO_3*alkalinity generated internally could not be predicted *ab initio* because the concentrations of the proteins and various organic acid/base salts could not be determined. The H_2CO_3*alkalinity generated was about 0,1 mgH_2CO_3*alkalinity (as $CaCO_3$) per mg base influent COD. Imposing a recycle from the effluent to the influent, the H_2CO_3*alkalinity generated in the bed and appearing in the effluent, is recycled to the influent; the dilution due to the recycle reduces the base influent COD to an effective influent COD, COD_e [COD_e = base influent COD/(1 + recycle ratio)]. As the recycle ratio increases the effective influent COD concentration decreases, with the effluent (i.e. recycled) H_2CO_3*alkalinity remaining constant the H_2CO_3*alkalinity/COD_e ratio increases causing the minimum bed pH to increase.

(6) The base influent COD concentrations ranged from 20 000 to 30 000 mg/ℓ. Dilution of the base influent COD to an effective influent COD (COD_e) of about 900 mg/ℓ, by applying a recycle ratio of 33:1, appeared to have no adverse effect on the process performance. Thus, it would seem that the lower limit of the effective influent COD of 2500 mg/ℓ, proposed by Sam–Soon *et al.* (1991) for satisfactory operation, can be substantially lowered.

(7) The effect of different effective influent COD (COD_e) concentrations on the minimum bed pH was evaluated at a constant COD loading rate of 9

kg/(m^3 sludge bed.d), a base influent COD of 27 000 mg/ℓ and an effluent H_2CO_3*alkalinity of about 3700 mg/ℓ (as $CaCO_3$), by applying three different recycle ratios of 33:1, 20:1 and 7:1 giving COD_e concentrations of 790 mg/ℓ, 1290 mg/ℓ and 3380 mg/ℓ respectively. The minimum bed pH decreased from 7,5 with COD_e = 790 mg/ℓ to 7,3 with COD_e = 1290 mg/ℓ and to 6,8 with COD_e = 3380 mg/ℓ. Hence by changing COD_e via the recycle the minimum bed pH changed considerably. COD removal was not significantly affected by the change in COD_e.

(8) The effect of change in effluent H_2CO_3*alkalinity on the minimum bed pH was evaluated at a constant COD loading rate of 9 kg/(m^3 sludge bed.d) and constant base influent COD. The effluent H_2CO_3*alkalinity was changed by adding a strong acid to the influent. Two different COD_e concentrations of 2300 mg/ℓ and 1170 mg/ℓ were tested. For COD_e of 1170 mg/ℓ (recycle ratio 22:1) the minimum bed pH changed from 7,5 to 6,8 when the effluent H_2CO_3*alkalinity decreased from 3500 to 1800 mg/ℓ (as $CaCO_3$). To maintain a minimum bed pH $\simeq$ 7 the effluent H_2CO_3*alkalinity required was about 2200 mg/ℓ (as $CaCO_3$) at a recycle ratio of 22:1. For COD_e of 2300 mg/ℓ (recycle ratio 12:1) the minimum bed pH changed from 7,2 to 6,8 when the effluent H_2CO_3*alkalinity decreased from about 3000 to 2200 mg/ℓ (as $CaCO_3$). To maintain a minimum bed pH $\simeq$ 7 the effluent H_2CO_3*alkalinity required was approximately 2800 mg/ℓ (as $CaCO_3$) at a recycle of 12:1. Hence, the effluent H_2CO_3*alkalinity requirements to maintain a near neutral minimum bed pH decrease with a decrease in COD_e (i.e. with an increase in recycle ratio). Consequently if the internally generated H_2CO_3*alkalinity decreases (with the base influent COD remaining constant), the recycle ratio can be increased to maintain the same near neutral minimum bed pH.

(9) The effect of different COD loading rates on the minimum bed pH was evaluated by using a constant base influent COD concentration (29 000 mg/l) and changing the base influent flow. The recycle ratio was kept constant at 12:1 giving a COD_e of 2230 mg/ℓ. The effluent H_2CO_3*alkalinity was constant at 3100 mg/ℓ (as $CaCO_3$). When the COD loading rate was increased from 7 to 19 kg/(m^3 sludge bed.d) by increasing the base flow the minimum bed pH decreased from 7,1 to 6,8. It would appear that for the same base influent COD *concentration* and a constant

recycle ratio the minimum bed pH remained relatively stable despite an almost threefold change in COD loading rate.

(10) The pH profiles in the bed exhibited only a slight depression (to the minimum pH) for recycle ratios of 33:1 and 20 :1 (base influent COD of 27 000 mg/ℓ and COD_e concentrations of 790 and 1290 mg/ℓ). This tendency to smooth out the "dip" in the pH profile at low effective influent CODs, conforms with the observations of Sam–Soon *et al.* (1991).

(11) From the experiments on recycling carried out in this laboratory scale study, it appears that the base influent COD should be diluted by the recycle to an effective influent COD range of about 1500 to 2000 mg/ℓ. Within this range of COD_e, for a COD loading rate of about 10 kg/(m^3 sludge bed.d) the different batches of wine distillery wastes generated sufficient internal H_2CO_3*alkalinity to maintain a near neutral minimum sludge bed.

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CHAPTER 9

TREATMENT OF CASEIN IN A UASB REACTOR
AND
INFLUENCE OF pH CHANGE ON PROCESS PERFORMANCE

ABSTRACT

Biological pellet formation was readily established in a flow through laboratory scale upflow anaerobic sludge bed (UASB) reactor treating a proteinaceous waste, casein. Pellets were small (< 2 mm), fragile and black. From a two in–series reactor system, in the first reactor, operated in high hydrogen partial pressure state, the specific VSS yield was 0,26 mgVSS/mgCOD removed, but two–thirds of the VSS were discharged from the sludge bed as debris; deamination generated inorganic nitrogen in excess of nitrogen requirements for pellet formation, and generated sufficient alkalinity to buffer the minimum bed pH to > 6,2. When the minimum bed pH in the first reactor was increased to about 7, by addition of $NaHCO_3$ to the influent, the minimum bed pH in the second reactor increased to 7,6; the resulting increase in the NH_3 species gave rise to increased levels of propioniate in the second reactor effluent, possibly due to inhibition of hydrogenotrophs; with time adaptation to the increased concentrations of NH_3 took place. In the flow through single UASB system with an influent COD of 10 500 mg/ℓ, COD loading rates up to 65 kgCOD/(m^3 sludge bed. d) were applied without signs of failure, with COD removals from influent to filtered effluent > 95 percent.

9.1 INTRODUCTION

In Chapters 7 and 8 treatment of lauter tun (brewery) and wine distillery wastes in UASB systems respectively were reported. The $H_2CO_3^*$alkalinity requirements for these two wastes in order to maintain a near neutral minimum bed pH at different recycle ratios, were investigated. For the lauter tun waste virtually all the $H_2CO_3^*$alkalinity had to be supplied from an external source. For wine distillery waste no $H_2CO_3^*$alkalinity needed to be supplied from an external source; $H_2CO_3^*$alkalinity was generated in the sludge bed by deamination of proteins to inorganic nitrogen (NH_3/NH_4^+) and by fermentation of organic acid salts (e.g. potassium malate, potassium bitartrate), and was reused by imposing an appropriate recycle from the effluent to the influent.

Although deamination of protein to inorganic nitrogen (NH_3/NH_4^+) is beneficial to the UASB process in that it provides H_2CO_3*alkalinity, it raises the possibility that the increased levels of inorganic nitrogen, in particular NH_3, may be inhibitory to anaerobic microorganisms: McCarty (1964) found NH_4^+ to be inhibitory at 3000 mgN/ℓ and ammonia at 80 mgN/ℓ, that is, NH_3 is far more inhibitory to the anaerobic process than NH_4^+. The relationship between inorganic nitrogen and pH is demonstrated in the log species diagram, Fig 2.1b; as the pH increases above about 7,4 so the fraction of ammonia becomes increasingly dominant. Thus, substrates having a high organic nitrogen content may yield such high inorganic nitrogen from deamination, that above neutral pH the ammonia (NH_3) concentration may become inhibitory.

Up to the present little information is available on treatment of wastes with a high proteinaceous content in a UASB system. Accordingly an investigation was undertaken to enquire into the treatment of a pure proteinaceous substrate casein in a UASB system, i.e. into pelletisation, protein deamination, alkalinity generation, COD removal, and, ammonia inhibition due to pH increase.

9.2 ASSESSMENT OF CASEIN AS SUBSTRATE

According to Sam-Soon *et al.* (1987) prerequisites for pelletisation by the hydrogenotroph *M* Strain *AZ*, now known as *Methanobrevibacter arboriphilus*, are: (1) a high hydrogen partial pressure, (2) excess supply of inorganic nitrogen, (3) pH buffered to near neutrality, and (4) limited source of the amino acid cysteine. These prerequisites are satisfied in the acidogenic phase of a UASB reactor receiving a carbohydrate substrate provided the influent has an adequate supply of inorganic nitrogen, and sufficient alkalinity to control the minimum pH to near neutrality.

In anaerobic fermentation, a proteinaceous substrate follows the same phases of breakdown as a carbohydrate substrate, acidogenesis, acetogenesis etc. (Gujer *et* *al.*, 1983). In the acidogenic phase the amino acids are deaminated to yield ammonia and short–chain fatty acids (SCFA); some amino acids also yield H_2; if the H_2 should be yielded under high hydrogen partial pressure (high $\bar{p}H_2$), and if deamination should produce an excess amount of inorganic nitrogen, two of the prerequesites for pellet formation should be satisfied. Deamination also yields OH^- ions, i.e. will generate alkalinity, and hence will buffer against pH change; if the buffer action is such that the pH is maintained near neutral the system may not need alkalinity addition. With regard to the 4th prerequisite, cysteine deficiency, it is not possible to state *ab initio* whether this will be satisfied or not; most proteins contain cysteine which, if available will reduce the potential for pelletisation, Sam Soon *et al.* (1987). However, cysteine may be deaminated in the acidogenic phase, in which event its availability to *M* Strain *AZ* might be limited and the possibility for pelletisation improved.

9.3 BIOCHEMISTRY OF AMINO ACID FERMENTATION

We have stated earlier that fermentation of amino acids follows the same phases as those for a carbohydrate, i.e. acidogenesis, acetogenesis and methanogenesis (Gujer *et al.*, 1983). The acetogenic and methanogenic pathways always would be independent of the substrate, provided the appropriate intermediates they act on are produced. The acidogenic pathways for amino acids however differ from those for carbohydrates and differ greatly even between the different amino acids.

For most amino acids the acidogenic phase of fermentation takes place in two stages, (1) a deamination stage with release of ammonia and various organic products depending on the amino acid deaminated, and (2) an oxidation stage where the products from (1) are oxidized to short chain fatty acids (SCFA) principally butyric, propionic and acetic acids (White *et al.*, 1973).

(1) Deamination stage

Deamination occurs either via (i) oxidative, (ii) reductive or (iii) oxidative/reductive coupled deamination reactions, all these reactions releasing ammonia.

(i) *Oxidative deamination*: Examples of amino acids which undergo oxidative deamination are alanine, valine, leucine, isoleucine. Considering alanine, the oxidative deamination process is,

$$\text{2 alanine} + \text{2 NAD} \rightarrow \text{2 pyruvic acid} + 2\,NH_3 + \text{2 NADH} \tag{9.1}$$

(Formulation of Eq (9.2), using 2 moles of alanine, becomes clear in discussing the oxidative stage below, under high $\bar{p}H_2$). This reaction terminates unless the NADH can be oxidized, see oxidative stage (2) below.

(ii) *Reductive deamination*: Examples of amino acids that undergo reductive deamination include glycine, proline, tryptophan. Considering glycine, the reductive deamination process is,

$$\text{glycine} + \text{NADH} \rightarrow \text{acetic acid} + NH_3 + \text{NAD} \tag{9.2}$$

(iii) *Coupled deamination*: An amino acid undergoing oxidative deamination can be coupled with another undergoing reductive deamination giving rise to the so-called Stickland coupled deamination reaction. The NADH generated in the oxidative reaction forms the NADH source for the reductive reaction. The sum of Eqs (9.1 and 9.2) gives the coupled reaction,

$$\text{glycine} + \text{alanine} \rightarrow \text{pyruvic acid} + \text{acetic acid} + 2\,NH_3 \tag{9.3}$$

This coupled reaction is independent of $\bar{p}H_2$.

In the deamination stage always NH_3 is produced together with SCFA or SCFA and pyruvate. In terms of the general theory for weak acid/base systems, for glycine for example, when HAc and NH_3 are produced, the H_2CO_3/HAC/HPr/NH_4^+–alkalinity will increase (see Chapter 2). At near neutral pH conditions, the NH_3/NH_4^+ weak acid/base ($pK_{an} \simeq 9{,}4$) acts as a strong base which buffers against a pH decrease resulting from the presence of SCFA and CO_2. This aspect is dealt with in greater detail in Chapter 2.

(2) Oxidative stage

The organic products and NADH generated in the oxidative deamination stage [e.g. Eq (9.1)] can be oxidized via various pathways depending on the nature of the organic products and $\bar{p}H_2$. As an illustration consider the products pyruvate and NADH in Eq (1) under low and high $\bar{p}H_2$.

Low $\bar{p}H_2$: Where $\bar{p}H_2$ is less than 10^{-6} atm, oxidation of NADH to NAD and H_2 is thermodynamically feasible. In Eq (9.1) above the NADH generated during deamination is oxidized (dehydrogenated) as follows:

$$2\ \text{NADH} \rightarrow 2\ \text{NAD} + H_2 \tag{9.4}$$

The pyruvic acid is oxidized to acetyl CoA as follows:

$$\text{CoASH} + \text{pyruvic acid} + \text{NAD} \rightarrow \text{acetyl CoA} + CO_2 + \text{NADH} \tag{9.5}$$

and acetyl CoA is converted to acetic acid:

$$\text{acetyl CoA} + \text{ADP} + \text{P} \rightarrow \text{acetic acid} + \text{ATP} + \text{CoASH} \tag{9.6}$$

Thermodynamically, equation (9.6) is a highly favourable reaction. Again the NADH formed in Eq (9.5) is oxidized spontaneously to NAD and H_2, as in Eq (9.4). The net result of the reactions in Eqs (9.4, 9.5 and 9.6) is that pyruvate is oxidized to acetic acid and hydrogen with the production of energy, ATP.

High $\bar{p}H_2$: In Eq (9.4) as the $\bar{p}H_2$ rises, NADH oxidation is increasingly inhibited. When $\bar{p}H_2$ exceeds 10^{-6} atm, NADH oxidation is no longer thermodynamically feasible. With high $\bar{p}H_2$ ($> 10^{-6}$atm) oxidation of the 2 mol of NADH, generated in Eq (9.1), takes place by reducing 1 mol of pyruvic acid to propionic acid,

$$\text{pyruvic acid} + 2\ \text{NADH} \rightarrow \text{propionic acid} + 2\ \text{NAD} \tag{9.7}$$

and the remaining mole of pyruvic acid to acetyl CoA and NADH,

$$\text{NAD} + \text{pyruvic acid} + \text{CoASH} \rightarrow \text{acetyl CoA} + CO_2 + \text{NADH} \tag{9.8}$$

In Eq (9.8) NADH is produced; energy is required to oxidize the NADH to NAD and H_2; this is achieved by coupling into the energetically favourable reaction Eq (9.6) to give,

$$\begin{aligned}&\text{acetyl CoA} + \text{NADH} + \text{ADP} + \text{P} \rightarrow \text{acetic acid} + \text{NAD}\\&+ \text{CoA} + H_2 + \text{ATP}\end{aligned} \qquad (9.9)$$

The net result of the reactions shown in Eqs (9.7, 9.8 and 9.9) is that pyruvate is oxidized to propionic acid, acetic acid and hydrogen with production of energy, ATP.

The description above applies to amino acids in which pyruvate and hydrogen are products in the acidogenesis pathway. Pyruvate and hydrogen also are common intermediates in the acidogenic breakdown of carbohydrates. Further breakdown of pyruvate will be the same irrespective of whether it originates from carbohydrates or amino acids. Hence, where pyruvate and hydrogen are products in the acidogenic breakdown of proteins, development of a high $\bar{p}H_2$ is as likely with such a substrate as with carbohydrate substrate. Should a high $\bar{p}H_2$ develop, prerequisite (1) for pelletisation would be satisfied; production of NH_3 in the acidogenic fermentation of proteins should assist in satisfying prerequisite (2). The amino acid cysteine present in the influent protein may be deaminated or be so low, to be insufficient to satisfy the requirements for balanced hydrogenotrophic organism growth, in which event prerequisite (4) would be satisfied. Provided the alkalinity generation during deamination is sufficient to buffer the pH to near neutrality, it would seem that, from a biochemical point of view, pelletisation in a UASB system could take place with a protein type substrate.

9.4 EXPERIMENTAL OBJECTIVES

To study the effect of a proteinaceous substrate on pelletisation in a UASB system, a pure protein, casein, was selected as substrate for reason that it was readily available, and relatively inexpensive compared to other pure proteins.

The experimental investigation comprised:

- *Feasibility study*: To obtain information on the system response via product formation (COD, SCFA, pH, NH_4^+-N), potential for pellet production, and alkalinity requirements.

- *Sludge yield*: To determine the sludge yield.

- *Effect of pH change on system performance:* To study the effect of high NH_3 species concentrations on the sludge yield and product formation.

9.5 EXPERIMENTAL SET UP

Apparatus

To investigate the response of the UASB system to a proteinaceous substrate a laboratory scale, steady state study was undertaken using two different UASB reactor configurations:

- ***High/low*** $\bar{p}H_2$ ***system*** : This system comprised a *single* reactor with a sufficiently large bed to incorporate both high and low $\bar{p}H_2$ zones. The unit comprised a vertical 94 mm diameter perspex cylinder with a conically shaped inlet at the bottom and a solid liquid separation unit at the top (see Fig 9.1a); twelve ports were installed up the wall of the reactor for sampling along the line of flow. The total volume of the reactor was 10,5ℓ. Temperature was maintained at 30°C ± 1 degC by a thermostat controlled electrical heating tape wrapped around the reactor.

- ***Two in-series reactor system*** : In this system the first reactor was operated with a sludge volume sufficiently small to isolate the high $\bar{p}H_2$ zone, i.e. operated at a volume such that the propionate profile showed a steady increase throughout the bed (Sam-Soon *et al.*, 1987). The second reactor received the effluent discharged from the first reactor and operated principally under a low $\bar{p}H_2$. The first reactor had a volume of 3,5ℓ, and the second a volume the same as the high/low $\bar{p}H_2$ reactor, 10,5ℓ (Fig 9.1b). Both reactors were controlled at 30°C.

Substrate feed:

During the starting-up period, with the single high/low $\bar{p}H_2$ reactor, the feed was a mixture of diluted apple juice concentrate and peptone (casein). Over a period of about 50 d the feed was changed gradually from a mixture of peptone-apple

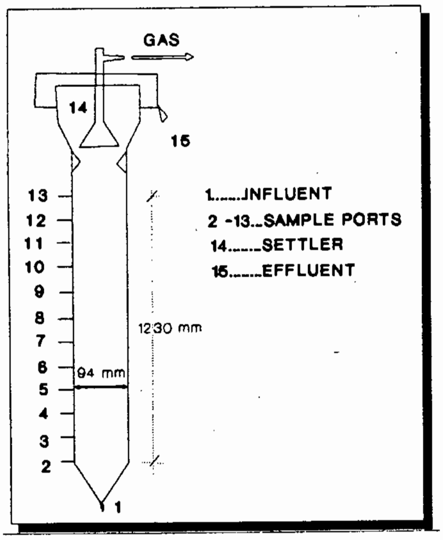


Fig 9.1a: Laboratory scale UASB reactor for high/low $\bar{p}H_2$ reactor experiment.

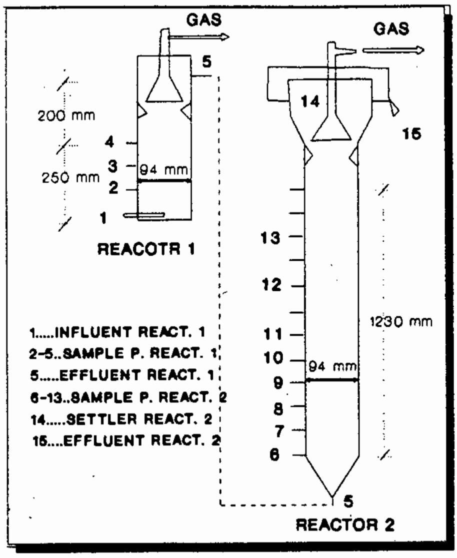


Fig 9.1b: Laboratory scale UASB reactors for two single in-series reactor experiment.

juice (50:50 in terms of COD) to 100 per cent peptone which remained the substrate for the rest of the experiment. The peptone, supplied by Merck, consisted of nearly 100 per cent casein with a TKN/COD ratio of 0,12 and a NH_3-N/COD ratio of 0,02; the various amino acids contained in casein are listed in Table 9.1.

Nutrients and trace elements:

To ensure adequate nutrients and trace elements for growth, solutions of these were made up, following the recipe of Zehnder and Wuhrmann (1977), see Table 9.2.

Operational mode:

The systems were operated in a flow through mode, that is, no recycle was imposed. This mode was followed because the interest was more in the effect of pH on product formation and sludge yield than in bed pH control – the principles of pH control via a recycle were adequately understood from the work on the lauter tun (Chapter 7) and wine distillery wastes (Chapter 8).

Table 1: Approximate amino acid composition of casein calculated to 16 percent nitrogen

Amino Acids	per cent
Arginine	4,1
Histidine	2,5
Lysine	6,9
Tyrosine	6,4
Tryptophan	1,8
Phenylalanine	5,2
Cysteine	0,36
Methionine	3,5
Serine	6,7
Threonine	3,9
Leucine	12,1
Isoleucine	6,5
Valine	7,0
Glutamic acid	22,8
Aspartic acid	6,3
Glycine	0,5
Alanine	5,6
Proline	8,2
Hydroxyproline	2

Table 2: Nutrient and trace element stock solutions

Trace element	Concentration g/ℓ
H_3BO_3	0,05
$FeC\ell_2.{}_2H_2O$	2,00
$ZnC\ell_2$	0,05
$MnSO_4$	0,5
$CuC\ell_2\ 2H_2O$	0,03
$(NH_4)_6\ MO_7\ O_{24}.4\ H_2O$	0,05
$AlC\ell_3.6H_2O$	0,05
$CoC\ell_2.6H_2O$	2,00
$MnC\ell_2$	0,25
$MgC\ell_2$	1,00
EDTA	0,05
$Ni\ C\ell_2.6H_2O$	0,25
$HC\ell$	1mℓ
Nutrients	**Concentration g/ℓ**
$NH_4C\ell$	10,00
K_2HPO	4,00

Parameters measured:

The following parameters were measured at 1 to 2 day intervals:

- unfiltered influent and filtered and unfiltered effluent COD,
- unfiltered influent and filtered effluent TKN and NH_3-N,
- pH in the influent, settler and effluent,
- substrate flow rate.

In addition, at appropriate times, profiles of COD, TKN, inorg-N, the SCFA (propionic (HPr) and acetic (HAc)), were measured along the axis of flow of the reactors. Samples were taken at each sample port, starting at the top. Samples were filtered using ordinary filter paper, Schleicher and Schuell 595. For the SCFA, samples were refiltered through a 0,45 micron filter paper (millipore) and the various SCFA measured by gas chromatography using a 60/80 Carbo pack C/0,3% Carbo wax packing. COD, TKN and inorg–N were measured in accordance with Standard Methods (1989). Total alkalinity, i.e. $H_2CO_3^*/H_2PO_4^-/HAc/HPr/NH_4^+$ alkalinity, was approximated using the Gran plot to determine the mass of strong acid added to give a zero first Gran Function value which is the mass of strong acid to be added to the equivalence point (in this case an approximate equivalence point) for this total alkalinity, Loewenthal *et al.* (1989). This total alkalinity was measured because at the time when this experiment was carried out the 5 pH point titration method (in which the $H_2CO_3^*$alkalinity and SCFA are determined as unknowns) was not yet available, see Chapter 5).

9.6 FEASIBILITY STUDY

In order to study the potential for development of pelletised sludge in a UASB reactor system with casein as substrate the single high/low $\overline{p}H_2$ reactor was set up. This study may be divided into the following stages:

- starting up
- steady state
- high loading.

These different stages are now set out in more detail.

Starting up

The starting up period can be divided into two phases of 20 and 30 days. During the first phase the sludge was adapted from a substrate of pure carbohydrate waste to one containing both carbohydrate and casein. During the second phase the sludge was adapted to a casein substrate only.

First phase : The reactor was seeded with approximately 1,5ℓ of pelletised sludge from a UASB reactor treating diluted apple juice concentrate as substrate. A constant substrate mix of 50:50 per cent of apple juice concentrate and casein (in terms of COD) was fed. The flow rate was kept constant at 5 ℓ/d but the influent COD concentration of the mix was increased in increments, from 800 to 3 500 mgCOD/ℓ. Throughout this phase 25 mℓ of nutrient solution (including ammonium chloride at 10 $gNH_4Cl/ℓ$), 2 mℓ of trace element solution and 6,5 $gNaHCO_3$ per litre of influent were added to the feed. The sludge bed volume remained virtually unchanged at 1,5 ℓ during the first 20 days giving a COD loading rate of 2,7 kgCOD/(m^3 sludge bed.d) at the beginning, and was incrementally increased to 11,7 kgCOD/(m^3 sludge bed.d) at the end of the first phase. Despite the increasing COD loading rate the filtered effluent COD decreased, indicating that the sludge was adapting well. The filtered effluent COD eventually stabilized at about 300 mg/ℓ for a 3 500 mg/ℓ influent COD consisting of 50 per cent casein and 50 per cent apple juice concentrate.

Second phase: In the second phase, to adapt the sludge to a 100 per cent casein substrate, the flow was maintained at 5ℓ/d and the influent COD at approximately 3 500 mgCOD/ℓ. Over the next 30 days the casein fraction was increased incrementally, from 50 to 100 per cent. Addition of alkalinity (6,5 g $NaHCO_3$), trace element (2 mℓ) and nutrient (25 mℓ) per litre of influent remained as before except for the inorg-N; after 18 days into the second period the inorg-N (70 mg/ℓ influent) was left out of the nutrient solution – as the casein fraction of the influent feed increased, the effluent concentration of ammonia did likewise, so that nitrogen deficiency was no longer likely. COD removal remained above 90 per cent throughout the second period, indicating that the sludge was adapting to the changing substrate.

After 30 days the sludge mass appeared to have been fully adapted to a 100 per cent casein substrate. Thereafter over a period of 81 days the COD loading rate was progressively increased from 17,5 gCOD/d (3 500 mgCOD/ℓ at 5 ℓ/d) to 135 gCOD/d (5 200 mgCOD/ℓ at 26 ℓ/d). Alkalinity supplementation remained at 6,5 g $NaHCO_3$/ℓ influent. Despite this significant increase in COD loading rate the COD concentration in the effluent remained virtually unchanged even at the highest COD loading rate, indicating that the system was not overloaded. At the end of this phase the sludge bed mass had increased from 1,5ℓ to 2,8ℓ giving a bed depth of 230 mm and a loading rate of 135/2,8 = 48 kgCOD/(m^3 sludge bed. d). Because the increase in bed mass indicated that pelletisation was active up to the maximum COD loading rate, it was decided to allow steady state conditions to develop at this COD loading rate and investigate the systems response in detail.

Steady state

At the steady state COD loading rate of 48 kgCOD/(m^3 sludge bed.d) the system responses with respect to COD, TKN, inorg-N (NH_3, NH_4^+) and org-N were the following:

COD removal: Average COD removal was 95 per cent (5029 mgCOD/ℓ removed). The pelletised sludge volume remained constant at approximately 2,8 ℓ.

TKN uptake: Uptake of nitrogen, calculated from the difference in the TKN concentration in the influent and filtered effluent, was 72 mgN/ℓ. In a 'normal' anaerobic process the following ratios for the utilization of nitrogen, COD and associated VSS generation apply (ten Brummeler *et al.*, 1985):

TKN/COD ratio for protoplasm = 0,086 mgN/mgCOD
COD/VSS ratio for protoplasm = 1,42 mgCOD/mgVSS
i.e. TKN/VSS = 0,086·1,42 = 0,122 mgN/mgVSS
Biomass yield = 0,03 VSS/COD removed .

Thus in a 'normal' anaerobic system the protoplasm generated would be

0,03·5029 mgVSS/ℓ influent; with a TKN/VSS ratio of 0,122 the TKN removal for synthesis would be 0,03·5029·0,122 = 13,4 mgN/ℓ influent. The observed nitrogen removal, however, was 72 mgN/ℓ; this is more than 5 times higher than that normally expected – the disappearance of nitrogen could not be explained by protoplasmic mass generation only.

Inorganic nitrogen: Org-N in the influent was 466 mgN/ℓ and in the effluent 21 mgN/ℓ, that is, about 95 per cent of the org-N was converted to inorg-N (this aspect is discussed in greater detail later).

Profiles : To obtain detailed information on the bed's response, profiles of total alkalinity, acetic acid (HAc), propionic acid (HPr), TKN, inorg-N and pH were measured, shown in Fig 9.2. For the moment the most significant profile is that of pH. The pH was relatively high throughout the reactor, with the lowest pH 7,4 near the bottom of the bed at sample port 2, and the highest pH 7,7 in the upper zone of the bed. Methanogens operate optimally around pH 7,0 and acidogens below pH 7 so that the pH was high for both species. To lower the pH to more favourable values, $NaHCO_3$ addition was terminated. After the system had stabilized another profile was measured (see Fig 9.3). There was now a significantly lower pH throughout the bed with a minimum pH 6,6 at sample port 2. The generally lower pH had little effect on the pattern of COD removal, TKN uptake and organic nitrogen conversion. However there was a slight increase in the concentrations of HAc and HPr, most likely due to increased activity of the acidogens and decrease in activity of the methanogens at the lowered pH. In both Figs 9.2 and 9.3 HAc and HPr profiles indicated complete conversion to methane after passing through 70 per cent of the bed – the system still appeared to be underloaded.

High loading

To obtain information under yet higher COD loading rates, the daily COD load was increased in two steps, by setting the flow rate at 28 ℓ/d and increasing the COD concentration to 7 500 and subsequently to 10 500 mgCOD/ℓ [50 and 65 kgCOD/(m^3 sludge bed. d)] respectively. There was *no alkalinity supplementation* of the influent, resulting in an influent pH of 6,6. Under each COD loading rate the sludge mass was allowed to increase and when the effluent COD indicated steady state, profiles were measured. These are shown in Figs 9.4 and 9.5 respectively. Both profile sets showed similar trends, hence, only the set

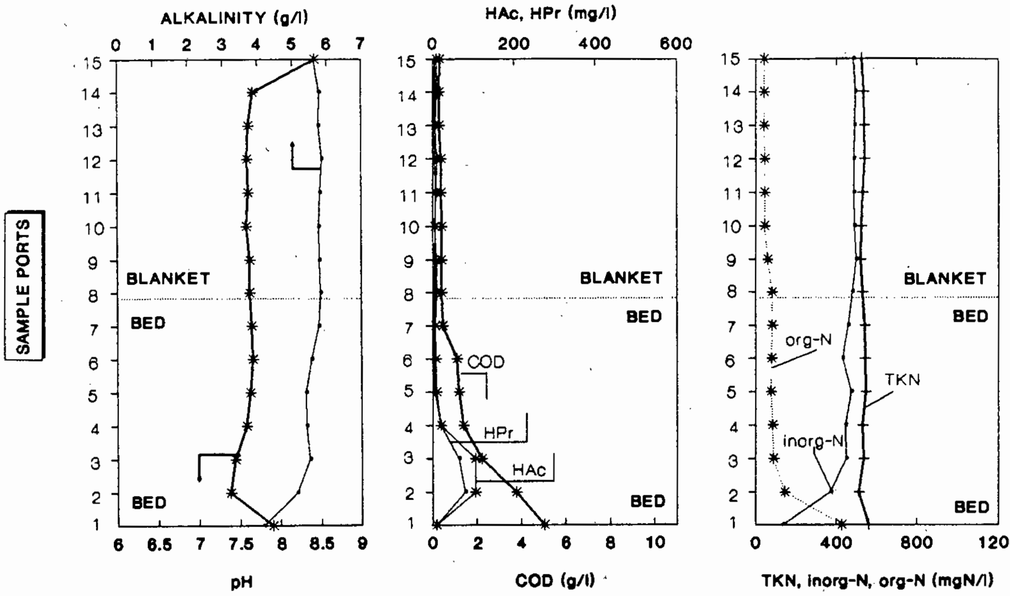


Fig 9.2: High/low $\bar{p}H_2$ single reactor system: profiles of pH, total alkalinity as $CaCO_3$, org-N, inorg-N, TKN, COD, acetic (HAc) and propionic acid (HPr). Addition of 6,5 g $NaHCO_3$ per litre influent; flow rate 25 ℓ/d; influent COD 5320 mg/ℓ; COD load on pelletised sludge 48 kg COD/m³.d.

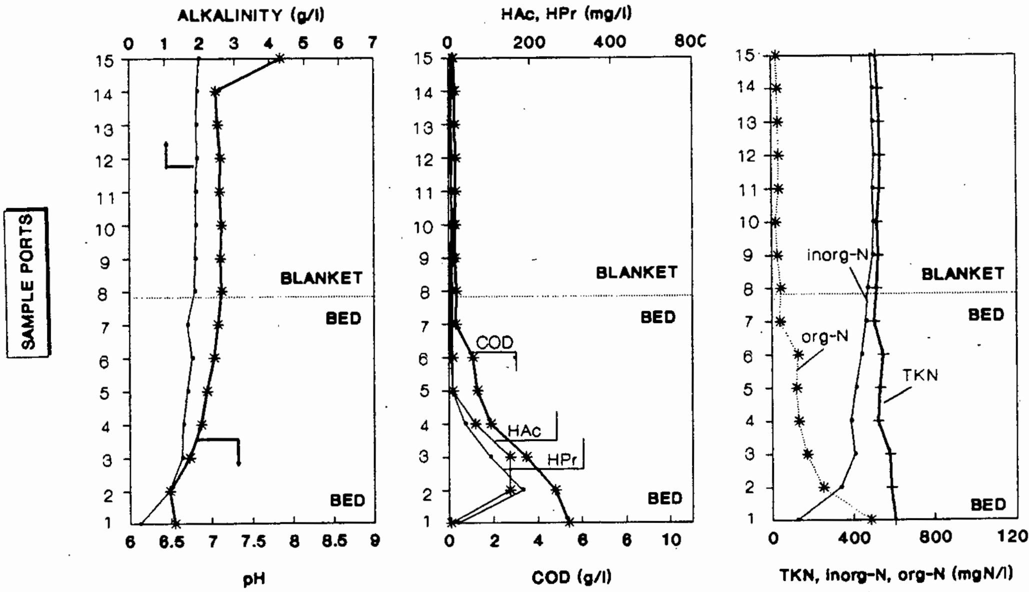


Fig 9.3: High/low $\bar{p}H_2$ single reactor system: profiles of pH, total alkalinity as $CaCO_3$, org-N, inorg-N, TKN, COD, acetic (HAc) and propionic acid (HPr). No addition of $NaHCO_3$ to feed; flow rate 25 ℓ/d; influent COD 5300 mg/ℓ; COD load on pelletised sludge 48 kg COD/m³.d.

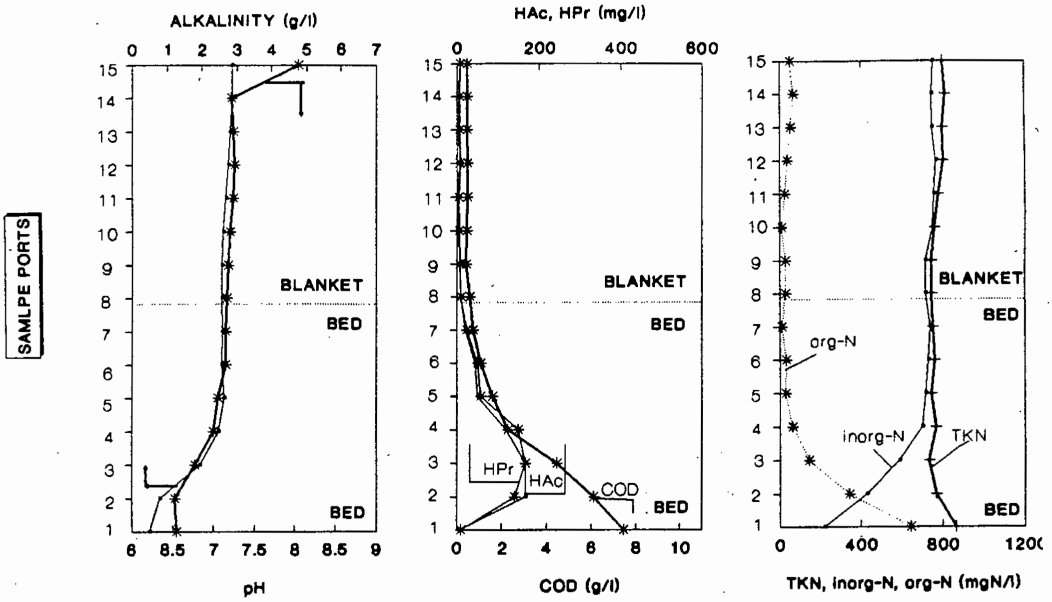


Fig 9.4: High/low $\bar{p}H_2$ single reactor system: profiles of pH, total alkalinity as $CaCO_3$, org-N, inorg-N, TKN, COD, acetic (HAc) and propionic acid (HPr). No addition of $NaHCO_3$ to feed; flow rate 25 ℓ/d; influent COD 7500 mg/ℓ; COD load on pelletised sludge: 55 kg COD/m^3.d).

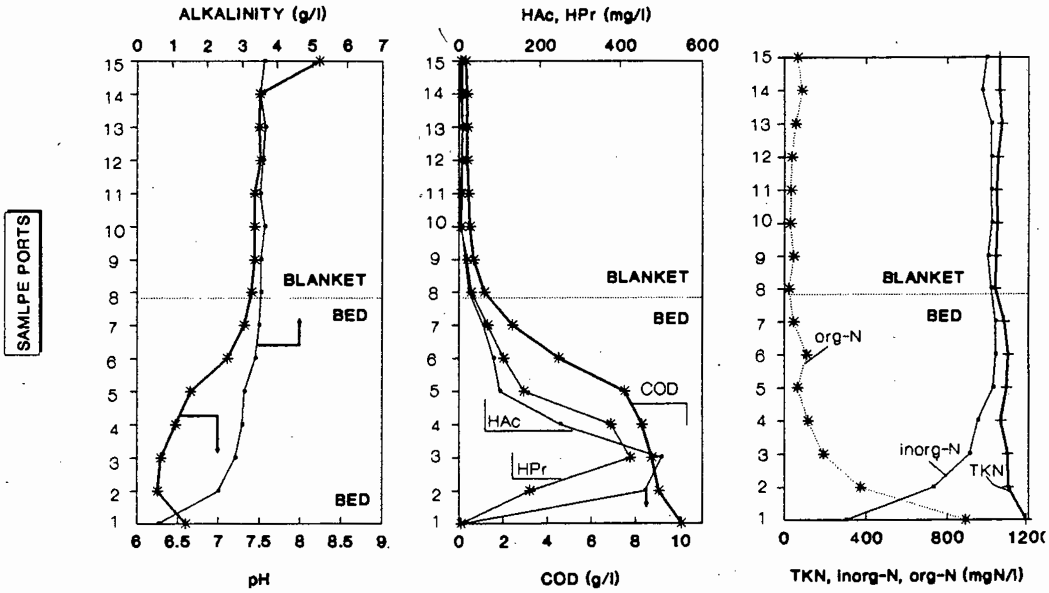


Fig 9.5: High/low $\bar{p}H_2$ single reactor system: profiles of pH, total alkalinity as $CaCO_3$, org-N, inorg-N, TKN, COD, acetic (HAc) and propionic acid (HPr). No addition of $NaHCO_3$ to feed; flow rate 25 l/d; influent COD 10 500 mg/l; COD load on pelletised sludge: 65 kg COD/m^3.d).

representing the higher COD loading rate [sludge bed volume 4,5ℓ, loading rate 65 kgCOD/(m^3 sludge bed .d)], shown in Fig 9.5, is discussed in detail below:

pH : Within the bed the pH declined to 6,2; and thereafter pH increased steadily to 7,6 at the top of the bed, and in the sludge blanket above the bed and in the settler (Fig 9.5). The causes giving rise to the behaviour pattern appear to be similar to those in UASB reactor treating carbohydrate substrate; in the lower bed zone the fall in pH was principally due to the high SCFA (HAc and HPr 500 mg/ℓ and 420 mg/ℓ maximum respectively)and the high partial pressure of CO_2. This fall in pH was moderated by the conversion of org-N to NH_4^+ during deamination. In the upper bed zone the rise in pH was principally due to the reduction in the SCFA. In the effluent bucket the pH rose to about 8,2, due to loss of CO_2.

Alkalinity : Referring to Fig 9.5, the approximate $H_2CO_3/H_2PO_4^-/HAc/HPr/NH_4^+$ alkalinity increased rapidly from the influent value (12 mmol/ℓ, 600 mg/ℓ as $CaCO_3$) to a relatively stable higher level in the upper part of the bed (72 mmol/ℓ, 3600 mg/ℓ as $CaCO_3$). Comparing the alkalinity increase with the org-N conversion to inorg-N, about 60 mmol org-N/ℓ influent were converted to inorg-N and this is reflected in a corresponding observed increase of 60 mmol of alkalinity per litre influent; this conforms to the theoretical expectation that the conversion of 1 mol org-N produces approximately 1 mol $H_2CO_3^*$alkalinity (the $H_2CO_3^*/H_2PO_4/HAc/HPr/NH_4$ alkalinity measured in the effluent is closely equal to the $H_2CO_3^*$alkalinity because the titration is affected only to a small degree by the other subsystems). The shape of the inorg-N curve is virtually identical with that of the alkalinity indicating that generation of alkalinity was due to conversion of org-N to inorg–N.

Nitrogen conversion and uptake : Org-N and inorg-N profiles are shown in Fig 9.5. Conversion of org-N took place primarily in the lower zone of the bed – 50 per cent conversion prior to sample port 2. The conversion rate decreased continuously up the bed, eventually to zero at the top of the bed (port 6), with a minimum org-N of about 20 mg/ℓ; this concentration did not change in the sludge blanket. The TKN (org-N + inorg-N) profile shows an uptake of about 90 mgN/ℓ, mainly in the bottom part of the bed. In the section 'TKN uptake' above, nitrogen requirements of about $0{,}03 \cdot 0{,}122 \sim 0{,}0037$ mgN/mgCOD utilized were predicted for normal anaerobic digestion. Accepting that (10 000–500) = 9500 mgCOD/ℓ was processed in the bed, the nitrogen requirements should have been 9500·0,0037 ~ 35 mgN/ℓ. Thus the nitrogen utilization was in excess of the requirements for protoplasmic growth and may be accounted for by accepting polypeptide formation.

COD : The COD profile, Fig 9.5, indicates a relatively low COD removal rate up to sample port 5 and thereafter a rapid increase in this rate. The lower COD removal in the bottom part of the bed was probably due to the relatively low pH (< 6,6) in that region (Fig 9.5) which could have inhibited methanogenesis – once the pH attained a value above 6,6 the COD removal rate appeared to improve significantly.

Propionate and acetate : The profiles (Fig 9.5) indicate a lower zone, in which HAc and HPr increased monotonically up to sample port 3, and an upper zone in which these decreased to a minimum value, thereafter remaining constant. Generation of HPr occurs where the $\bar{p}H_2$ is relatively high (> $10^{-4,1}$atm) so that a rising HPr profile defines the high $\bar{p}H_2$ zone with which is associated pellet generation (Sam-Soon *et al.*, 1987); oxidation of HPr indicates a low $\bar{p}H_2$, so that the declining HPr profile defines the low $\bar{p}H_2$ zone. Hence, according to Sam-Soon *et al.* (1987), pellet generation would be confined to the high $\bar{p}H_2$ zone, up to port No. 3.

Conversion HPr to HAc and conversion of HAc to methane were virtually complete just below the top of the bed. At higher loading rates it is likely these conversions would have been incomplete at the top of the bed and specifically, HPr discharged to the sludge blanket. These data indicate therefore that the system was near its maximum loading capacity for methane production; at higher loading the system very likely would have shown signs of 'failure', by increased HPr in the blanket.

Summary of feasibility study

The feasibility study provided the following principal points of information:

(1) A flow through UASB system treating a proteinaceous substrate casein developed a pelletised bed.

(2) Up to the highest COD loading rate [65 kgCOD/(m^3 pelletised bed)] the COD removal remained above 95 per cent.

(3) The system could be operated without alkalinity supplementation of the influent.

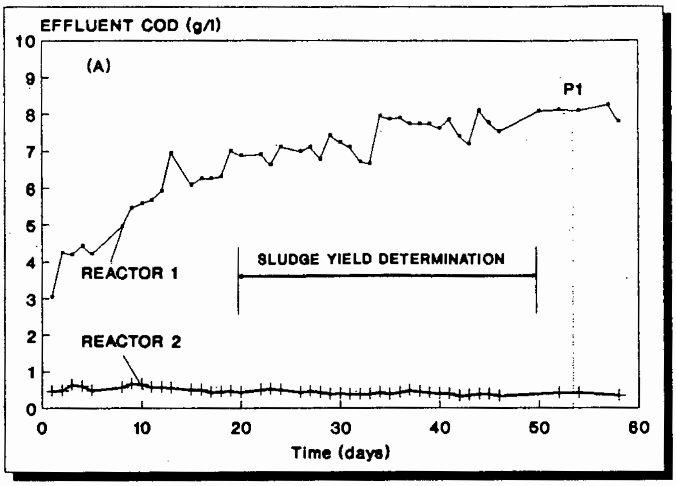
(4) The profiles of product formation along the line of flow of the reactor were similar to those reported by Sam–Soon *et al.* (1987) treating a carbonaceous substrate in a flow through UASB reactor. As in Sam–Soon's study, uptake of nitrogen was well in excess of that observed in 'normal' anaerobic fermentation – Sam–Soon's conclusion that this was due to pellet formation appears to be supported.

The response observed above established that casein is a suitable substrate for treatment in a UASB system and merited a more detailed study. Although the response of the UASB system appeared to be similar to to that of a UASB system treating a carbohydrate type substrate, the similarity may not persist under all situations; an increase in the minimum pH (6,2) observed with casein should improve the conditions for hydrogenotrophic growth, particularly that of *M* Strain *AZ* which, according to Sam–Soon *et al.* (1987), is responsible for pelletisation. That is, raising the minimum pH might increase the pellet yield reported in the feasibility study above. There–against high influent concentrations of casein will give rise to high inorganic nitrogen concentrations due to deamination; this in a higher pH environment (> 7) could give rise to appreciable concentrations of NH_3 species which may act inhibitory on the biological response. To obtain information on these aspects it was decided to study and compare the system's response under low and high pH conditions. Of particular importance would be evaluation of the effect of pH on the volatile solids/pellet production. Accordingly in Section 5 and 6, below the response characteristics under low and high pH conditions were investigated. All these studies were undertaken continuing to use a flow through mode of operation.

9.7 RESPONSE UNDER LOW pH CONDITIONS

In the high/low $\bar{p}H_2$ single reactor study in Section 4 above, it was evident that the high $\bar{p}H_2$ zone, as indicated by the increasing HPr profile, extended only up to about port No.3 (see Fig 9.4). Sam-Soon *et al.* (1987) showed that pellet formation takes place in the high $\bar{p}H_2$ zone and observed pellet break up in the low $\bar{p}H_2$ zone in upper region of the sludge bed. To obtain data on the VSS yield in the high $\bar{p}H_2$ zone the system was changed to operate as two in-series reactor system with the sludge volume in the first reactor limited to represent the high $\bar{p}H_2$ zone only. The units are shown in Fig 9.1(b). The high $\bar{p}H_2$ zone in the single high/low $\bar{p}H_2$ reactor extended up to between port 3 and 4 (volume ∼ 1,5ℓ) and accordingly 1,5ℓ of sludge from this zone was transferred to the first in-series reactor. The previous high/low $\bar{p}H_2$ reactor served as the second in-series reactor and contained the remaining 3ℓ of pelletised sludge. The COD loading rate imposed on the system was set at 210 gCOD/d (flow rate 20 ℓ/d, influent COD 10 500 mgCOD/ℓ). This COD loading rate was lower than the near maximum on the single high/low $\bar{p}H_2$ (≃ 280 COD g/d) system to give greater surety that the system would operate in a stable fashion. Trace element and nutrient solution additions remained the same as for the single high/low $\bar{p}H_2$ system experiment at high COD loading conditions, i.e. no alkalinity and no NH_4^+ additions.

The in-series system was run for some time to ensure that steady state was attained. Progress towards steady state was assessed as follows: Every day org-N, inorg-N and COD were measured on the filtered effluent of both reactors and pH monitored in the settler of the first and second reactor. In Fig 9.6(a) is shown the time plot of the filtered COD in the effluent from the first and second reactor. Fig 9.6(b) shows the pH in the settlers of the two reactors. The sludge bed in the high $\bar{p}H_2$ reactor was allowed to build up to sample port No 4 (1,7ℓ) and thereafter controlled to this level by regular wasting. Excess pellets from the first reactor were not transferred to the low $\bar{p}H_2$ reactor because of difficulties in introducing the pellets into the bed at the bottom of this reactor. At the beginning, the COD in the effluent from the first reactor was about 3500 mg/l (in the single high/low $\bar{p}H_2$ reactor at a slightly higher COD loading rate the COD at sample port 4 had been about 7000 mg/l (see Fig 9.4) so that initially the effluent COD from the first reactor of 3500 mg/l was much lower than at the corresponding sludge bed level in the single high/low $\bar{p}H_2$ system. However, within 20 days the effluent COD in the high $\bar{p}H_2$ reactor increased to ± 7000 mg/ℓ so that at this bed level



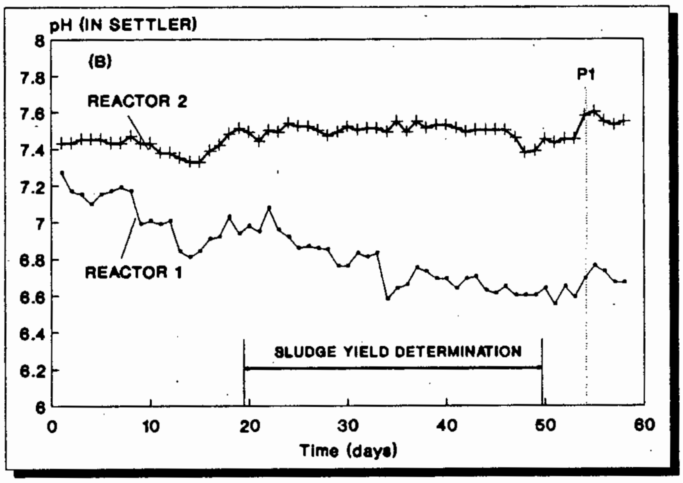


Fig 9.6: Two in–series reactor system: COD and pH changes vs time after converting from a high/low $\bar{p}H_2$ single system (see Fig 7.5) to a two in–series reactor system: (a) COD effluent concentration from first and second reactor. (b) pH in settlers of first and second reactor. No addition of $NaHCO_3$ to feed; flow rate 20 l/d; influent COD 10 500 mg/l; COD load on pelletised bed: 36 kg COD/(m.d). P1 indicates the time location of profile set 1.

the responses were approximately the same in the high $\bar{p}H_2$ and the high/low $\bar{p}H_2$ systems. It was concluded that the system had attained near steady state by day 20 and it was possible to commence investigations into the sludge production.

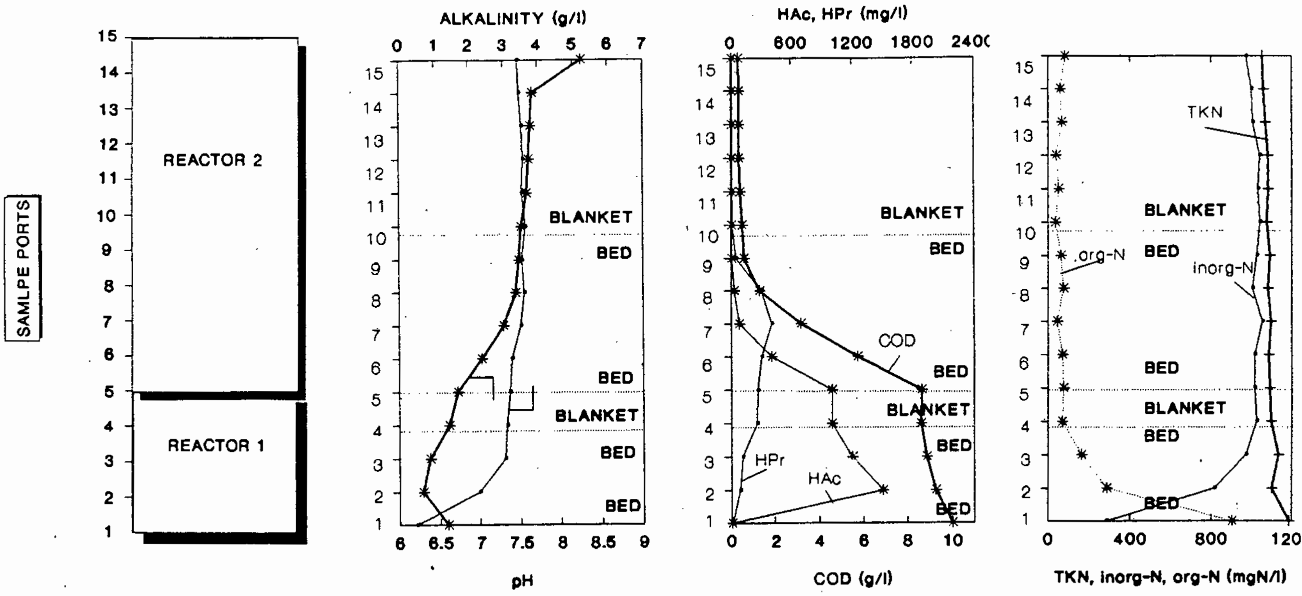
Sludge yield determination under low pH conditions

Once steady state was attained the system was run for a period of 30 days (day 20 to day 50) when sludge mass generation in the high $\bar{p}H_2$ reactor was measured, to determine the sludge age (R_s) and the sludge yield per COD utilized. At the end of this period profiles of pH, COD, TKN, org N, inorg-N, alkalinity, HAc and HPr in the two reactors were measured (on day 54, see Fig 9.7), to detail product formation.

Sludge mass generation in the high $\bar{p}H_2$ (first in-series) reactor : The sludge bed mass was controlled to port No.4 (1,7ℓ). To determine the yield the sludge mass was allowed to increase above sample port 4 for sequential periods of 5 days. At the end of each period the sludge generated (i.e. pellets and VSS in the bulk liquid above sample port N_0 4) was drained into a measuring cylinder, thoroughly mixed and a sample taken to determine the mass of VSS. Every day the VSS in the effluent from the high $\bar{p}H_2$ reactor was determined by subtracting the filtered COD (ordinary filter paper) from unfiltered COD and calculating the effluent VSS via the mean measured COD/VSS ratio of the sludge (1,38 mgCOD/mgVSS). Multiplying this value by the flow over the 5 day period (100ℓ) gave the mass of VSS loss in the effluent. Total mass of VSS produced over the 5 day period was the sum of the masses of VSS increase in the pelletised bed and the blanket, and the mass of VSS loss in the effluent. The concentration of COD utilized for metabolic purposes in the first reactor was obtained daily by subtracting the filtered effluent COD from the influent COD. The average difference in concentration multiplied by the flow over the 5 day period (100ℓ) gave the mass of COD removed: Average influent COD = 10 500 mg/ℓ, average filtered effluent COD of the high $\bar{p}H_2$ reactor = 6 850 mgCOD/ℓ, i.e. COD utilized in the bed = 3 650 mg/ℓ, hence mass of COD removed/d = 20·3 650 = 73 gCOD/d. On an average 19 gVSS/d were generated. The specific yield, Y, is given by:

$$Y = \frac{\text{mass of VSS generated/d}}{\text{mass of COD utilized/d}} = \frac{19}{73} = 0{,}26 \text{ gVSS/gCOD utilized}$$

Of the total mass of sludge generated (19 gVSS/d), 38 per cent was retained in



<u>Fig 9.7:</u> Two in-series reactor system: profiles of pH, total alkalinity (as $CaCO_3$), org-N, inorg-N, TKN, COD, acetic (HAc) and propionic acid (HPr). Flow rate 20 l/d; influent COD 10 500 mg/l; COD load on pelletised bed: 36 kg COD/(m^3.d).

the pelletised bed, the rest was lost to the blanket above the bed and some was eventually discharged to the second reactor in the series. Thus, the net specific *pellet* yield was 0,26 · 0,38 = 0,1 mgVSS/mgCOD removed.

The specific yield in the high $\bar{p}H_2$ reactor (0,26 mgVSS/mgCOD utilized) was lower than that obtained by Sam-Soon *et al.* (1987) treating apple juice waste (0,36 mgVSS/COD utilized) and the pellets were smaller (< 2mm), more fragile and black in colour. In their high $\bar{p}H_2$ reactor study, Sam-Soon *et al.* (1987) reported no sludge debris discharge from the bed to the liquid above, whereas with the proteinaceous substrate large quantities of sludge debris discharged from the bed, to form a blanket above, and some discharged in the effluent. However, the two substrates are so dissimilar that one can only conjecture as to the differences in the specific yield.

***Sludge mass generation in the low $\bar{p}H_2$ (second in-series) reactor*:** In the two in-series reactor system sludge production was measured only in the first (high $\bar{p}H_2$) reactor. To obtain an estimate on the yield of VSS in the second reactor the following assumptions were made: Assume that the second in-series reactor operated under low $\bar{p}H_2$ conditions and no or insignificant pellet production took place (this is not unreasonable because little nitrogen was removed in the second reactor, see Fig 9.7). Also over the whole period of the experiment the sludge bed depth remained substantially constant. Sludge production would be due mainly to conversion of H_2 (under low $\bar{p}H_2$) and acetate to methane. Under those conditions a yield value of 0,03 mgVSS/mgCOD utilized would seem applicable (ten Brummeler *et al.*, 1985). It was stated above that 3 650 mgCOD/ℓ were removed in the first reactor. The effluent COD concentration in the second reactor was 500 mgCOD/ℓ. Hence, the COD removal in the second in-series reactor could be estimated as approximately: 10 500 – 3 650 – 500 = 6 350 mgCOD/ℓ. Thus the VSS generation per day in the second reactor was 6 350·0,03·20 = 3,8 gVSS/d. This value may be combined with the VSS yield in the first in-series reactor to give the overall yield of the system.

Overall sludge generation in two in-series reactor system : Combining the sludge generation per day of the two individual reactors gives: (19+3,8) = 22,8 gVSS/d. Hence the overall specific yield = 22,8/(20·10 000/1 000) = 0,114 gVSS/gCOD utilized.

Sludge age : The sludge age, R_s, in the high $\bar{p}H_2$ reactor (in days) is defined by:

$$R_s = \frac{\text{mass of sludge in the bed}}{\text{mass of sludge removed per day}}$$

The mass of sludge in the high $\bar{p}H_2$ reactor was determined from the bed volume (1,7ℓ) and the sludge density. Draining the sludge bed and measuring the VSS gave a density of 37,5 gVSS/ℓ. Hence: R_s = 1,7·37,5/19 = 3,4 days.

Profiles

After 54 days from the start of the in-series reactor experiment, profiles of pH, COD, total alkalinity, inorg-N, org-N, HAc and HPr were measured in the two reactors (see Fig 9.7).

The pH, COD, total alkalinity, inorg-N and org-N profiles show trends similar to those observed in the high/low $\bar{p}H_2$ single reactor system (c.f. Fig 9.5). However, the HAc and HPr profiles differed – in the two in-series reactor system the maximum value of the HAc in the high $\bar{p}H_2$ reactor exceeded that in the high/low $\bar{p}H_2$ single reactor system by about 3 times; the HPr profile of the two in-series reactors reached its maximum at a higher point in the bed (in the second reactor) but was less in the lower zone of the bed (in the first reactor), than in the high/low $\bar{p}H_2$ single reactor system. Overall the separation of the high $\bar{p}H_2$ zone (first reactor) from the remaining sludge bed did not significantly affect the pattern of the system's response with respect to these parameters. The different behaviour pattern observed might have been due to the absence of any intermixing of sludge from the low $\bar{p}H_2$ reactor with the sludge of the high $\bar{p}H_2$ reactor. Sam-Soon *et al.* (1989) indicated that there is a measure of intermixing between the layers in a UASB reactor. In the separated two in-series reactor system, the lack of intermixing very likely would have given rise to selective pressure on the bacterial population in the high $\bar{p}H_2$ reactor as a result of the relatively short sludge age (3,4 d). The selection pressure would be particularly pronounced with a proteinaceous substrate because of the differences in acidogenic pathways for the various amino acids.

<u>Discussion – low pH conditions</u>

- The response of the systems treating proteinaceous substrate were similar to the same system treating carbohydrate substrate in that in the high $\bar{p}H_2$ zone there was an uptake of nitrogen in excess of that required for protoplasmic growth and a high specific yield of volatile suspended solids in both systems.

- The specific yield of volatile suspended solids in the high $\bar{p}H_2$ zone (first reactor) was 0,26 mgVSS/mgCOD removed; 38 per cent of the generated VSS was retained in the bed as pellets, 62 per cent was lost from the bed to the blanket and discharged to the second reactor. The overall specific yield of suspended volatile solids including both reactors were estimated to be about 0,114 mgVSS/mgCOD removed. This estimate of specific yield at best can only be approximate as it is not possible to identify whether any of the sludge had been hydrolysed in the second reactor. The specific yield in the high $\bar{p}H_2$ reactor was significantly lower than that obtained by Sam Soon *et al.* (1987) treating a carbonaceous substrate. Two causes for this low yield can be postulated: The first is the nature of the substrate itself. The second is the low pH in the high $\bar{p}H_2$ zone. During the period in which the sludge production was measured in the high $\bar{p}H_2$ reactor, where the main generation of sludge took place, the pH in the effluent declined from about 7,0 to 6,6. The minimum pH in the first reactor during this period may be estimated from Fig 9.7 and possibly ranged from 6,2 to 6,4. Thus, an appreciable fraction of the bed in this reactor was below. a pH of 6,6 – a pH level below which pelletisation is inhibited according to Sam Soon *et al.* (1987). The magnitude of the second cause, i.e. low pH, can be assessed by operating the system at a higher pH level in the high $\bar{p}H_2$ reactor. This study is reported in Section 9.8 below.

9.8 RESPONSE UNDER HIGH pH CONDITIONS

In order to study the effect of a higher pH on the system's response, and in particular on the sludge yield, the minimum pH in the high $\bar{p}H_2$ (first) reactor of the in–series system was raised in two steps, from 6,2 to 6,6 then to 7,0, by addition of $NaHCO_3$ to the influent. The reactor system remained the same as before, as described in Section 5, i.e. two in–series reactors, with sludge volumes of 1,7ℓ in the first reactor and 3,5ℓ in the second, influent COD 10 500 mg/ℓ and flow rate 20ℓ/d. The time schedule of addition of $NaHCO_3$ for the two in–series experiment is shown in Fig 9.8. Zero time was selected to be that at start of the two in–series investigation, i.e. including the study described in Section 5 with no alkalinity addition. This figure also includes the time schedule for addition of NH_4Cl at elevated pH levels which followed the study of the effect of increased pH levels.

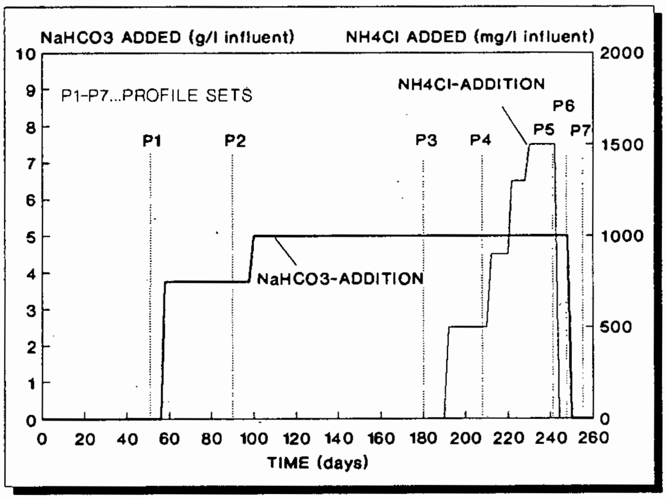


Fig 9.8: Two in–series reactor system: Time schedule of alkalinity ($NaHCO_3$) and ammonium (NH_4Cl) addition and time locations when various profile sets (P1 – P7) were measured over the duration of the two in–series reactor experiment. Zero time at start of two in–series reactor experiment.

Increase of minimum pH to 6,6

To increase the minimum pH from 6,2 to 6,6, a mass of 3,75 $gNaHCO_3/\ell$ influent was added on day 57 (see Fig 9.8). In Fig 9.9 the effluent COD's of the first and second reactor are shown plotted, including the period during which no alkalinity was added. In Fig 9.10 the COD removal per litre of influent in each of the reactors is shown. This plot is not very useful in illustrating the changes in performance of the second reactor because the influent COD to the second reactor was not constant as a result of the changes occurring in the first reactor. Plots of the percentage COD removal in each reactor with respect to their respective influent COD concentration are more informative, Fig 9.11. These show that with alkalinity addition, and the concomitantly higher pH, the percentage COD

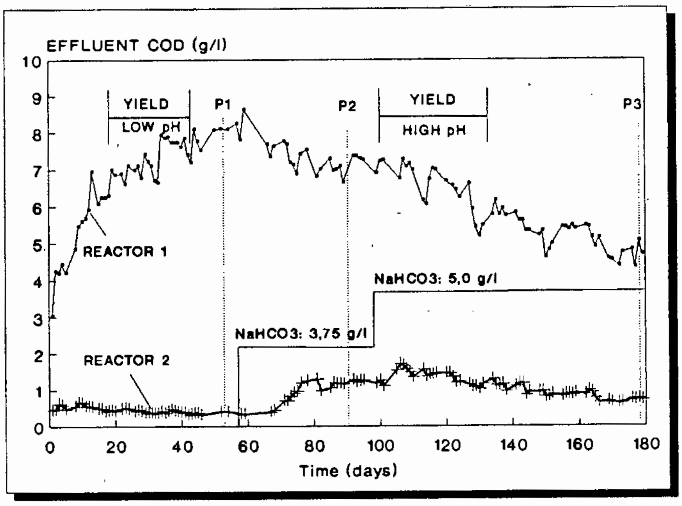


Fig 9.9: Two in-series reactor system: COD concentration in the effluent of the first and second reactor during time period with and without alkalinity addition. P1, P2 and P3 indicate time locations of profile sets. Zero time at start of two in-series reactor experiment. Flow rate 20 l/d; influent COD 10 500 mg/l; COD load on pelletised bed: 36 kg COD/(m.d). The terms "yield (low)" and "yield (high)" indicate the time period for sludge yield determination under low and high pH conditions respectively.

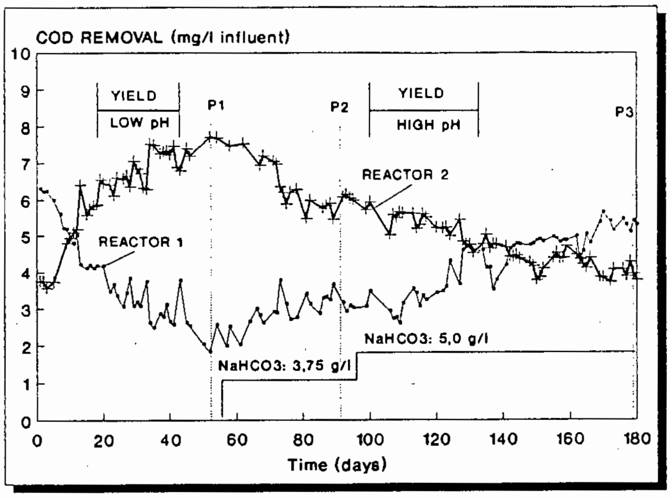


Fig 9.10: Two in-series reactor system: COD removal per litre of influent in first and second reactor. P1, P2 and P3 indicate time locations for profile sets. Flow rate 20 l/d; influent COD 10 500 mg/l; COD load on pelletised bed: 36 kg COD/(m.d).

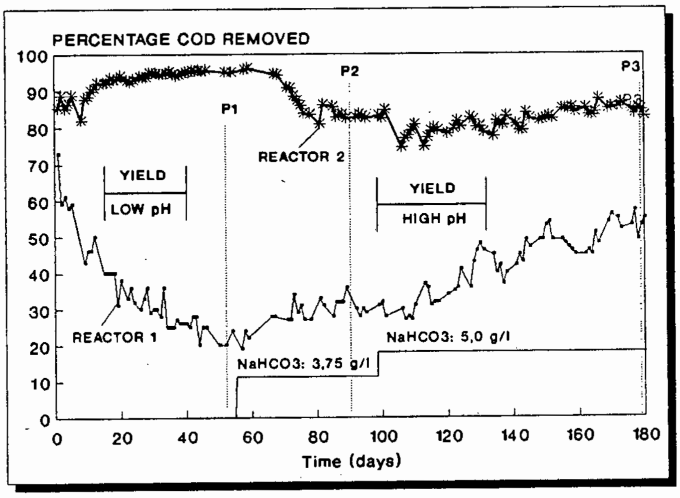


Fig 9.11: Two in-series reactor system: Percentage COD removal in first and second reactor calculated as: (filtered influent COD con. - filtered effluent COD con.)/(filtered influent COD con.). The influent COD concentration to the second reactor is identical to the effluent COD concentration of the first reactor. P1, P2 and P3 indicate time locations for profile sets. Flow rate 20 l/d; influent COD 10 500 mg/l; COD load on pelletised bed: 36 kg COD/(m.d).

removal increased slightly in the first reactor but *declined* in the second reactor. Detailed changes in behaviour become apparent by comparing the set of profiles P2 taken on day 90 (after the first step of alkalinity augmentation) with set P1 taken on day 54 (before alkalinity addition). Both sets are plotted together in Fig 9.12a,b,c,d,e (There is also a third set of profiles P3 plotted in Fig 9.12a,b,c,d,e; this set reflects profiles at yet higher alkalinity addition and will be described later).

Comparing profiles P1 (no alkalinity addition) and profiles P2 (alkalinity addition), changes are noticeable in pH, COD, HAc, HPr and inorg–N:

pH : Addition of 3,75 g$NaHCO_3$ per litre of influent caused a significant increase in pH in the first and second reactor (P2 profile). In the first reactor the pH profile retained its shape but increased by a constant amount of 0,4 pH units [Fig 9.12(a)]. In the second reactor the pH profile changed significantly; the pH increased at the bottom of the bed by about 0,5 pH units but thereafter the increase declined up the bed to merge with the P1 profile near the top of the bed.

COD : From profiles P1 and P2, in the *first* reactor, Fig 9.12(b), on addition of alkalinity the COD removal *rate* clearly improved; this appeared to have been due to the higher pH, that is, the pH increase to near neutrality improved the performance of some organism species. However, in the second reactor, a marked drop in the COD removal rate was observed: the COD concentration in the effluent from the second reactor increased considerably from about 600 mg/ℓ to 1500 mg/ℓ, despite the fact that the influent COD (effluent from the first reactor) had declined and the pH was still below an upper limit of $\simeq$ 7,4. These effects are reflected also in the percentage COD removal plots in Fig 9.11. From COD profiles in the first and second reactor alone no conclusion could be drawn as to which bacterial group had been affected by the change in pH. However, comparison of the individual SCFA, acetic and propionic acids, provide more useful information in this regard.

Acetic acid : For the first reactor, Fig 9.12(c) shows the profiles of HAc measured in sets P1 and P2. In the lower pH profile (minimum pH $\simeq$ 6,2) the HAc peak is markedly higher than in the higher pH profile (minimum pH $\simeq$ 7,0). This may be because the acetoclastic methanogens are pH neutrophiles and would therefore gain an advantage from the pH increase of about 0,4 pH units; concomittantly this improvement is reflected in the COD removal rate in the first reactor, Fig 9.12(b). In the second reactor the two HAc profiles are nearly identical. From these profiles, for the second reactor it may be concluded that the performance of the acetoclastic microbial population in this reactor was not significantly affected by the increase in pH, and hence the HAc component of the COD was not the cause of the higher COD in the effluent. An explanation for the deterioration in the COD removal is forth coming by examining the HPr profiles.

Propionic acid: At the higher pH levels in both the first and second reactor the HPr profile P2, unlike the HAc profile, showed a marked increase relative to that in profile P1, Fig 9.12(d). One explanation that can be hypothesized for this increase in HPr may be the inhibition of *acetogens* which convert HPr to HAc plus H_2 – a reduced conversion rate of HPr would lead to an accumulation of HPr in the system. However, it is unlikely that this inhibition was a direct result of the pH increase since the pH stayed within the limits favourable to acetogens (pH range from 6,6 to 7,5). Another hypothesis is that inhibition arose from the increased NH_3 species concentration which resulted from the higher pH. McCarty (1964) and van Velsen (1979) amongst others have reported that NH_3 species can act inhibitory in anaerobic fermentation. To date little information is available which bacterial group might be affected; the accumulation of HPr points towards inhibition of the acetogens. However, this inhibition could be a *direct* or an *indirect* one. *Direct* inhibition would mean that the activity of the acetogens themselves is affected by the NH_3 species. *Indirect* inhibition would arise, not due to NH_3 inhibition of the acetogens but due to NH_3 inhibition of the *hydrogenotrophs*, as follows: Conversion of HPr by acetogens can take place only below a $\bar{p}H_2$ of 10^{-4} atm (Mc Innery et al., 1979); if the hydrogenotrophs were inhibited by NH_3 they would not reduce the $\bar{p}H_2$ and this would prevent the acetogens to convert HPr to HAc and H_2.

An alternative explanation for the accumulation of HPr under increased pH conditions might be that a shift in production of this intermediate took place, that the elevated HPr levels were a result of increased HPr production at the increased pH. However, a comparison of the HPr profiles measured on the high/low $\bar{p}H_2$ single reactor during the feasibility study (see Fig 9.2 and Fig 9.3) indicates a *reduced* HPr production under high pH conditions (minimum pH $\simeq$ 7,2). Due to the lower inorganic nitrogen concentration in the sludge bed (400 mgN/l), the

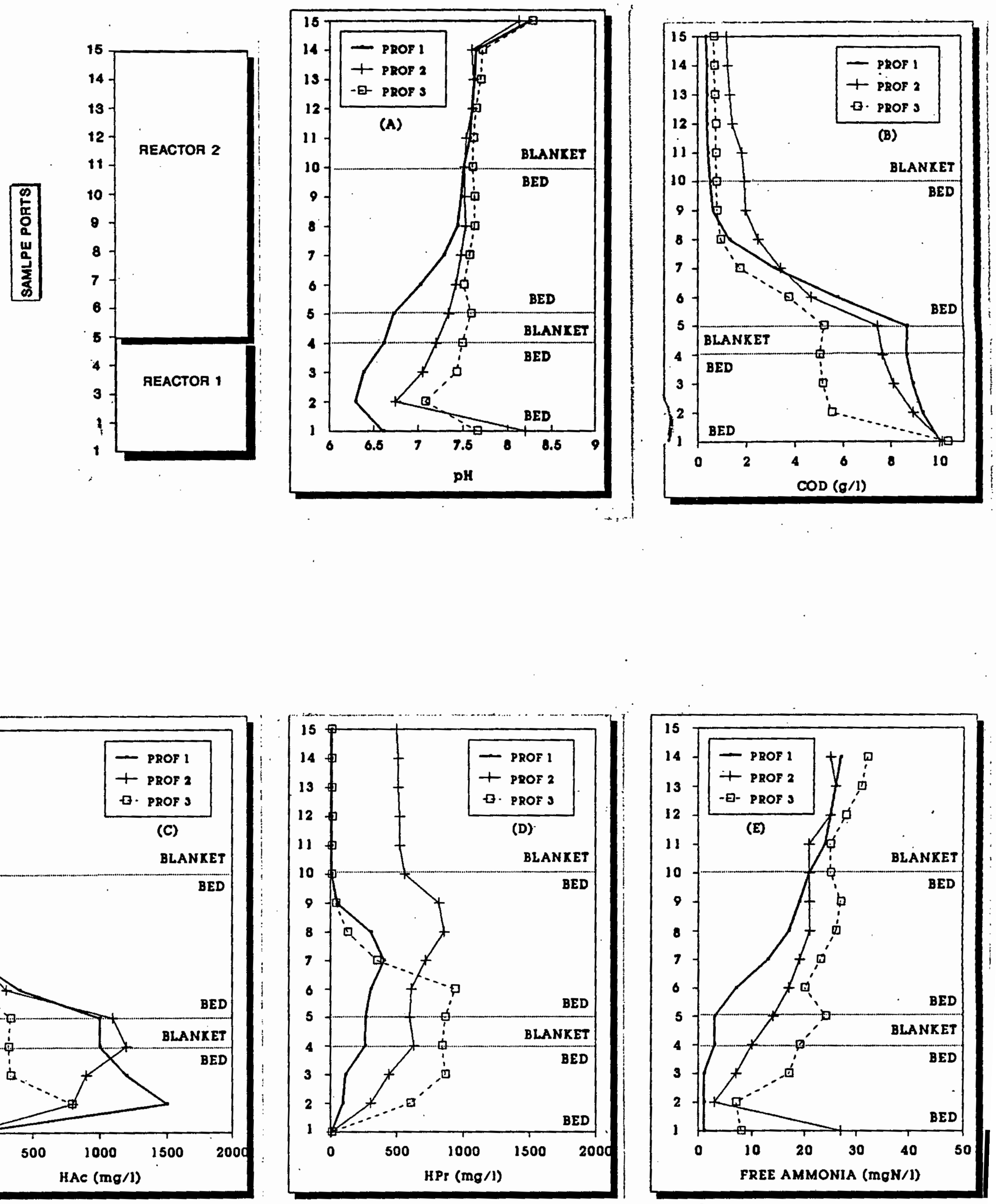


Fig 9.12: Two in-series reactor system: Comparison of profiles of pH (a), COD (b), HAc (c), HPr (d) and NH_3 (e) measured in profile P1, P2 and P3 representing the following conditions: P1: zero alkalinity addition; P2: 3,75 $gNaHCO_3/l$ influent supplementation, P3: 5 $gNaHCO_3/l$ influent supplementation. No ammonium supplementation to influent. Flow rate 20 l/d; influent COD 10 500 mg/l; COD load on pelletised bed: 36 kg COD/(m.d).

NH_3 concentrations under those conditions were unlikely to cause any inhibition and product formation would be influenced only by the change in pH. It was concluded therefore that the increase in HPr at the higher pH level, observed at this stage of the study, did not result from an increase in HPr production.

Cause of inhibition

To study whether the hydrogenotrophs were affected by the increase in NH_3 species the following reasoning was applied. Sam Soon *et al.* (1987) hypothesised that sludge growth in a high $\bar{p}H_2$ environment is mainly due to hydrogenotrophs which grow optimally at neutral pH (Zehnder *et al.*, 1977). Accepting this hypothesis it may be expected that the sludge yield in the high $\bar{p}H_2$ reactor (0,26 mgVSS/mg COD) which was measured under unfavourably low pH conditions (see Section 5) would improve at near neutral pH conditions. An increase in pH, however, also increases the concentration of the NH_3 species which possibly might inhibit the hydrogenotrophs. Such an inhibition would be indicated by a reduction in specific yield due to a higher NH_3 concentration when the minimum pH increases from 6,2 to about 7. A study into the specific yield in the high $\bar{p}H_2$ reactor at near neutral pH conditions therefore was indicated.

In order to ensure optimal pH conditions for the hydrogenotrophs, the minimum pH in the first reactor was increased to *circa* 7 by adding 5 g $NaHCO_3/\ell$ influent instead of 3,75 g from day 98, see Fig 9.8. Except for the $NaHCO_3$ addition no other changes were made. The system was allowed to stabilize for 15 days (day 98 to 113 , Fig 9.11) before measurements of VSS production were undertaken.

Sludge yield under near neutral pH conditions: The method to determine the sludge yield in the high $\bar{p}H_2$ reactor remained the same as that under low pH conditions described earlier in Section 5. Measurements on the VSS production were taken over a period of 35 days (from day 113 to 148).

In the high $\bar{p}H_2$ reactor the sludge and COD removal measurements gave a specific yield of 0,17 mg VSS/mg COD utilized (c.f. 0,26 mg VSS/mg COD utilized under low pH conditions, see above). From the mass of sludge generated, only 11 per cent was retained in the reactor as pellets whereas the rest, 89 per cent, was discharged from the bed in the effluent from the first reactor. From Fig 9.11 it can be seen that from the first augmentation of alkalinity addition, on day 98, the percentage COD removal in the *first* reactor increased steadily. This increased COD removal had been ascribed above to the improved acetoclastic action, i.e. improved conversion of HAc to methane. This effect alone would give rise to an apparent *reduced* specific yield because the increase in mass generated by the acetoclastic bacteria per COD removed is very small (0,03 mg VSS/mg COD). However, by comparing the absolute mass of sludge produced per day under the lower and higher pH conditions, a decision may be reached as to whether the hydrogenotrophs were inhibited or not - a reduced absolute sludge yield would strongly point towards inhibition of the hydrogenotrophs by NH_3. This indeed happened; under the higher pH conditions (minimum pH $\simeq$ 7) 12 g VSS were generated per day as compared to 19 g VSS per day under the lower pH conditions (minimum pH $\simeq$ 6,2). These findings suggest that the mass of sludge produced by the hydrogenotrophs was reduced significantly at higher pH conditions; thus the decrease in the specific sludge yield was not a result of the improved COD removal due to increased cleavage of acetate.

Noting the reduced specific sludge yield of 0,17 mg VSS/mg COD (under higher pH conditions) compared with the specific sludge yield of 0,26 mg VSS/mg COD (under lower pH conditions) *and* the reduced absolute sludge production per day (12 g/d and 19 g/d respectively), the hypothesis that the NH_3 inhibits the hydrogenotrophs appears to be supported. Reduced activity of the hydrogenotrophs is further supported by the deteriorating quality of the pelletised sludge which was reflected in the high fraction of debris from the first reactor bed of 89 per cent, reported earlier.

System adaptation

In the second reactor, after alkalinity addition commenced on day 57 (Fig 9.8), initially there was a deterioration in COD removal but thereafter COD removal *increased* steadily and continued to do so. In the first reactor a steady increase in COD removal occurred immediately after commencement of alkalinity addition. To investigate the steadily improving performance of the two reactors with time, a further set of profiles P3 was measured on day 180 and is shown plotted together with set P1 (no addition of alkalinity) and set P2 in Fig 9.12(a,b,c,d,e). Profile set P2 represents the response of the system after the first step of alkalinity increase and was measured on day 90. Profile set P3 represents the system's response after the second step of alkalinity increase (see Fig 9.8). A comparison of profiles P2 and P3 provides information with regard to the system's response to increased levels of pH (and associated increase in NH_3 species):

pH: The pH profile of P3 shows a considerable increase (compared to pH profile P2) of about 0,4 pH units in the first reactor where the minimum pH is raised to *circa* 7. In the second reactor the pH profiles of P3 and P2 are nearly identical.

COD: The COD profile P3 shows marked improvements in COD removal in both the first and second reactors. The cause for the improvements must be sought in the SCFA profiles.

Acetic acid: The P3 profile for HAc (at minimum pH $\simeq$ 7) showed improved removal over the P2 profile (minimum pH $\simeq$ 6,6) in both the first and second reactors. This confirms the conclusion already reached when comparing the P1 and P2 profiles (at minimum pH of 6,2 and 6,6 respectively), that the acetoclastic microbial population gained an advantage from the increase in pH to near neutral and showed no signs of inhibition due to increased levels of NH_3.

Propionic acid: The HPr profile P3 [Fig 9.12(d)] shows an increase in the HPr concentration in the first reactor but improved HPr conversion in the second reactor relative to the P2 profile. The increased HPr concentration in the first reactor might be caused by the elevated level of NH_3 species, see Fig 9.12(e); one would expect that this should apply also to the second reactor response because the NH_3 species also increased in this reactor. However the opposite happened – HPr conversion *improved* in the second reactor. The only explanation that can be proposed is that a measure of *adaptation* of the hydrogenotrophs to NH_3 developed with time (which caused a drop in $\bar{p}H_2$ and hence enabled the acetogens to convert HPr to HAc and H_2). This effect was not apparent in the first reactor because the hydrogenotrophs in this reactor probably did not have sufficient contact time with NH_3 for adaptation as the sludge age was only about 3 – 5 days.

To investigate if the conclusion that adaptation of the hydrogenotrophs to NH_3 species was taking place was valid, it was decided to keep the pH unchanged and increase the inorganic nitrogen concentration by adding NH_4Cl to the influent, see below.

9.9 RESPONSE TO HIGH pH AND AND NH_4CL

In the investigation into the possible adaptation of the hydrogenotrophs to the NH_3 species, the experiment was divided into two periods. The first period started on day 192 (see Fig 9.8) when 500 mg NH_4Cl–N were added to the influent, and lasted for 18 days. After this followed a second period during which the NH_4Cl addition was increased to 1500 mg/ℓ influent as N, in three steps.

In the first reactor the pH remained substantially the same as before any NH_4^+ addition (Fig 9.13); the COD in the effluent also showed little change (Fig 9.14). In the second reactor, as in the first reactor, the pH also remained almost unchanged (Fig 9.13); the effluent COD, however, increased with time, particularly after the NH_4CL addition was raised to 1500 mg/ℓ, the COD increased rapidly for about 8 days up to 2200 mg/l. This indicated that some form of inhibition was present. However, after the 8 day period the COD commenced to fall sharply to 1500 mg/l in about 7 days. From this it was concluded that the

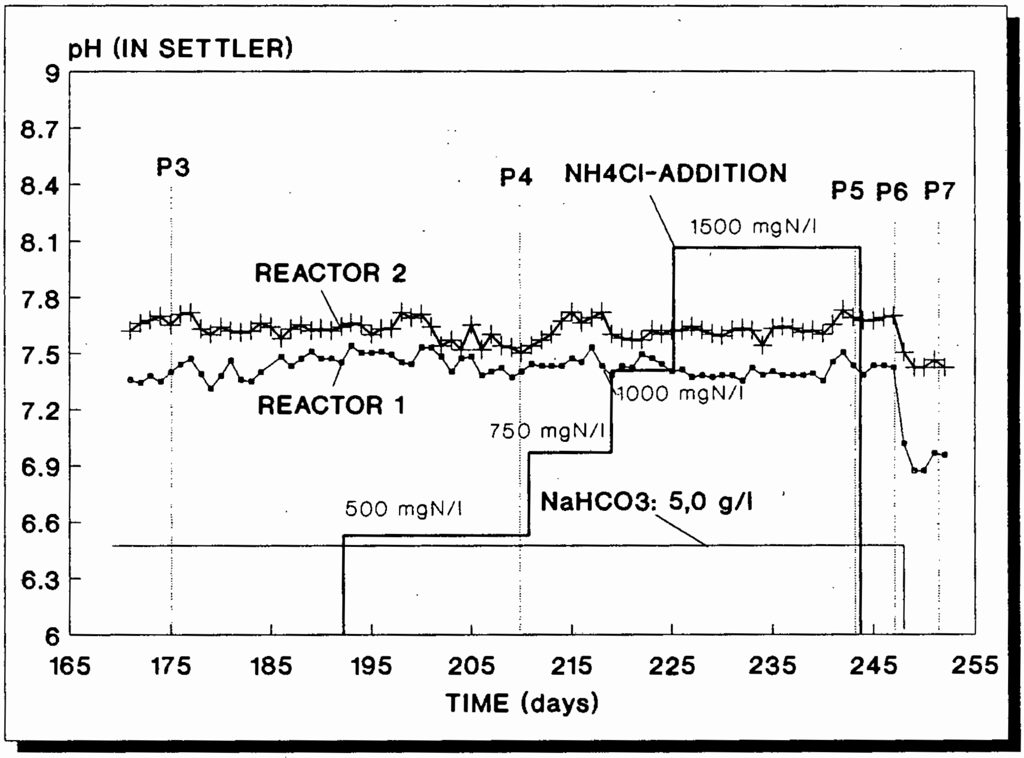


Fig 9.13: Two in–series reactor system: pH vs time in settlers of first and second reactor during time period of alkalinity and alkalinity/ammonium supplementation. Flow rate 20 l/d; influent COD 10 500 mg/l; COD load on pelletised bed: 36 kg COD/(m.d).

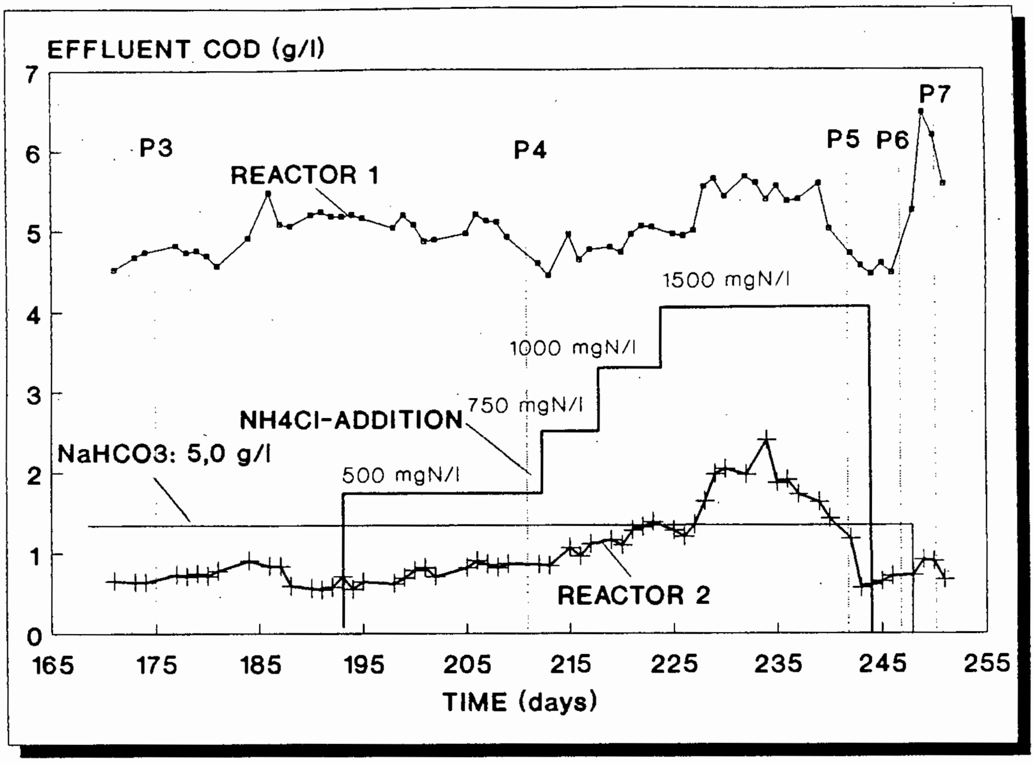


Fig 9.14: Two in-series reactor system: filtered COD concentration in effluent of first and second reactor during time period of alkalinity and alkalinity/ammonium supplementation. Flow rate 20 l/d; influent COD 10 500 mg/l; COD load on pelletised bed: 36 kg COD/(m.d).

organism assembly was adapting to the high NH_3 concentration. At this point because the effluent improvement appeared to be well established, ammonium addition was terminated (Fig 9.8).

At the end of the each period with 500 and 1500 mgN/l addition of NH_4Cl a set of profiles was measured - termed P4 and P5 respectively. These are shown plotted together with profile P3, see Fig 9.15(a,b,c,d,e). Comparison of profiles P3, P4 and P5 shows little difference. The similarity between the profiles P4 and P5 arises because P5 was taken after adaptation had caused the effluent COD to improve to about the same value as that when the profile P4 was measured. Only insignificant differences are apparent with one exception:

Acetic acid: During the first period of NH_4Cl addition (500 mgN/l) HAc removal improved further relative to P3 (alkalinity addition only) which again demonstrated the tolerance of acetoclastic bacteria towards NH_3. This bacterial group only showed signs of inhibition after the NH_4Cl addition was increased to 1500 mgN/l i.e. inorg–N concentrations of about 2400 mgN/ℓ. This can be seen from P5 in Fig 9.15(c) which shows a decline in HAc removal during the second period in first reactor.

After this period of NH_4Cl and alkalinity addition it was of interest to investigate the system's response to (1) withdrawal of NH_4Cl but continuing alkalinity addition and (2) withdrawal of NH_4Cl and alkalinity addition. This would provide information on the system's recovery.

9.10 SYSTEM RECOVERY

On day 243 (see Fig 9.8) the addition of NH_4Cl was terminated. To examine the immediate effect of this change a set of profiles P6 was measured 4 days later. After measuring this set of profiles the supplementation of alkalinity was terminated and another set of profiles P7 measured 7 days later. These sets of profiles are shown plotted together with P5 in Fig 9.16(a,b,c,d,e):

Figure 9.16b shows the pH profiles P5 (NH_4Cl and alkalinity addition), P6 (withdrawal of NH_4Cl but alkalinity addition) and P7 (withdrawal of NH_4Cl and alkalinity supplementation). On terminating NH_4^+ addition there was only a small change in the pH profile (*cf* P5 and P6) and COD removal improved in the second reactor. On withdrawing alkalinity addition a significant drop in pH occurred throughout the two reactors – especially in the first reactor (*cf* P6 and P7). The pH profile P7 now reverted to near that in P1. The COD, HAc and HPr profiles in P7 also show a change towards those in P1, that is the system rapidly changed to the response observed when no alkalinity or NH_4^+ was added.

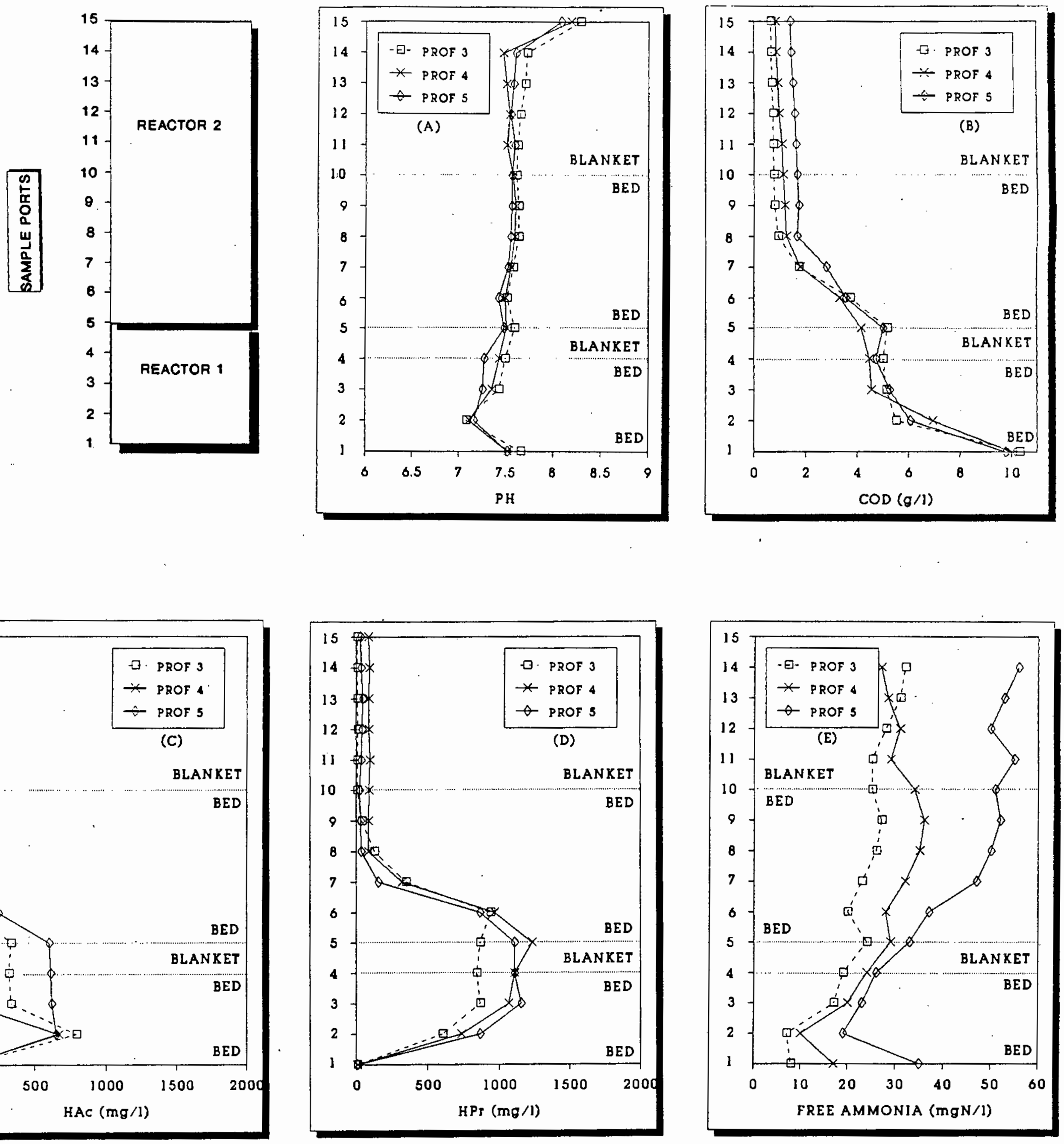


Fig 9.15: Two in–series reactor system: Comparison of profiles of pH (a), COD (b), HAc (c), HPr (d) and NH_3 (e) measured in sets P3, P4 and P5 representing the following conditions: P3: 5,0 $gNaHCO_3/l$ influent and zero ammonium; P4: 5,0 $gNaHCO_3/l$ influent and 500 mgN/l influent as NH_4Cl; P5: 5,0 $gNaHCO_3/l$ influent and 1500 mgN/l influent as NH_4Cl. Flow rate 20 l/d; influent COD 10 500 mg/l; COD load on pelletised bed: 36 kg COD/(m.d).

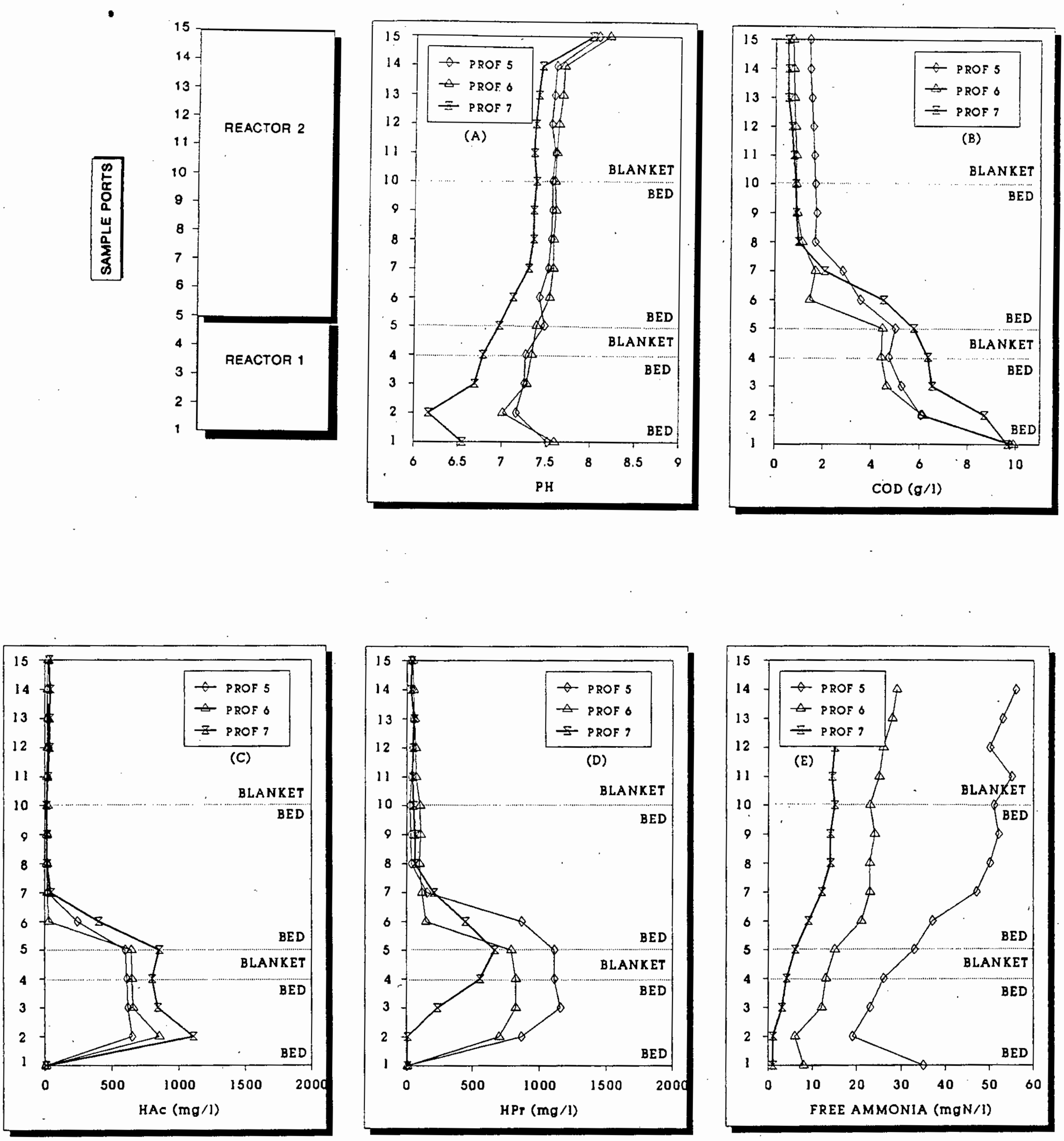


Fig 9.16: Two in-series reactor system: Comparison of profiles of pH (a), COD (b), HAc (c), HPr (d) and NH_3 (e) measured in sets P5, P6 and P7 representing the following conditions: P5 : 5,0 $gNaHCO_3/l$ influent and 1500 mgN/l influent as NH_4Cl supplementation, P6: 5,0 $gNaHCO_3/l$ influent and zero ammonium supplementation; P7: zero alkalinity and zero ammonium supplementation. Flow rate 20 l/d; influent COD 10 500 mg/l; COD load on pelletised bed: 36 kg COD/(m.d).

9.11 CONCLUSIONS

From this study on the treatment of the proteinaceous substrate, casein, the following conclusions are formed:

Feasibility:

- A UASB system treating the proteinaceous substrate casein developed a pelletised bed.

- Up to the highest loading rate applied (65 kgCOD/m^3 sludge bed. d) the COD removal remained above 95 per cent.

- The system could be operated in a flow through mode without alkalinity addition to the influent, for influent COD concentrations up to 10 000 mg/ℓ, even though at the highest COD loading rate the minimum bed pH declined to 6,2.

- The profiles of product formation along the line of flow of the reactor were similar to those reported by Sam Soon *et al.* (1987) when treating a carbonaceous substrate in a UASB reactor.

- Uptake of nitrogen was well in excess of that observed in "normal anaerobic fermentation", and appears to be associated with pellet formation.

Sludge production:

- The specific sludge yield obtained in a high hydrogen partial pressure reactor, under the prevailing low pH conditions (minimum bed pH $\simeq$ 6,2) was 0,26 mgVSS/mgCOD utilized. In the first reactor the VSS retained as pellets was 38 per cent of the VSS produced; the remaining 62 per cent was lost from the bed to the effluent. In general the pellets were small (< 2 mm), fragile and black in colour.

- The overall sludge yield of the high and low hydrogen partial pressure reactors combined (with a minimum bed pH $\simeq$ 6,2 in the first reactor) was estimated to be 0,11 mgVSS/mgCOD utilized.

- When the minimum bed pH in the system was raised (pH ≃ 7,0) by addition of alkalinity to the influent, the specific sludge yield in the high hydrogen partial pressure reactor declined to 0,17 mgVSS/COD utilized. The VSS retained as pellets was 11 percent and the remaining 89 per cent was lost to the effluent.

- The lower specific sludge yield measured under near neutral minimum bed pH conditions was contradictory to Sam Soon's hypothesis on pelletisation which predicts a higher sludge yield at neutral pH levels because of increased activity of the hydrogenotrophs. From an experimental study of this problem the decrease in sludge production at near neutral pH levels is ascribed to inhibitory effects of the increased NH_3 species concentration on the hydrogenotrophic organisms when pH neutrality is approached.

Inhibition effects:

- On addition of alkalinity, to raise the minimum pH from 6,2 to 7 in the first reactor, the conversion of HAc to CH_4 and CO_2 improved considerably which resulted in an increased COD removal. However, there was now an increase in HPr in the profile and decrease in pellet/VSS production, from 0,26 to 0,17 mgVSS/mgCOD utilized in the high $\bar{p}H_2$ reactor. It was concluded that these very likely were due to inhibition of the hydrogenotrophs which resulted in an increase in $\bar{p}H_2$, thereby preventing the conversion of HPr to HAc and H_2 by the acetogenic bacteria and a reduction in polypeptide formation.

- The cause of the inhibition appeared to be due to an increase in NH_3 species concentration when the pH was raised. The higher NH_3 concentration appeared to inhibit primarily the hydrogenotrophs, not the acetogens nor the acetoclastic organisms.

- The methanogens appeared to adapt to a large degree to the increased NH_3 concentrations when the inorganic nitrogen concentration was raised in steps from 900 to 1400 to 2400 mgN/l influent at a pH range within the reactor of 7,0 to 7,5. The system's overall COD removal showed only temporary loss in COD conversion. However, from the VSS measurements taken over a relatively short period it would appear that VSS generation was reduced and the fraction of VSS retained as pellets had become smaller.

- On termination of NH_4^+ and alkalinity addition the system reverted back rapidly to the response observed before these additions were made.

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CHAPTER 10

CONCLUSIONS

This investigation started with the objective to evaluate the feasibility for treatment of a pure proteinaceous substrate (casein), lauter tun (brewery) and wine distillery wastes in UASB systems. During these feasibility studies the need for monitoring and control of the UASB systems became apparent: Two principal parameters identified as being of crucial importance were: (1) pH buffering (via H_2CO_3*alkalinity) for pH control and (2) short–chain fatty acids (SCFA) for monitoring of process stability. From the need for pH control and SCFA monitoring the following objectives were set for the investigation:

- Development of a simple method for simultaneous determination of the H_2CO_3*alkalinity and SCFA concentration in anaerobic systems. This method would be used for (1) assessing the H_2CO_3*alkalinity requirements for different types of wastes when treated in UASB systems, (2) monitoring process stability when treating these wastes under different operating conditions, e.g. different recycle ratios.

- Assessment of H_2CO_3*alkalinity requirements when treating lauter tun (brewery) waste in UASB systems. This waste generates very little H_2CO_3*alkalinity internally; consequently virtually all H_2CO_3*alkalinity has to be supplied externally. It was of special interest to evaluate the effect of recycling the effluent to the influent thereby recovering the effluent H_2CO_3*alkalinity and diluting the base influent COD to an effective influent COD, COD_e, defined as: base influent COD/(1 + recycle ratio).

- Assessment of H_2CO_3*alkalinity requirements when treating wine distillery waste in UASB systems. This waste generates a substantial mass of H_2CO_3*alkalinity internally due to deamination of proteins to ammonium/ammonia, reduction of sulfates to sulfides and removal of organic acid salts such as potassium bitartrate. Similar to the brewery waste, it was of interest to evaluate the effect of recycling on process performance and the requirements of H_2CO_3*alkalinity at different recycle ratios, i.e. different COD_e concentrations.

- Assessment of a pure proteinaceous waste, casein, for treatment in a UASB system: This substrate provides the opportunity to study the H_2CO_3*alkalinity generation from deamination and the effect of pH changes on process performance of systems with high levels of inorganic nitrogen. With high levels of inorganic nitrogen generated in the reactor liquid the likelihood of inhibitory effects increases developing due to increased ammonia (NH_3) levels at higher than neutral pH values. It was of interest to evaluate the effect of pH change on process performance due to the NH_3 inhibition.

Because of the differing nature of these aspects each will be dealt with separately, describing the problems encountered and the solutions achieved.

Measurement of H_2CO_3*alkalinity and SCFA

In the literature a number of methods had been proposed to measure (1) some form of alkalinity which approximates the H_2CO_3*alkalinity only, (2) the SCFA concentration only, and (3) some form of alkalinity approximating the H_2CO_3*alkalinity *and* the SCFA by using strong acid/base titrations. Since the objective in this investigation was to measure alkalinity *and* SCFA concentration, only methods measuring both these parameters needed to be considered. Two approaches to quantify the SCFA *and* approximate forms of the H_2CO_3*alkalinity concentrations in anaerobic digestor liquids had been proposed, one by Powell and Archer (1989) and one by Colin (1984). Both methods involve strong acid *and* base titrations over a large pH range which imposes a rather cumbersome titration procedure, increases uncertainty in the correctness of the pH readings, and may give rise to precipitation phenomena, all these resulting in loss of accuracy of the derived values.

In this investigation a 5 pH point acid titration was developed for determining the SCFA and H_2CO_3*alkalinity in aqueous solutions containing known concentrations of other weak acid/bases such as the phosphate, ammonium or sulfide. The method requires only acid titration over the middle range of pH (initial pH to pH 6,7; 5,9; 5,2 and 4,3) so that the pH probe needs to be calibrated only for a relatively narrow pH range and precipitation phenomena are unlikely.

The most common additional weak acid/bases in anaerobic digestion are phosphate and ammonium. In some situations the total species concentrations of these two weak acid/bases might not be known; it was shown that if the concentration of the ammonium weak acid/base is neglected, the errors induced in the determination of the SCFA and $H_2CO_3^*$alkalinity are very small and usually negligible. However, if the concentration of the phosphate weak acid/base is neglected, the error in the determination of the SCFA always will be minor but the error in the $H_2CO_3^*$alkalinity can be substantive, being large if the phosphate concentration is large and small if the phosphate concentration is small.

The method can be readily automated if the initial pH of the sample is > 6,7; in this event only a strong acid titration is required to four lower pH points. If however the initial pH of the sample is < 6,7 the pH needs to be raised to 6,7 by addition of strong base. The requirement is only to raise the pH; it is not necessary to standardize the strong base or to measure the mass of strong base added – the mass of titrant from $pH_1 = 6,7$ (± 0,1) to the lower pH values only needs to be monitored because the method *inter alia* determines the total carbonate species concentration (C_T) from the titration between pH points 6,7 to 4,3 and, therefore C_T is not affected by the preliminary titration to pH = 6,7.

The method allows a check on the pH probe in that it provides an estimate of the 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 estimate of the systematic pH error, however, requires that the carbonate subsystem dominates over the SCFA system, i.e. the total species concentration of the SCFA (as acetic acid) must not exceed half of C_T (measured as $CaCO_3$).

For monitoring the process performance via SCFA and $H_2CO_3^*$alkalinity and for pH control of anaerobic systems, the 5 pH point titration method appears to have decided advantages over existing methods in, (1) attainable accuracy, (2) testing time required, and (3) simplicity of testing procedure.

Feasibility study and assessment of $H_2CO_3^*$alkalinity requirements for lauter tun (brewery) waste

The study of lauter tun waste in a laboratory scale UASB reactor at 30° C was undertaken with three principal objectives in mind:

- to investigate the potential for pelletisation,

- to study the H_2CO_3*alkalinity requirements to maintain a near neutral minimum sludge bed pH when a recycle was imposed from the reactor effluent back to the influent and,

- to investigate the effect of recycling on process performance.

From the experimental study the following conclusions were drawn:

- Lauter tun waste was amenable to treatment in a UASB system and the waste developed a pelletised sludge bed. The pattern of product formation along the line of flow of the reactor was very similar to that observed under similar conditions when treating a pure carbohydrate type substrate.

- The TKN/COD ratio of the lauter tun waste was 0,011 mgN/mgCOD; for unimpeded pelletisation when treating glucose in a UASB system Sam–Soon *et al.* (1990) suggested a TKN/COD ratio of 0,02 mgN/mgCOD. In this study the feed was supplemented with NH_4Cl to give a TKN/COD ratio of 0,024; the observed TKN uptake was 0,015 mgN/mg undiluted influent COD. Thus it appears that (1) lauter tun waste needs to be supplemented with nitrogen when treated in UASB system to achieve unimpeded pelletisation and, (2) the TKN/COD uptake was lower than that for glucose substrate; the most likely cause for this reduction is that in lauter tun waste carbohydrates form only a fraction of the COD whereas in glucose the carbohydrates constitute 100 percent of the COD (the carbohydrates generate a high hydrogen partial pressure during acidogenesis, which provides the basis for pelletisation and the concomitantly high uptake of inorganic nitrogen per mass of COD removed). Besides the requirement for nitrogen augmentation there was a "suspicion" that lauter tun waste may be deficient in some trace elements. For this study, to ensure that such a deficiency positively was not present, trace elements were added. Because this aspect was not clarified it would be advisable in design to take cognisance of a possible need for trace element addition.

- The pellets produced were smaller and less compact than with glucose as feed substrate. This contributed to the pellets being lifted by the escaping gas to the gas seperator and the settler when the COD loading rate exceeded about 10 kg/(m^3 sludge bed.d) and in this manner set the upper limit for the COD loading rate.

- Lauter tun waste generates insignificant concentrations of internal pH buffer; pH buffer needs to be supplied from an external source to control the minimum pH in the reactor to $6,8 < pH < 7,2$. When supplying H_2CO_3*alkalinity via a strong base (NaOH) to the base feed flow, the pH increased to such high levels that some of the trace elements apparently precipitated becoming unavailable to the microorganisms which gave rise to partial failure of the process. Hence, the dosing point needs to be selected such that a drastic pH increase at the dosing point is avoided. In this study an appropriate dosing point was found to be the recycle stream; the presence of dissolved CO_2 and H_2CO_3*alkalinity in the recycle stream buffered the pH downstream of the point of strong base addition to a $pH < 8,5$, instead of a pH of > 11 when NaOH was added to the influent flow.

- Dilution of the base influent COD from 13 000 mg/ℓ to an effective influent COD (COD_e) of 570 mg/ℓ, by applying a recycle ratio of 22:1, appeared to have no adverse effect on process performance, in COD removal and SCFA conversion to methane and carbon dioxide (the percentage COD removal never declined below 90 percent). Thus it would seem that the lower limit of the COD_e of 2500 mg/ℓ, tested by Sam–Soon *et al.* (1991), can be substantially lowered.

- With the target minimum bed pH of $\simeq 7$ the pH profile in the bed exhibited only a slight depression at the minimum value for a recycle ratio of 6:1 (base influent COD diluted by the recycle to 1860 mg/ℓ) and no significant depression at higher recycle ratios. This tendency to smooth out the "dip" in the pH profile when the effective influent COD is reduced by increasing the recycle ratio, conforms with the observations of Sam–Soon *et al.* (1991).

- The alkalinity requirement (mg H_2CO_3*alkalinity/ℓ base influent) to maintain a selected minimum pH in the bed, was reduced by imposing a recycle. Sam–Soon *et al.* (1991) formulated the alkalinity requirement/ℓ influent as $C \cdot$ (base influent COD, mg/ℓ)/(1 + recycle ratio) where $C =$ mgH_2CO_3*alkalinity/(mg base influent COD). This study showed that for a selected COD loading rate of 9 kg/(m^3 sludge bed.d) and a selected minimum pH ≃ 7, C is not constant but increases as the recycle ratio, r, increases, from C = 1,5 (r = 6) to C = 2,4 (r = 22). Despite this increase, the recycle factor 1/(1 + r) still induced a significant reduction in H_2CO_3*alkalinity requirements per litre base influent flow with increase in r. For example, to maintain a minimum sludge bed pH ≃ 7, at a COD loading rate of 9 kg/(m^3 sludge bed.d), a base influent COD concentration of 13 000 mg/ℓ and a recycle ratio of 22:1, the pH buffer requirements, expressed as H_2CO_3*alkalinity as $CaCO_3$, were 1350 mg/(ℓ base influent flow) as $CaCO_3$; with the recycle ratio 6:1, the requirement was 2980 mg/(ℓ base influent flow) as $CaCO_3$. Virtually all of the pH buffer needed to be supplied from an external source.

Feasibility study and assessment of H_2CO_3*alkalinity requirements for wine distillery waste

The study of wine distillery waste in a laboratory scale UASB reactor at 30°C, similar to the study on lauter tun waste, was undertaken with three principal objectives in mind:

- to investigate the potential for pelletisation,
- to study the H_2CO_3*alkalinity required to maintain a near neutral minimum sludge bed pH when recycling the reactor effluent back to the influent,
- to investigate the effect of recycling on process performance.

From the experimental study the following conclusions were drawn:

- Wine distillery waste was amenable to treatment in a UASB system and developed a pelletised sludge bed. The pattern of product formation along the line of flow of the reactor was very similar to that observed under similar conditions when treating a pure carbohydrate type substrate.
- The TKN/COD ratio of the wine distillery waste was about 0,014 mgN/mgCOD. For unimpeded pelletisation when treating glucose in a UASB system, Sam–Soon *et al.* (1990) suggested a TKN/COD ratio of 0,02 mgN/mgCOD. However, in this study the average mass of TKN uptake per mass of COD for wine distillery waste was substantially less, 0,01 mgN/mgCOD. This reduced TKN uptake may be ascribed to the nature of the

waste: Part of the COD (short chain fatty acids and other organic acids) did not induce high hydrogen partial pressure conditions; hence, only reduced biopolymer production would take place. From the measured TKN uptake of about 0,01 mgN/mgCOD it would appear that in most cases wine distillery waste would require no addition of nitrogen, or only a little.

- Pellet production in the high hydrogen partial pressure region of the reactor was 0,14 mgVSS/(mgCOD removed). This pellet yield was significantly lower than that reported by Sam–Soon *et al.* (1987), 0,36 mgVSS/(mgCOD removed), when treating apple juicing wastes. This observation is in agreement with the reduced TKN uptake and lends further support to the conclusion above that wine distillery waste would not induce pelletisation to the same extent as pure carbohydrate substrates.

- Visually the pellets produced were smaller and less compact than those observed with glucose and appeared to have a sightly filamentous surface texture. This contributed to the pellets being lifted by the escaping gas to the gas seperator and the settler when the COD loading rate exceeded about 15 kg/(m^3 sludge bed.d) and in this manner set the upper limit for the COD loading rate.

- When pH buffer was added in the form of NaOH to the undiluted feed, with addition of 1 gNaOH per litre feed the pH did not increase above 8,0 because the waste pH was very low due to the presence of short–chain fatty acids (SCFA) and other organic acids. Wine distillery waste generated significant internal buffer, H_2CO_3*alkalinity, due to the interaction of OH^- ions with dissolved CO_2; the OH^- ions were generated by the removal of H^+ ions due to deamination of proteins and the removal of organic weak acid/base salts. The mass of H_2CO_3*alkalinity generated could not be predicted *ab initio* because the influent concentrations of the proteins and various organic acid/base salts could not be determined. The H_2CO_3*alkalinity generated internally was experimentally determined to be about 0,1 mgH_2CO_3*alkalinity as $CaCO_3$ per mg base influent COD (from H_2CO_3*alkalinity measured in the effluent). Imposing a recycle from the effluent to the influent, the H_2CO_3*alkalinity generated in the bed, and appearing in the effluent, is recycled to the influent; the dilution due to the recycle reduces the base influent COD to an effective influent COD, COD_e [COD_e = base influent COD/(1 + recycle ratio)]. In the measure the recycle ratio increases, the effective influent COD concentration decreases, but the effluent (i.e. recycled) H_2CO_3*alkalinity remains constant (because the H_2CO_3*alkalinity generated per base influent COD remains constant). Consequently the H_2CO_3*alkalinity/COD_e ratio increases, causing the minimum pH to increase.

- The base influent COD concentration ranged from 20 000 to 30 000 mg/ℓ. Dilution of the base influent COD to an effective influent COD (COD_e) as low as 900 mg/ℓ, by applying a recycle ratio of 33:1, appeared to have no adverse effect on the process performance (the percentage COD removal never declined below 90 percent). This provides further evidence (see section lauter tun waste) that the lower limit of the effective influent COD of 2500 mg/ℓ, tested by Sam–Soon *et al.* (1991) with satisfactory operation, can be substantially lowered.

- In a UASB system with a recycle, in assessing the H_2CO_3*alkalinity supplementation to maintain a selected minimum bed pH, the effluent H_2CO_3*alkalinity must serve as a reference parameter because this H_2CO_3*alkalinity includes any H_2CO_3*alkalinity generated in the bed and accordingly reduces the H_2CO_3*alkalinity to be supplied externally.

- The effect of different effective influent COD (COD_e) concentrations on the minimum bed pH was evaluated at a constant COD loading rate of 9 kg/(m^3 sludge bed.d), a base influent COD of 27 000 mg/ℓ and an effluent H_2CO_3*alkalinity of about 3700 mg/ℓ as $CaCO_3$, by applying three different recycle ratios of 33:1, 20:1 and 7:1 to give COD_e concentrations of 790 mg/ℓ, 1290 mg/ℓ and 3380 mg/ℓ respectively. The minimum bed pH decreased from 7,5 with COD_e = 790 mg/ℓ to 7,3 with COD_e = 1290 mg/ℓ and to 6,8 with COD_e = 3380 mg/ℓ. Hence, by changing COD_e via the recycle the minimum bed pH changed considerably and indicated that the minimum pH ≃ 7 could be readily controlled by increasing or decreasing the recycle ratio. COD removal was not significantly affected by the change in COD_e.

- The effect of lowering the effluent H_2CO_3*alkalinity (i.e. the H_2CO_3*alkalinity generated per litre of base influent), by adding HCl to the base influent flow, was evaluated at a constant COD loading rate of 9 kg/(m^3 sludge bed.d). This experiment showed that, at a constant COD loading rate;

(1) for the same COD_e the minimum bed pH increases with increase of effluent H_2CO_3*alkalinity, and,

(2) for the same minimum bed pH, the higher the COD_e (the lower the recycle ratio) the higher the effluent H_2CO_3*alkalinity requirements.

- The effect of different COD loading rates on the minimum bed pH was evaluated by using a constant base influent COD concentration (29 000 mg/l) and changing the base influent flow. The recycle ratio was kept constant at 12:1 giving a COD_e of 2230 mg/ℓ. The effluent H_2CO_3*alkalinity was constant at 3100 mg/ℓ (as $CaCO_3$). When the COD loading rate was increased from 7 to 19 kg/(m^3 sludge bed.d) by increasing the base flow, the minimum bed pH decreased from 7,1 to 6,8. It would appear that for the same base influent COD *concentration* and a constant recycle ratio the minimum bed pH remains relatively stable despite an almost threefold change in COD loading rate.

- The pH profiles in the bed exhibited only a slight depression (to the minimum pH) for recycle ratios of 33:1 and 20:1 (base influent COD of 27 000 mg/ℓ and COD_e concentrations of 790 and 1290 mg/ℓ). This tendency to smooth out the "dip" in the pH profile at low effective influent CODs, conforms with the observations of Sam-Soon *et al.* (1991). It would seem, therefore, that provided the effective influent COD is maintained in the range, say, 1000 to 1500 mg/ℓ the pH up the bed will be substantially constant and it can be monitored at any point in the bed.

- In wine distillery waste [at a practical COD loading rate of 10 kg/(m^3 sludge bed.d) with a base influent COD of 20 000 to 30 000 mg/ℓ] with the internal alkalinity generation, as the recycle ratio was increased (COD_e is decreased) so the external supplementation of alkalinity was reduced until at a $COD_e < 2000$ mg/ℓ (approximately) the process generated sufficient internal H_2CO_3*alkalinity to maintain a near neutral minimum sludge bed.

Feasibility study for a pure proteinaceous substrate, casein, and effects of pH changes on process performance

Sam-Soon *et al.* (1987 and 1991a) investigated two basic types of organic substrates with regard to their potential to form pellets in a UASB system: carbohydrates (glucose) and fats and oils (oleic acid). They found that pelletisation occurred with glucose but did not occur with oleic acid. Besides these two basic types of organic substrates there is a third – proteins. There was but little information available on the behaviour of UASB systems receiving pure proteinaceous substrates. Accordingly an investigation was undertaken into the behaviour of a pure proteinaceous substrate, casein, in a laboratory scale UASB system with the objectives to:

- study the feasibility of treatment of casein in a UASB system,

- measure sludge production and,

- investigate the effect of the high inorganic nitrogen concentrations (generated due to deamination of high concentrations casein) on the process with changes in pH. Depending on the concentration of proteins, deamination may generate high concentrations of inorganic nitrogen. The species concentration of inorganic nitrogen is dependent on the pH, i.e. the concentration of ammonia increases with an increase in pH. From the literature, methanogenic organisms are inhibited even at low ammonia (NH_3) concentrations. It was of interest therefore to study possible inhibition effects due to increased levels of ammonia at pH levels above neutral.

The feasibility study was done on a single reactor unit, that is, the sludge bed that included both the high and low hydrogen partial pressure regions. The study on sludge production and inhibition effects was done on a two in–series reactor system, the first reactor containing the high hydrogen partial pressure region, and the second reactor containing the low hydrogen partial pressure region of the sludge bed respectively. From the study on the treatment of the proteinaceous substrate, casein, in these two laboratory UASB systems the following conclusions were formed:

Feasibility:

- The UASB system treating the proteinaceous substrate casein developed a pelletised bed.

- Up to the highest loading rate applied (65 kgCOD/m^3 pelletised bed.d) the COD removal remained above 95 per cent.

- The system could be operated without alkalinity addition to the influent.

- The profiles of product formation along the line of flow of the reactor were similar to those reported by Sam Soon *et al.* (1987) when treating a carbonaceous substrate in a UASB reactor.

- Uptake of nitrogen was well in excess of that observed in "normal anaerobic fermentation" – Sam Soon's conclusion that this was due to pellet formation appears to be supported.

Sludge production:

- The specific sludge yield obtained in a high hydrogen partial pressure reactor, under the prevailing low pH conditions (minimum bed pH ≃ 6,2) was 0,26 mgVSS/mgCOD utilized. In the first reactor the VSS retained as pellets were 38 percent of the VSS produced; the remaining 62 percent were lost from the bed to the effluent of the first reactor. The overall sludge yield of the high and low hydrogen partial pressure reactors combined (with a minimum bed pH ≃ 6,2 in the first reactor) was estimated at 0,11 mgVSS/mgCOD utilized. The pellets were small < 2 mm diameter, dark in colour and less compact than those with glucose as feed substrate.

- When the minimum bed pH in the first reactor was raised from about 6,2 by addition of alkalinity to the influent to 7, the specific sludge yield in the high hydrogen partial pressure reactor declined from 0,26 to 0,17 mgVSS/COD utilized. The VSS retained as pellets was 11 percent and the remaining 89 per cent was lost to the effluent. The lower specific sludge yield measured under near neutral pH conditions was contradictory to Sam Soon's hypothesis on pelletisation, which predicts a higher sludge yield at neutral pH levels because of increased activity of the hydrogenotrophs. The decrease in sludge production at near neutral pH levels might be ascribed to inhibitory effects of the increased NH_3 species concentration on the hydrogenotrophic organisms as pH neutrality was approached, see below.

Inhibition effects:

- In the first reactor, on addition of alkalinity (which raised the minimum bed pH from 6,2 to 7), the concentration of HAc decreased, the COD removal increased but there was now an increase in HPr in the profile and a decrease in VSS production from 0,26 to 0,17 mgVSS/mgCOD utilized in the high $\bar{p}H_2$ reactor. Accepting the hypothesis on pelletisation by Sam–Soon *et al.* (1987), i.e. increased VSS production due to the action of the hydrogenotroph *M* strain AZ, it was concluded that the reduced VSS production was due to inhibition of the hydrogenotrophs. Inhibition of the hydrogenotrophic microorganisms was further supported by the fact that the HPr advanced higher up the sludge bed. HPr can only be converted at low hydrogen partial pressure. Inhibition of hydrogenotrophs reduced the rate of H_2 utilization thereby extending the region of high hydrogen partial pressure up the sludge bed, in this manner retarding the conversion of HPr to HAc and H_2.

- The cause of the inhibition appeared to be the increase in NH_3 species concentration when the pH was raised to pH 7. The higher NH_3 concentrations appeared to inhibit primarily the hydrogenotrophs, not acetoclastic organisms.

- With time the hydrogenotrophs appeared to adapt, to a large degree, to the increased NH_3 concentrations. When the inorganic nitrogen concentration was raised in steps from 900 to 1400 to 2400 mgN/(ℓ influent) with pH maintained within the reactor between 7,0 to 7,5, the system's overall COD removal showed only temporary loss in COD conversion at each step.

- On termination of ammonium and alkalinity addition the system reverted rapidly back to the response observed before these additions were made.

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APPENDIX A

CALCULATION OF THE ACTIVITY COEFFICIENTS WITH THE AID OF THE DAVIS EQUATION

In low salinity waters (TDS < 2500 mg/ℓ) activity coefficients of ions can be determined from the Debye–Hueckel theory or some modification of it. The most widely used modification of this theory is that by Davis (Butler, 1964); viz.

$$\log f_i = -A\, Z_i^2 \left[\frac{\mu^{0,5}}{(1+\mu^{0,5})} - 0{,}3\,\mu\right] \qquad (A.1)$$

where f_i = activity coefficient for ionic species i, written as f_m and f_d for mono and divalent ions respectively

μ = ionic strength

= $0{,}5\, \Sigma\, C_i\, Z_i^2$

C_i = concentration of the i^{th} ionic species, (mol/ℓ)

Z_i = charge of the i^{th} species, equal to 1 for monovalent and 2 for divalent ions

A = temperature dependent constant

= $1{,}825 \cdot 10^6 \cdot (78{,}3\ T)^{-1,5}$

= 0,504 at 25 °C

T = temperature in Kelvin

To calculate the ionic strength, μ, requires a complete analysis of the water. However, the activity coefficients determined from the Davis equation are not very sensitive to the ionic strength so that an approximate estimate of μ from empirical methods usually is sufficient. Two empirical equations are available (Kemp, 1971), i.e.

$$\mu \simeq 2{,}5 \cdot 10^{-5} \cdot (\mathrm{TDS} - 20) \tag{A.2}$$

where TDS = total inorganic dissolved solids, (mg/ℓ).

$$\mu \simeq 1{,}68 \cdot 10^{-4} \cdot \mathrm{SC} \tag{A.3}$$

where SC = specific conductivity, (mS/m)
(1 mS/m = 10 μ mho/cm)

Examples:

The monovalent activity coefficient, f_m, for a solution with ionic strength of 0,010 at 25 °C is

$$\begin{aligned} \log f_m &= -0{,}504 \cdot (1)^2 \cdot [0{,}010^{0\text{’}5}/(1 + 0{,}010^{0\text{’}5}) - 0{,}3 \cdot 0{,}010] \\ &= -0{,}0443 \\ f_m &= 10^{-0\text{’}0443} = 0{,}903 \end{aligned}$$

For the same solution the divalent activity coefficient, f_d, is

$$\begin{aligned} f_d &= -0{,}504 \cdot (2)^2 \cdot [0{,}010^{0\text{’}5}/(1 + 0{,}010^{0\text{’}5}) - 0{,}3 \cdot 0{,}010] \\ &= -0{,}1772 \\ f_d &= 10^{-0\text{’}1772} = 0{,}665 \end{aligned}$$

REFERENCES

Butler J N (1964) Ionic equilibrium: A mathematical approach. Addison Wesley, Reading, Mass., USA

Kemp P H (1967) Chemistry of natural water. 1/M Fundamental relationships. Water Research, 5, pp 297 – 311.

APPENDIX B

APPARATUS FOR TITRATION EXPERIMENTS

The apparatus to develop and test the 4 and 5 pH point titration methods comprised the following components:

(1) titration burette,
(2) pH meter,
(3) pH probe,
(4) pH buffer solutions,
(5) pipettes,
(6) magnetic stirrer and stirrer bar, and,
(7) sample vessel.

Titration burette

The titration burette used throughout the investigation was of a manually operated "piston burette" type with switching valve at the top to regulate the inflow and outflow of the titration acid. Teflon tubing connected the acid bottle containing the acid stock solution to the intake side of the valve, and the valve outlet to the dropping pipette in the test solution. The accuracy of the burette was repeatedly tested by weighing 10 mℓ of acid stock solution; on average it was found to be 99,7 percent accurate.

pH meter

The electrometric measurements were carried out with a digital high precision pH meter, supplied by Radiometer, pHM64. This pH meter displays the pH to three decimal places. For the 4 and 5 pH point titration pH readings are required only to the second decimal. Hence all the readings were rounded to the second decimal.

pH probe

A combined glass electrode, GK2401C, supplied by Radiometer, was used throughout the investigation

pH buffer solutions

Calibration of the combined glass electrode was carried out using two NBS standard buffer solutions, (1) 0,05 M potassium hydrogen phthalate buffer (pH = 4,00 at 25 °C), and (2) 0,0275 M disodium hydrogen phosphate / 0,025 M potassium dihydrogen phosphate buffer (pH 7,00 at 25 °C).

Pipettes

The pipettes were 5, 10, 20, 25 and 50 mℓ pipettes (A grade). Similar to the titration burette, each pipette was tested for accuracy; all showed an accuracy of 99,7 percent or better.

The effect of inaccuracies of the titration burette and pipettes, on the determination of H_2CO_3*alkalinity and SCFA by titration, were very small in comparison with the effect of errors in pH readings, or, or in the evaluation of the apparent pK_a values of the different weak acid/bases. With the accuracy with which the A grade pipettes are supplied, in practice the additional effort to calibrate the pipettes does not appear to be justified by the small increase in accuracy that can be achieved. For this investigation also *no* corrections were made for the small calibration errors in measuring the sample volumes with pipettes and errors in titrant dosage.

Magnetic stirrer and stirrer bar

The sample was stirred with a magnetic stirrer of variable speed and a stirrer bar of 25 mm length, at about 60 rpm.

Sample vessel

In this investigation 100 mℓ and 150 mℓ Erlenmeyer flasks were used.

APPENDIX C

INVESTIGATION INTO THE EFFECT OF A SYSTEMATIC pH ERROR ON THE CALCULATION OF H_2CO_2*ALKALINITY AND C_T

EXPERIMENTAL DATA AND RESULTS

The experimental data and calculated results are subdivided into two groups:

(1) Data and results *without* correction for systematic pH error: The individual titration data and calculated results are listed in tables designated Table C.1. The averaged results for the set of C_T and H_2CO_3*alkalinity concentrations are listed in Table C.2.

(2) Data and results *with* correction for systematic pH error by applying a constant pH correction factor, found by trial, of – 0,07. The individual titration data and calculated results are listed in tables designated Table C.3. The averaged results for the set of C_T and H_2CO_3*alkalinity concentrations (250, 500, 750 and 1000 mg/ℓ as $CaCO_3$) are listed in Table C.4.

TABLE C.1.1

No correction for systematic pH error

250 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 20°C

TDS: 420 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,36	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,40	5,99	1	0-1	260	259
2,68	5,80	2	0-2	259	258
2,90	5,59	3	0-3	256	255
3,06	5,39	4	0-4	255	254
3,16	5,22	5	0-5	255	254
3,24	4,99	6	0-6	253	252
3,28	4,83	7	0-7	253	252

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,35	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,40	6,01	1	0-1	264	263
2,68	5,82	2	0-2	262	261
2,94	5,57	3	0-3	258	257
3,06	5,42	4	0-4	257	256
3,18	5,20	5	0-5	255	255
3,26	4,96	6	0-6	254	253
3,30	4,78	7	0-7	253	252

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,4	6,00	1	0-1	262	261
2,68	5,80	2	0-2	259	258
2,90	5,61	3	0-3	258	257
3,06	5,40	4	0-4	256	254
3,18	5,16	5	0-5	254	253
3,24	4,98	6	0-6	253	252
3,28	4,81	7	0-7	252	251

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,36	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,40	5,99	1	0-1	260	259
2,68	5,80	2	0-2	259	258
2,90	5,60	3	0-3	257	256
3,06	5,40	4	0-4	256	255
3,16	5,22	5	0-5	255	254
3,24	4,98	6	0-6	253	252
3,28	4,82	7	0-7	253	251

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,40	5,99	1	0-1	260	259
2,68	5,79	2	0-2	258	256
2,90	5,60	3	0-3	257	256
3,06	5,39	4	0-4	255	254
3,16	5,20	5	0-5	254	253
3,24	4,96	6	0-6	252	251
3,28	4,80	7	0-7	252	251

TABLE C.1.2

No correction for systematic pH error

500 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 840 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,86	6,01	1	0-1	544	540
5,46	5,81	2	0-2	537	533
5,88	5,61	3	0-3	527	524
6,18	5,39	4	0-4	518	515
6,36	5,19	5	0-5	512	509
6,48	4,99	6	0-6	508	505
6,56	4,79	7	0-7	506	502

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,43	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,78	5,99	1	0-1	526	521
5,34	5,81	2	0-2	524	519
5,82	5,60	3	0-3	520	514
6,14	5,39	4	0-4	514	509
6,34	5,21	5	0-5	512	507
6,50	4,98	6	0-6	509	504
6,60	4,77	7	0-7	508	503

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,41	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,76	6,00	1	0-1	528	523
5,34	5,81	2	0-2	524	520
5,82	5,60	3	0-3	520	515
6,12	5,41	4	0-4	515	511
6,34	5,21	5	0-5	512	508
6,48	5,01	6	0-6	509	505
6,60	4,77	7	0-7	508	503

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,42	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,74	5,99	1	0-1	522	517
5,34	5,79	2	0-2	519	514
5,80	5,58	3	0-3	514	509
6,10	5,39	4	0-4	511	506
6,30	5,19	5	0-5	507	502
6,46	5,01	6	0-6	508	503

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,43	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,74	5,99	1	0-1	522	516
5,34	5,79	2	0-2	519	513
5,80	5,58	3	0-3	514	509
6,10	5,39	4	0-4	511	506
6,30	5,21	5	0-5	509	504
6,46	5,01	6	0-6	508	503

TABLE C.1.3

No correction for systematic pH error

750 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 22°C

TDS: 1260 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
7,08	6,00	1	0-1	796	789
8,00	5,80	2	0-2	789	782
8,66	5,59	3	0-3	776	769
9,16	5,39	4	0-4	771	764
9,46	5,20	5	0-5	765	759
9,66	5,00	6	0-6	760	754
9,80	4,79	7	0-7	756	750

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
7,06	5,97	1	0-1	776	769
7,96	5,77	2	0-2	772	766
8,60	5,58	3	0-3	767	761
9,06	5,39	4	0-4	763	756
9,38	5,20	5	0-5	759	752
9,60	5,01	6	0-6	756	750
9,76	4,79	7	0-7	753	747

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,38	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,96	5,99	1	0-1	776	769
7,86	5,80	2	0-2	775	768
8,56	5,59	3	0-3	766	760
9,04	5,41	4	0-4	765	758
9,38	5,21	5	0-5	760	753
9,60	5,03	6	0-6	758	751
9,76	4,84	7	0-7	756	747

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
7,00	5,98	1	0-1	775	768
7,90	5,78	2	0-2	771	764
8,56	5,59	3	0-3	767	760
9,04	5,40	4	0-4	763	756
9,38	5,21	5	0-5	760	754
9,60	5,02	6	0-6	757	751
9,76	4,82	7	0-7	755	749

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,39	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,96	5,98	1	0-1	770	763
7,86	5,79	2	0-2	771	763
8,56	5,58	3	0-3	764	756
9,04	5,39	4	0-4	761	753
9,36	5,20	5	0-5	757	750
9,60	4,99	6	0-6	754	747
9,76	4,79	7	0-7	753	746

TABLE C.1.4

No correction for systematic pH error

1000 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 1680 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$alk	C_T
0 ml	8,39	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
9,36	5,99	1	0-1	1045	1034
10,54	5,78	2	0-2	1029	1018
11,40	5,60	3	0-3	1025	1015
12,10	5,38	4	0-4	1016	1006
12,52	5,20	5	0-5	1013	1003
12,84	4,99	6	0-6	1009	999
13,04	4,81	7	0-7	1009	998

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,38	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
9,42	6,00	1	0-1	1060	1050
10,6	5,80	2	0-2	1046	1036
11,48	5,60	3	0-3	1033	1023
12,20	5,37	4	0-4	1022	1012
12,60	5,18	5	0-5	1016	1006
12,86	5,00	6	0-6	1012	1002
13,06	4,79	7	0-7	1009	999

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,38	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
9,40	5,98	1	0-1	1042	1032
10,58	5,78	2	0-2	1033	1023
11,44	5,59	3	0-3	1025	1015
12,14	5,38	4	0-4	1020	1010
12,54	5,20	5	0-5	1015	1005
12,84	5,01	6	0-6	1012	1002
13,04	4,82	7	0-7	1009	1000

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,39	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
9,38	5,98	1	0-1	1040	1030
10,54	5,79	2	0-2	1035	1025
11,40	5,60	3	0-3	1026	1016
12,14	5,37	4	0-4	1017	1007
12,52	5,20	5	0-5	1013	1003
12,84	5,00	6	0-6	1011	1001
13,04	4,81	7	0-7	1009	999

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,39	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
9,38	5,98	1	0-1	1039	1029
10,54	5,78	2	0-2	1029	1018
11,40	5,60	3	0-3	1025	1015
12,10	5,38	4	0-4	1016	1006
12,52	5,20	5	0-5	1013	1003
12,84	5,00	6	0-6	1011	1000
13.04	4,81	7	0-7	1009	998

Table C.2

Averaged results

No correction for systematic pH error

250 mg/l as $CaCO_3$				
pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	261	260
5,80	2	0-2	259	258
5,60	3	0-3	257	256
5,40	4	0-4	256	255
5,20	5	0-5	255	254
5,00	6	0-6	253	252
4,80	7	0-7	253	251

500 mg/l as $CaCO_3$				
pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	528	523
5,80	2	0-2	525	520
5,60	3	0-3	519	514
5,40	4	0-4	514	509
5,20	5	0-5	510	506
5,00	6	0-6	508	504
4,80	7	0-7	508	503

750 mg/l as $CaCO_3$				
pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	779	772
5,80	2	0-2	776	769
5,60	3	0-3	768	761
5,40	4	0-4	765	757
5,20	5	0-5	760	754
5,00	6	0-6	757	751
4,80	7	0-7	755	748

1000 mg/l as $CaCO_3$				
pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	1045	1035
5,80	2	0-2	1034	1024
5,60	3	0-3	1027	1017
5,40	4	0-4	1018	1008
5,20	5	0-5	1014	1004
5,00	6	0-6	1111	1001
4,80	7	0-7	1009	999

TABLE C.3.1

Correction for systematic pH error: - 0,07

250 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 20°C

TDS: 420 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$alk	C_T
0 ml	8,36	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,40	5,99	1	0-1	249	249
2,68	5,80	2	0-2	251	250
2,90	5,59	3	0-3	250	250
3,06	5,39	4	0-4	251	251
3,16	5,22	5	0-5	252	252
3,24	4,99	6	0-6	252	251
3,28	4,83	7	0-7	251	251

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,35	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,40	6,01	1	0-1	252	252
2,68	5,82	2	0-2	253	253
2,94	5,57	3	0-3	252	252
3,06	5,42	4	0-4	253	253
3,18	5,20	5	0-5	253	253
3,26	4,96	6	0-6	252	252
3,30	4,78	7	0-7	252	252

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,40	6,00	1	0-1	250	250
2,68	5,80	2	0-2	251	250
2,90	5,61	3	0-3	252	252
3,06	5,40	4	0-4	252	252
3,18	5,16	5	0-5	251	251
3,24	4,98	6	0-6	251	251
3,28	4,81	7	0-7	251	251

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,36	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,40	5,99	1	0-1	249	249
2,68	5,80	2	0-2	251	250
2,90	5,60	3	0-3	251	251
3,06	5,40	4	0-4	252	252
3,16	5,22	5	0-5	252	252
3,24	4,98	6	0-6	251	251
3,28	4,82	7	0-7	251	251

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,40	5,99	1	0-1	249	249
2,68	5,79	2	0-2	249	249
2,90	5,60	3	0-3	251	251
3,06	5,39	4	0-4	251	251
3,16	5,20	5	0-5	251	251
3,24	4,96	6	0-6	251	251
3,28	4,80	7	0-7	251	251

TABLE C.3.2

Correction for systematic pH error: - 0,07

500 mg $H_2CO_3^*$ alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 840 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,86	6,01	1	0-1	518	516
5,46	5,81	2	0-2	518	517
5,88	5,61	3	0-3	515	513
6,18	5,39	4	0-4	510	508
6,36	5,19	5	0-5	507	505
6,48	4,99	6	0-6	505	503
6,56	4,79	7	0-7	503	502

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,43	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,78	5,99	1	0-1	502	499
5,34	5,81	2	0-2	506	503
5,82	5,60	3	0-3	508	504
6,14	5,39	4	0-4	507	503
6,34	5,21	5	0-5	507	504
6,50	4,98	6	0-6	506	503
6,60	4,77	7	0-7	506	503

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,41	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,76	6,00	1	0-1	528	523
5,34	5,81	2	0-2	524	520
5,82	5,60	3	0-3	520	515
6,12	5,41	4	0-4	515	511
6,34	5,21	5	0-5	512	508
6,48	5,01	6	0-6	509	505
6,60	4,77	7	0-7	508	503

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,42	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,74	5,99	1	0-1	498	495
5,34	5,79	2	0-2	502	499
5,80	5,58	3	0-3	503	500
6,10	5,39	4	0-4	503	500
6,30	5,19	5	0-5	502	499
6,46	5,01	6	0-6	504	501
6,60	4,77	7	0-7	506	503

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,43	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,74	5,99	1	0-1	498	495
5,34	5,79	2	0-2	502	498
5,80	5,58	3	0-3	503	499
6,10	5,39	4	0-4	503	500
6,30	5,21	5	0-5	503	500
6,46	5,01	6	0-6	504	501
6,60	4,76	7	0-7	505	502

TABLE C.3.3

Correction for systematic pH error: - 0,07

750 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 22°C

TDS: 1260 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
7,08	6,00	1	0-1	758	754
8,00	5,80	2	0-2	762	758
8,66	5,59	3	0-3	757	754
9,16	5,39	4	0-4	759	755
9,46	5,20	5	0-5	757	754
9,66	5,00	6	0-6	755	751
9,80	4,79	7	0-7	753	750

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
7,06	5,97	1	0-1	740	737
7,96	5,77	2	0-2	744	747
8,60	5,58	3	0-3	750	746
9,06	5,39	4	0-4	750	747
9,38	5,20	5	0-5	751	747
9,60	5,01	6	0-6	751	747
9,76	4,79	7	0-7	750	746

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,37	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
7,00	5,98	1	0-1	739	736
7,90	5,78	2	0-2	745	741
8,56	5,59	3	0-3	748	745
9,04	5,40	4	0-4	750	747
9,38	5,21	5	0-5	752	748
9,60	5,02	6	0-6	751	748
9,76	4,82	7	0-7	751	748

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,38	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,96	5,99	1	0-1	739	736
7,86	5,80	2	0-2	748	744
8,56	5,59	3	0-3	748	745
9,04	5,41	4	0-4	748	752
9,38	5,21	5	0-5	752	748
9,60	5,03	6	0-6	752	748
9,76	4,84	7	0-7	752	749

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,39	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,96	5,98	1	0-1	734	730
7,86	5,79	2	0-2	744	740
8,56	5,58	3	0-3	746	742
9,04	5,39	4	0-4	749	744
9,36	5,20	5	0-5	749	745
9,60	4,99	6	0-6	749	745
9,76	4,79	7	0-7	750	746

TABLE C.3.4

Correction for systematic pH error: - 0,07

1000 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 1680 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$alk	C_T
0 ml	8,39	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
9,36	5,99	1	0-1	996	989
10,54	5,78	2	0-2	995	988
11,40	5,60	3	0-3	1001	994
12,10	5,38	4	0-4	1001	994
12,52	5,20	5	0-5	1002	996
12,84	4,99	6	0-6	1002	996
13,04	4,81	7	0-7	1004	997

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,38	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
9,42	6,00	1	0-1	1009	1003
10,60	5,80	2	0-2	1010	1004
11,48	5,60	3	0-3	1008	1002
12,20	5,37	4	0-4	1007	1001
12,60	5,18	5	0-5	1006	1000
12,86	5,00	6	0-6	1005	999
13,06	4,79	7	0-7	1004	998

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,38	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
9,40	5,98	1	0-1	994	988
10,58	5,78	2	0-2	998	993
11,44	5,59	3	0-3	1001	995
12,14	5,38	4	0-4	1004	998
14,54	5,20	5	0-5	1004	998
12,84	5,01	6	0-6	1004	999
13,04	4,82	7	0-7	1004	999

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,39	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
9,38	5,98	1	0-1	991	985
10,54	5,79	2	0-2	999	993
11,40	5,60	3	0-3	1001	994
12,14	5,37	4	0-4	1002	995
12,52	5,20	5	0-5	1002	996
12,84	5,00	6	0-6	1003	997
13,04	4,81	7	0-7	1004	997

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,39	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
9,38	5,98	1	0-1	991	985
10,54	5,78	2	0-2	995	988
11,40	5,60	3	0-3	1001	994
12,10	5,38	4	0-4	1001	994
12,52	5,20	5	0-5	1002	996
12,84	5,00	6	0-6	1003	997
13,04	4,81	7	0-7	1004	997

Table C.4

Averaged results

Correction for systematic pH error: - 0,07

250 mg/l as $CaCO_3$

pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	250	250
5,80	2	0-2	251	250
5,60	3	0-3	251	251
5,40	4	0-4	252	252
5,20	5	0-5	252	252
5,00	6	0-6	251	251
4,80	7	0-7	251	251

500 mg/l as $CaCO_3$

pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	509	506
5,80	2	0-2	510	507
5,60	3	0-3	510	506
5,40	4	0-4	508	504
5,20	5	0-5	506	503
5,00	6	0-6	506	503
4,80	7	0-7	506	503

750 mg/l as $CaCO_3$

pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	742	739
5,80	2	0-2	749	746
5,60	3	0-3	750	747
5,40	4	0-4	751	749
5,20	5	0-5	752	749
5,00	6	0-6	752	748
4,80	7	0-7	751	748

1000 mg/l as $CaCO_3$

pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	996	990
5,80	2	0-2	999	993
5,60	3	0-3	1002	996
5,40	4	0-4	1003	996
5,20	5	0-5	1003	997
5,00	6	0-6	1003	997
4,80	7	0-7	1004	998

APPENDIX D

INVESTIGATION INTO THE EFFECT OF ADDITION OF NaCl ON THE SYSTEMATIC pH ERROR AND THE CALCULATION OF H_2CO_3*ALKALINITY AND C_T.

EXPERIMENTAL DATA AND RESULTS

The experimental data and calculated results are subdivided into two groups:

(1) Data and calculated results [H_2CO_3*alkalinity, C_T and ΔpH (delta pH)] for tests performed to evaluate the influence of ionic strength (by addition of different masses of NaCl) on the systematic pH error: The individual data and calculated results are listed in tables designated Table D.1. The averaged results obtained with the different NaCl concentrations are listed in Table D.2. (Calculation procedure set out in Chapter 3).

(2) Data and calculated results (H_2CO_3*alkalinity, C_T and ΔpH) for tests performed to investigate the possibility of eliminating the systematic pH error [ΔpH (delta pH)] by addition of 7,8 gNaCl/ℓ to the sample: The individual data and calculated results are listed in tables designated Table D.3. The averaged results for the set of C_T and H_2CO_3*alkalinity concentrations (250, 500, 750 and 1000 mg/ℓ as $CaCO_3$) are listed in Table D.4. (Calculation procedure set out in Chapter 3).

TABLE D.1.1

Effect of ionic strength on syst. pH error

NaCl addition: 0 g/l

Effect of ionic strength

Sample size [undiluted]: 40 ml

Sample size [diluted]: 40 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 1680 mg/l

Individual data and results

TEST No 1

V_x	pH_x	delta pH	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,46	- 0,05		
9,56	5,40		996	985
10,38	4,78			

Test 2

V_x	pH_x	delta pH	$H_2CO_3^*$alk	C_T
0	8,46	- 0,05	996	985
9,56	5,40			
10,38	4,78			

Test 3

V_x	pH_x	delta pH	$H_2CO_3^*$alk	C_T
0	8,46	- 0,05	986	985
9,56	5,40			
10,38	4,77			

TABLE D.1.2

Effect of ionic strength on syst. pH error

NaCl addition: 3,5 g/l

Sample size [undiluted]: 40 ml

Sample size [diluted]: 40 ml

Normality of strong acid: 0,075 mol/l

Temperature: 22°C

TDS: 5180 mg/l

Individual data and results

TEST No 1

V_x	pH_x	delta pH	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,35	- 0,04		
9,42	5,40		994	983
10,32	4,79			

Test 2

V_x	pH_x	delta pH	$H_2CO_3^*$alk	C_T
0	8,35	- 0,02	995	982
9,40	5,39			
10,30	4,78			

Test 3

V_x	pH_x	delta pH	$H_2CO_3^*$alk	C_T
0	8,36	- 0,03	995	982
9,40	5,40			
10,30	4,79			

TABLE D.1.3

Effect of ionic strength on syst. pH error

NaCl addition: 7,0 g/l

Sample size [undiluted]: 40 ml

Sample size [diluted]: 40 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 8680 mg/l

Individual data and results

TEST No 1

V_x	pH_x	delta pH	$H_2CO_3^*$alk mg/las $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,24	- 0,01	992	984
9,32	5,39			
10,30	4,73			

Test 2

V_x	pH_x	delta pH	$H_2CO_3^*$alk	C_T
0	8,24	- 0,01	992	984
9,32	5,39			
10,26	4,79			

Test 3

V_x	pH_x	delta pH	$H_2CO_3^*$alk	C_T
0	8,24	- 0,01	990	982
9,30	5,39			
10,24	4,79			

TABLE D.1.4

Effect of ionic strength on syst. pH error

NaCl addition: 10,5 g/l

Sample size [undiluted]: 40 ml

Sample size [diluted]: 40 ml

Normality of strong acid: 0,075 mol/l

Temperature: 22°C

TDS: 12180 mg/l

Individual data and results

TEST No 1

V_x	pH_x	delta pH	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,19	+ 0,01	991	984
9,20	5,40			
10,20	4,80			

Test 2

V_x	pH_x	delta pH	$H_2CO_3^*$alk	C_T
0	8,19	+ 0,02	991	983
9,20	5,39			
10,20	4,79			

Test 3

V_x	pH_x	delta pH	$H_2CO_3^*$alk	C_T
0	8,22	+ 0,03	993	983
9,20	5,39			
10,20	4,79			

TABLE D.1.5

Effect of ionic strength on syst. pH error

NaCl addition: 14,0 g/l

Sample size [undiluted]: 40 ml

Sample size [diluted]: 40 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 15680 mg/l

Individual data and results

TEST No 1

V_x	pH_x	delta pH	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,15	+ 0,04		
9,16	5,40		995	988
10,20	4,81			

Test 2

V_x	pH_x	delta pH	$H_2CO_3^*$alk	C_T
0	8,20	+ 0,06	992	981
9,08	5,40			
10,18	4,78			

Test 3

V_x	pH_x	delta pH	$H_2CO_3^*$alk	C_T
0	8,19	+ 0,05	993	984
9,12	5,40			
10,20	4,77			

TABLE D.2

Influence of ionic strength [expressed as TDS] on systematic pH error: Averaged results for individual results with different NaCl concentrations ranging from zero to 14gNaCl/l [see Tables D1.1 - D1.5]

NaCl added mg/l	TDS mg/l	delta pH	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	1680	- 0,05	996	985
3500	5180	- 0,03	995	982
7000	8680	- 0,01	992	983
10 500	12 180	+ 0,02	992	983
14 000	15 680	+ 0,05	993	984

TABLE D.3.1

Addition of 9,0 g NaCl per litre sample

250 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 22°C

TDS: 9420 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$alk	C_T
0 ml	8,10	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,41	6,00	1	0-1	249	249
2,44	5,80	2	0-2	250	250
2,72	5,61	3	0-3	252	252
2,94	5,40	4	0-4	252	252
3,08	5,22	5	0-5	253	253
3,20	4,99	6	0-6	253	253
3,28	4,76	7	0-7	253	253

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,08	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,10	6,01	1	0-1	251	251
2,44	5,82	2	0-2	253	253
2,74	5,61	3	0-3	254	254
2,94	5,41	4	0-4	253	253
3,08	5,22	5	0-5	253	253
3,18	5,02	6	0-6	252	252
3,26	4,79	7	0-7	252	252

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,09	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,10	6,00	1	0-1	249	249
2,44	5,80	2	0-2	250	250
2,72	5,60	3	0-3	251	251
2,94	5,40	4	0-4	252	252
3,08	5,22	5	0-5	253	253
3,20	4,99	6	0-6	253	253
3,28	4,77	7	0-7	253	253

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,09	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,40	6,00	1	0-1	249	249
2,44	5,80	2	0-2	250	250
2,72	5,60	3	0-3	251	251
2,94	5,40	4	0-4	252	252
3,08	5,22	5	0-5	253	253
3,20	5,00	6	0-6	253	253
3,28	4,77	7	0-7	253	253

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,09	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
2,10	6,00	1	0-1	249	249
2,44	5,80	2	0-2	250	251
2,72	5,60	3	0-3	251	252
2,94	5,40	4	0-4	252	252
3,08	5,22	5	0-5	253	253
3,20	4,99	6	0-6	253	253
3,28	4,77	7	0-7	253	253

TABLE D.3.2

Addition of 8 g NaCl per litre sample

500 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 9680 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,09	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,34	6,01	1	0-1	516	517
5,00	5,81	2	0-2	514	514
5,54	5,60	3	0-3	510	510
5,94	5,40	4	0-4	509	510
6,20	5,20	5	0-5	507	507
6,38	4,98	6	0-6	504	504
6,48	4,82	7	0-7	503	504

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,13	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,30	6,00	1	0-1	507	506
5,00	5,79	2	0-2	507	506
5,50	5,61	3	0-3	508	507
5,90	5,42	4	0-4	509	508
6,22	5,21	5	0-5	509	508
6,42	5,00	6	0-6	508	507
6,56	4,77	7	0-7	507	506

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,11	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,30	5,98	1	0-1	499	498
4,92	5,80	2	0-2	502	502
5,50	5,60	3	0-3	506	506
5,90	5,40	4	0-4	506	506
6,20	5,19	5	0-5	506	505
6,40	4,98	6	0-6	505	505
6,54	4,76	7	0-7	505	505

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,12	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,28	5,98	1	0-1	496	496
4,90	5,81	2	0-2	503	502
5,48	5,60	3	0-3	504	504
5,88	5,41	4	0-4	506	505
6,18	5,21	5	0-5	506	505
6,38	5,00	6	0-6	505	504
6,52	4,80	7	0-7	505	505

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,11	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
4,26	5,99	1	0-1	498	495
4,90	5,81	2	0-2	503	498
5,46	5,61	3	0-3	505	499
5,88	5,40	4	0-4	504	500
6,18	5,20	5	0-5	505	500
6,38	4,99	6	0-6	504	501
6,52	4,79	7	0-7	505	502

TABLE D.3.3

Addition of 8,2 g NaCl per litre sample

750 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 22°C

TDS: 1260 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,14	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,36	5,98	1	0-1	727	735
7,34	5,81	2	0-2	753	751
8,16	5,59	3	0-3	748	746
8,76	5,40	4	0-4	751	749
9,20	5,20	5	0-5	752	750
9,48	5,01	6	0-6	752	750
9,68	4,81	7	0-7	751	750

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,14	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,38	5,99	1	0-1	745	743
7,34	5,80	2	0-2	748	743
8,16	5,60	3	0-3	751	749
8,76	5,40	4	0-4	751	749
9,22	5,19	5	0-5	752	750
9,48	5,01	6	0-6	752	750
9,66	4,80	7	0-7	749	748

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,15	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,36	5,99	1	0-1	742	740
7,34	5,80	2	0-2	748	746
8,16	5,60	3	0-3	751	748
8,76	5,40	4	0-4	751	749
9,20	5,20	5	0-5	752	750
9,48	5,01	6	0-6	752	749
9,68	4,81	7	0-7	751	749

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,16	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,36	5,99	1	0-1	742	740
7,34	5,80	2	0-2	748	746
8,16	5,59	3	0-3	747	745
8,76	5,39	4	0-4	749	746
9,20	5,19	5	0-5	750	748
9,48	5,00	6	0-6	751	748
9,68	4,79	7	0-7	750	748

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,16	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,36	5,99	1	0-1	742	740
7,34	5,79	2	0-2	744	741
8,16	5,59	3	0-3	747	745
8,76	5,39	4	0-4	749	746
9,20	5,19	5	0-5	750	748
9,48	5,00	6	0-6	751	748
9,68	4,79	7	0-7	750	748

TABLE D.3.4

Addition of 7,8 g NaCl per litre sample

1000 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 9480 mg/l

Individual data and results

TEST No 1

V_x	pH_x	No	pH pair	$H_2CO_3^*$alk	C_T
0 ml	8,14	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
8,42	6,00	1	0-1	992	989
9,80	5,80	2	0-2	999	997
10,94	5,59	3	0-3	1002	1000
11,74	5,39	4	0-4	1003	1001
12,32	5,19	5	0-5	1005	1003
12,70	4,99	6	0-6	1005	1002
12,96	4,79	7	0-7	1005	1002

TEST No 2

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,14	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
8,42	6,00	1	0-1	992	989
9,80	5,80	2	0-2	999	997
10,94	5,59	3	0-3	1002	1000
11,74	5,39	4	0-4	1003	1001
12,32	5,19	5	0-5	1005	1003
12,70	4,99	6	0-6	1005	1002
12,96	4,80	7	0-7	1006	1003

TEST No 3

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,15	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
8,42	6,00	1	0-1	991	988
9,80	5,80	2	0-2	999	996
10,94	5,59	3	0-3	1002	999
11,74	5,39	4	0-4	1003	1000
12,32	5,18	5	0-5	1003	1000
12,70	4,99	6	0-6	1005	1002
12,96	4,79	7	0-7	1005	1002

TEST No 4

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,16	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
8,42	6,00	1	0-1	991	987
9,80	5,80	2	0-2	999	995
10,94	5,59	3	0-3	1002	999
11,74	5,39	4	0-4	1003	1000
12,32	5,19	5	0-5	1005	1001
12,70	4,99	6	0-6	1005	1001
12,96	4,79	7	0-7	1005	1001

TEST No 5

V_x	pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
0 ml	8,16	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
8,42	6,00	1	0-1	991	987
9,80	5,80	2	0-2	999	995
10,94	5,59	3	0-3	1002	999
11,74	5,41	4	0-4	1009	1006
12,32	5,20	5	0-5	1007	1003
12,70	4,99	6	0-6	1003	1001
12,96	4,79	7	0-7	1006	1002

Table D.4

Averaged results

$NaHCO_3$ solutions with addition of NaCl

250 mg/l as CaCO^3

pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	249	249
5,80	2	0-2	251	251
5,60	3	0-3	252	252
5,40	4	0-4	252	252
5,20	5	0-5	253	253
5,00	6	0-6	253	253
4,80	7	0-7	253	253

500 mg/l as CaCO^3

pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	503	503
5,80	2	0-2	506	505
5,60	3	0-3	507	506
5,40	4	0-4	507	507
5,20	5	0-5	507	506
5,00	6	0-6	505	505
4,80	7	0-7	505	505

750 mg/l as CaCO^3

pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	740	740
5,80	2	0-2	748	746
5,60	3	0-3	749	747
5,40	4	0-4	750	748
5,20	5	0-5	751	749
5,00	6	0-6	752	749
4,80	7	0-7	750	749

1000 mg/l as CaCO^3

pH_x	No	pH pair	$H_2CO_3^*$ alk	C_T
8,40	0		mg/l as $CaCO_3$	mg/l as $CaCO_3$
6,00	1	0-1	991	988
5,80	2	0-2	999	996
5,60	3	0-3	1002	999
5,40	4	0-4	1004	1002
5,20	5	0-5	1005	1002
5,00	6	0-6	1005	1002
4,80	7	0-7	1005	1002

APPENDIX E

INVESTIGATION INTO THE EFFECT OF SELECTING pH DATA PAIRS SYMMETRICAL WITH RESPECT TO pK_{ac1}

EXPERIMENTAL DATA AND RESULTS

The effect of selecting pH pairs symmetrically around pK_{ac1} on C_T and H_2CO_3*alkalinity was investigated for $NaHCO_3$ solutions of 50, 100, 150, 200, 250 and 500 mg/ℓ as CaO_3. The individual data and calculated results (C_T and H_2CO_3*alkalinity) are listed in tables designated Table E, together with the respective averaged results. (Calculation procedure set out in Chapter 3).

TABLE E.1.1

Symmetrical pH pair titrations

50 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 40 ml

Sample size [diluted]: 40 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 84 mg/l

TEST No 1

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,90	0	0-5	50	51
0,04	7,44	1	1-4	49	51
0,16	6,81	2	2-3	48	49
0,44	5,76	3	Individual data and results		
0,50	5,28	4			
0,54	4,61	5			

TEST No 2

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,91	0	0-5	51	50
0,04	7,45	1	1-4	50	51
0,16	6,80	2	2-3	49	52
0,42	5,87	3	Individual data and results		
0,50	5,34	4			
0,54	4,67	5			

TEST No 3

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,85	0	0-5	50	52
0,04	7,39	1	1-4	50	51
0,16	6,76	2	2-3	49	50
0,42	5,84	3	Individual data and results		
0,48	5,46	4			
0,54	4,59	5			

TEST No 4

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,88	0	0-5	50	52
0,04	7,39	1	1-4	50	51
0,16	6,78	2	2-3	48	50
0,42	5,85	3	Individual data and results		
0,48	5,46	4			
0,54	4,62	5			

TEST No 5

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,88	0	0-5	50	52
0,04	7,39	1	1-4	50	51
0,16	6,78	2	2-3	48	50
0,42	5,85	3	Individual data and results		
0,48	5,47	4			
0,54	4,64	5			

TABLE E.1.2

Symmetrical pH pair titrations

100 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 45 ml

Sample size [diluted]: 45 ml

Normality of strong acid: 0,075 mol/l

Temperature: 20°C

TDS: 168 mg/l

TEST No 1

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,12	0	0-5	101	102
0,12	7,37	1	1-4	100	101
0,36	6,81	2	2-3	98	99
0,98	5,81	3	Individual data and results		
1,10	5,43	4			
1,20	4,65	5			

TEST No 2

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,10	0	0-5	100	101
0,12	7,36	1	1-4	99	100
0,36	6,80	2	2-3	97	98
0,98	5,78	3	Individual data and results		
1,10	5,39	4			
1,20	4,59	5			

TEST No 3

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,10	0	0-5	100	101
0,12	7,36	1	1-4	100	101
0,36	6,80	2	2-3	97	98
0,96	5,82	3	Individual data and results		
1,10	5,41	4			
1,20	4,58	5			

TEST No 4

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,10	0	0-5	100	101
0,12	7,36	1	1-4	99	100
0,36	6,79	2	2-3	98	99
0,96	5,82	3	Individual data and results		
1,10	5,40	4			
1,20	4,57	5			

TEST No 5

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,12	0	0-5	100	101
0,12	7,35	1	0-2	100	101
0,36	6,80	2	0-3	97	98
0,96	5,82	3	Individual data and results		
1,10	5,41	4			
1,18	4,83	5			

TABLE E.1.3

Symmetrical pH pair titrations

150 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 60 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,075 mol/l

Temperature: 20°C

TDS: 252 mg/l

TEST No 1

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,27	0	0-5	149	149
0,26	7,32	1	1-4	149	149
0,68	6,83	2	2-3	146	147
1,90	5,83	3	Individual data and results		
2,18	5,40	4			
2,36	4,62	5			

TEST No 2

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,30	0	0-5	149	149
0,24	7,35	1	1-4	149	149
0,68	6,81	2	2-3	147	147
1,90	5,81	3	Individual data and results		
2,18	5,38	4			
2,34	4,78	5			

TEST No 3

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,29	0	0-5	150	150
0,26	7,32	1	1-4	149	149
0,68	6,81	2	2-3	147	147
1.90	5,81	3	Individual data and results		
2,18	5,39	4			
2,34	4,82	5			

TEST No 4

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,27	0	0-5	149	149
0,24	7,34	1	1-4	149	149
0,68	6,80	2	2-3	147	147
1,90	5,80	3	Individual data and results		
2,16	5,41	4			
2,34	4,78	5			

TEST No 5

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,30	0	0-5	149	149
0,24	7,35	1	0-2	149	149
0,68	6,80	2	0-3	147	147
1,90	5,82	3	Individual data and results		
2,16	5,42	4			
2,34	4,78	5			

TABLE E.1.4

Symmetrical pH pair titrations

200 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 20°C

TDS: 336 mg/l

TEST No 1

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,39	0	0-5	199	198
0,28	7,34	1	1-4	199	198
0,78	6,81	2	2-3	193	192
2,14	5,78	3	Individual data and results		
2,42	5,39	4			
2,60	4,78	5			

TEST No 2

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,39	0	0-5	199	198
0,26	7,37	1	1-4	200	199
0,78	6,80	2	2-3	193	192
2,12	5,79	3	Individual data and results		
2,42	5,39	4			
2,60	4,76	5			

TEST No 3

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,40	0	0-5	200	199
0,26	7,39	1	1-4	200	198
0,78	6,80	2	2-3	195	193
2,14	5,78	3	Individual data and results		
2,42	5,40	4			
2,60	4,81	5			

TEST No 4

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,47	0	0-5	200	198
0,26	7,40	1	1-4	199	197
0,76	6,81	2	2-3	195	197
2,12	5,80	3	Individual data and results		
2,42	5,38	4			
2,60	4,81	5			

TEST No 5

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,47	0	0-5	200	198
0,26	7,40	1	0-2	199	196
0,76	6,80	2	0-3	197	195
2,12	5,79	3	Individual data and results		
2,40	5,41	4			
2,60	4,79	5			

TABLE E.1.5

Symmetrical pH pair titrations

250 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 420 mg/l

TEST No 1

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,44	0	0-5	251	250
0,40	7,28	1	1-4	251	249
0,98	6,79	2	2-3	249	249
2,66	5,81	3	Individual data and results		
3,06	5,37	4			
3,30	4,70	5			

TEST No 2

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,44	0	0-5	252	250
0,34	7,37	1	1-4	252	250
0,98	6,81	2	2-3	245	243
2,68	5,80	3	Individual data and results		
3,06	5,39	4			
3,28	4,81	5			

TEST No 3

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,44	0	0-5	253	250
0,34	7,37	1	1-4	252	249
0,98	6,80	2	2-3	245	242
2,66	5,80	3	Individual data and results		
3,06	5,38	4			
3,30	4,73	5			

TEST No 4

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,44	0	0-5	252	250
0,34	7,37	1	1-4	251	249
0,96	6,81	2	2-3	244	242
2,64	5,81	3	Individual data and results		
3,04	5,40	4			
3,28	4,79	5			

TEST No 5

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,44	0	0-5	252	250
0,34	7,37	1	0-2	251	249
0,96	6,80	2	0-3	247	244
2,64	5,81	3	Individual data and results		
3,04	5,40	4			
3,28	4,81	5			

TABLE E.1.6

Symmetrical pH pair titrations

500 mg $H_2CO_3^*$alk/l

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,075 mol/l

Temperature: 21°C

TDS: 840 mg/l

TEST No 1

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,43	0	0-5	498	493
0,62	7,39	1	1-4	501	496
1,90	6,81	2	2-3	483	478
5,24	5,80	3	Individual data and results		
6,00	5,41	4			
6,46	4,80	5			

TEST No 2

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,43	0	0-5	502	497
0,62	7,38	1	1-4	506	501
1,88	6,80	2	2-3	490	485
5,24	5,80	3	Individual data and results		
6,04	5,41	4			
6,54	4,74	5			

TEST No 3

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,44	0	0-5	503	497
0,64	7,39	1	1-4	502	496
1,88	6,80	2	2-3	497	491
5,26	5,81	3	Individual data and results		
6,04	5,40	4			
6,54	4,75	5			

TEST No 4

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,43	0	0-5	503	498
0,62	7,39	1	1-4	503	498
1,88	6,80	2	2-3	492	488
5,26	5,80	3	Individual data and results		
6,04	5,40	4			
6,54	4,76	5			

TEST No 5

V_x ml	pH_x	No	pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	8,43	0	0-5	503	498
0,64	7,38	1	0-2	502	497
1,88	6,79	2	0-3	494	489
5,24	5,80	3	Individual data and results		
6,04	5,40	4			
6,54	4,76	5			

AVERAGED RESULTS

for individual symmetrical pH pair titrations

[see Tables E.1 to E.6]

50 $mgH_2CO_3^*alk/l$		
pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
8,3 - 4,8 [0 - 5]	50	52
7,3 - 5,3 [1 - 4]	50	51
6,8 - 5,8 [2 - 3]	49	50

100 $mgH_2CO_3^*alk/l$		
pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
8,3 - 4,8 [0 - 5]	100	101
7,3 - 5,3 [1 - 4]	100	101
6,8 - 5,8 [2 - 3]	97	98

150 $mgH_2CO_3^*alk/l$		
pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
8,3 - 4,8 [0 - 5]	149	149
7,3 - 5,3 [1 - 4]	149	149
6,8 - 5,8 [2 - 3]	147	147

200 $mgH_2CO_3^*alk/l$		
pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
8,3 - 4,8 [0 - 5]	200	198
7,3 - 5,3 [1 - 4]	199	198
6,8 - 5,8 [2 - 3]	194	193

250 $mgH_2CO_3^*alk/l$		
pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
8,3 - 4,8 [0 - 5]	252	250
7,3 - 5,3 [1 - 4]	251	249
6,8 - 5,8 [2 - 3]	246	243

500 $mgH_2CO_3^*alk/l$		
pH pair	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
8,3 - 4,8 [0 - 5]	502	497
7,3 - 5,3 [1 - 4]	503	498
6,8 - 5,8 [2 - 3]	491	486

APPENDIX F

INVESTIGATION INTO THE EFFECT OF CO_2 LOSS ON THE DETERMINATION OF C_T

EXPERIMENTAL DATA AND RESULTS

Individual data and calculated results for Na_2CO_3 solutions giving C_T values ranging from 50 to 1700 mg/ℓ as $CaCO_3$ are listed in tables designated Table F, together with the respective averaged results. (Calculation procedure set out in Chapter 3).

TABLE F.1

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 50 mg/l as $CaCO_3$

Sample size [undiluted]: 55 ml

Sample size [diluted]: 55 ml

Normality of strong acid: 0,0754 mol/l

Temperature: 22°C

TDS: 106 mg/l

TEST No 1

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	10,59	1	
0,62	8,26	1	
1,32	4,79	1	48
1,32	4,78	10	48
1,32	4,83	20	49
1,32	4,88	30	49

TEST No 2

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	10,58	1	
0,62	8,30	1	
1,34	4,60	1	49
1,34	4,57	10	49
1,34	4,58	20	49
3,18	4,61	30	49

TEST No 3

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0,62	10,68	1	
1,34	8,29	1	
1,34	4,60	1	49
1,34	4,58	10	49
1,34	4,60	20	49
1,34	4,63	30	49

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	49
10	49
20	49
30	49

TABLE F.2

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 200 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0754 mol/l

Temperature: 22°C

TDS: 424 mg/l

TEST No 1

V_X ml	pH_X	Stirring time min	C_T mg/l as $CaCO_3$
0	10,96	1	
2,58	8,81	1	
5,26	4,77	1	206
5,26	4,80	10	207
5,26	4,88	20	208
5,26	4,98	30	210

TEST No 2

V_X ml	pH_X	Stirring time min	C_T mg/l as $CaCO_3$
0	11,00	1	
2,62	8,25	1	
5,26	4,78	1	204
5,26	4,77	10	204
5,26	4,86	20	205
5,26	4,94	30	207

TEST No 3

V_X ml	pH_X	Stirring time min	C_T mg/l as $CaCO_3$
0	10,97	1	
2,60	8,27	1	
5,26	4,77	1	205
5,26	4,78	10	205
5,26	4,86	20	206
5,26	4,96	30	208

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	205
10	205
20	206
30	208

TABLE F.3

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 350 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0754 mol/l

Temperature: 22°C

TDS: 742 mg/l

TEST No 1

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,06	1	
4,56	8,30	1	
9,14	4,75	1	352
9,14	4,79	10	353
9,14	4,88	20	356
9,14	4,99	30	360

TEST No 2

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	10,99	1	
4,54	8,28	1	
9,14	4,80	1	356
9,14	4,87	10	358
9,14	4,97	20	361
9,14	5,07	30	365

TEST No 3

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	10,96	1	
4,54	8,15	1	
9,16	4,76	1	359
9,16	4,83	10	361
9,16	4,94	20	364
9,16	5,05	30	369

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	356
10	357
20	360
30	365

TABLE F.4

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 500 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0748 mol/l

Temperature: 22°C

TDS: 1060 mg/l

TEST No 1

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,08	1	
6,54	8,31	1	
13,04	4,78	1	497
13,04	4,80	10	498
13,04	4,87	20	501
13,04	4,95	30	505

TEST No 2

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,06	1	
6,54	8,20	1	
13,04	4,77	1	500
13,04	4,82	10	502
13,04	4,90	20	505
13,04	4,99	30	510

TEST No 3

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,10	1	
6,54	8,29	1	
13,04	4,74	1	496
13,04	4,76	10	497
13,04	4,84	20	500
13,04	4,93	30	504

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	498
10	499
20	502
30	506

TABLE F.5

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 650 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,1808 mol/l

Temperature: 20°C

TDS: 1378 mg/l

TEST No 1

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,05	1	
3,56	8,18	1	
7,06	4,88	1	651
7,06	4,94	10	661
7,06	5,05	20	669
7,06	5,15	30	678

TEST No 2

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,07	1	
3,84	8,23	1	
7,08	4,80	1	659
7,08	4,86	10	662
7,08	4,98	20	669
7,08	5,07	30	676

TEST No 3

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,11	1	
3,54	8,26	1	
7,08	4,82	1	659
7,08	4,86	10	661
7,08	4,97	20	667
7,08	5,06	30	674

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	658
10	661
20	658
30	676

TABLE F.6

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 800 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,1808 mol/l

Temperature: 21°C

TDS: 1696 mg/l

TEST No 1

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,13	1	
4,38	8,22	1	
8,68	4,80	1	801
8,68	4,81	10	801
8,68	4,87	20	805
8,68	4,97	30	813

TEST No 2

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,16	1	
4,38	8,29	1	
8,68	4,80	1	797
8,68	4,84	10	800
8,68	4,94	20	807
8,68	5,03	30	815

TEST No 3

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,16	1	
4,38	8,28	1	
8,68	4,81	1	798
8,68	4,85	10	801
8,68	4,93	20	807
8,68	5,03	30	816

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	799
10	801
20	806
30	814

TABLE F.7

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 950 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,1808 mol/l

Temperature: 22°C

TDS: 2014 mg/l

TEST No 1

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,10	1	
5,18	8,34	1	
10,32	4,75	1	947
10,32	4,80	10	950
10,32	4,91	20	959
10,32	5,01	30	969

TEST No 2

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,15	1	
5,18	8,35	1	
10,32	4,80	1	950
10,32	4,86	10	954
10,32	4,96	20	963
10,32	5,06	30	975

TEST No 3

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,14	1	
5,20	8,25	1	
10,32	4,73	1	947
10,32	4,79	10	951
10,32	4,90	20	960
10,32	5,00	30	970

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	948
10	952
20	961
30	971

TABLE F.8

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 1100 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,1808 mol/l

Temperature: 22°C

TDS: 2332 mg/l

TEST No 1

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,13	1	
6,02	8,28	1	
11,92	4,80	1	1094
11,92	4,82	10	1096
11,92	4,92	20	1106
11,92	5,05	30	1122

TEST No 2

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,13	1	
6,02	8,21	1	
11,92	4,82	1	1101
11,92	4,88	10	1106
11,92	4,95	20	1114
11,92	5,07	30	1130

TEST No 3

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,10	1	
6,00	8,36	1	
11,94	4,78	1	1095
11,94	4,83	10	1099
11,94	4,93	20	1109
11,94	5,02	30	1120

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	1097
10	1100
20	1110
30	1124

TABLE F.9

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 1250 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,1808 mol/l

Temperature: 22°C

TDS: 2650 mg/l

TEST No 1

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,18	1	
6,88	8,31	1	
13,62	4,79	1	1247
13,62	4,82	10	1250
13,62	4,90	20	1258
13,62	5,03	30	1276

TEST No 2

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,19	1	
6,88	8,31	1	
13,62	4,80	1	1248
13,62	4,85	10	1253
13,62	4,95	20	1265
13,62	5,06	30	1281

TEST No 3

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,18	1	
6,88	8,28	1	
13,62	4,76	1	1246
13,62	4,82	10	1252
13,62	4,91	20	1262
13,62	5,01	30	1276

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	1247
10	1252
20	1262
30	1278

TABLE F.10

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 1400 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,1808 mol/l

Temperature: 25°C

TDS: 2968 mg/l

TEST No 1

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,21	1	
7,68	8,29	1	
15,20	4,77	1	1390
15,20	4,82	10	1396
15,20	4,93	20	1410
15,20	5,05	30	1431

TEST No 2

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,21	1	
7,68	8,33	1	
15,20	4,77	1	1387
15,20	4,87	10	1398
15,20	4,98	20	1415
15,20	5,08	30	1433

TEST No 3

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,20	1	
7,68	8,34	1	
15,20	4,84	1	1394
15,20	4,93	10	1406
15,20	5,04	20	1424
15,20	5,16	30	1450

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	1390
10	1400
20	1416
30	1438

TABLE F.11

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 1550 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,1808 mol/l

Temperature: 25°C

TDS: 3286 mg/l

TEST No 1

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,18	1	
8,52	8,31	1	
16,88	4,77	1	1544
16,88	4,84	10	1552
16,88	4,95	20	1569
16,88	5,00	30	1578

TEST No 2

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,20	1	
8,54	8,30	1	
16,90	4,81	1	1549
16,90	4,88	10	1559
16,90	5,00	20	1579
16,90	5,11	30	1603

TEST No 3

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,19	1	
8,54	8,28	1	
16,88	4,81	1	1548
16,88	4,86	10	1554
16,88	4,97	20	1572
16,88	5,05	30	1588

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	1547
10	1555
20	1573
30	1590

TABLE F.12

Influence of CO_2 loss on C_T determination;

C_T of sample [Na_2CO_3 solution]: 1700 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,1808 mol/l

Temperature: 22°C

TDS: 3604 mg/l

TEST No 1

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,19	1	
9,32	8,29	1	
18,46	4,78	1	1691
18,46	4,79	10	1692
18,46	4,90	20	1708
18,46	4,98	30	1723

TEST No 2

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,18	1	
9,32	8,32	1	
18,46	4,79	1	1689
18,46	4,82	10	1693
18,46	4,90	20	1705
18,46	4,99	30	1721

TEST No 3

V_x ml	pH_x	Stirring time min	C_T mg/l as $CaCO_3$
0	11,19	1	
9,32	8,31	1	
18,46	4,79	1	1690
18,46	4,83	10	1695
18,46	4,89	20	1704
18,46	4,98	30	1720

AVERAGED RESULTS FOR C_T

Stirring time min	CT mg/l as $CaCO_3$
1	1690
10	1693
20	1706
30	1721

APPENDIX G

DETERMINATION OF C_T AND H_2CO3_3*ALKALINITY IN LOW ALKALINITY SOLUTIONS USING THE FIRST GRAN FUNCTION METHOD

EXPERIMENTAL DATA AND RESULTS

Individual data and results for H_2CO_3*alkalinity (and C_T) calculated with the aid of the complete First Gran Function method are listed for $NaHCO_3$ solutions of 10, 20, 30, 40 and 50 mg/ℓ as $CaCO_3$ in tables designated Table G, together with the respective averaged results. The calculation procedure is that given by Loewenthal et al. (1989), (see reference in Chapter 3). The H_2CO_3*alkalinity and C_T of the *same* samples are also determined using the 4 pH point titration method, see Appendix H.

TABLE G.1

Determination of $H_2CO_3^*$alk and C_T with the aid of the First Gran Function

$NaHCO_3$ solution: 10 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,00736 mol/l

Temperature: 21°C

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,24	9,7	11,0
2,80	3,75		
3,10	3,67		
3,40	3,61		
3,70	3,55		

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,29	9,7	10,9
2,80	3,75		
3,10	3,67		
3,40	3,61		
3,70	3,55		

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,28	9,7	10,9
2,80	3,75		
3,10	3,67		
3,40	3,61		
3,70	3,55		

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,27	9,8	11,0
2,80	3,75		
3,10	3,67		
3,40	3,60		
3,70	3,55		

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
9,7	11,0

TABLE G.2

Determination of $H_2CO_3^*$alk and C_T with the aid of the First Gran Function

$NaHCO_3$ solution: 20 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,00736 mol/l

Temperature: 21°C

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,07	19,4	23,3
4,10	3,81		
4,30	3,73		
4,70	3,66		
5,00	3,61		

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,20	19,4	22,3
3,80	3,93		
4,20	3,80		
4,60	3,71		
5,00	3,63		

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,15	19,7	23,0
4,00	3,79		
4,40	3,68		
4,80	3,59		
5,20	3,52		

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,14	20,1	23,5
4,00	3,81		
4,40	3,69		
4,80	3,60		
5,20	3,53		

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
19,7	**23,0**

TABLE G.3

Determination of $H_2CO_3^*$alk and C_T with the aid of the First Gran Function

$NaHCO_3$ solution: 30 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,00736 mol/l

Temperature: 21°C

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,33	29,7	33,0
5,20	3,87		
5,60	3,74		
6,00	3,65		
6,40	3,57		

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,35	29,9	33,0
5,20	3,87		
5,60	3,75		
6,00	3,65		
7,40	3,57		

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,50	30,2	33,3
5,20	3,86		
5,60	3,73		
6,00	3,64		
6,40	3,57		

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,35	29,8	32,9
5,20	3,88		
5,60	3,75		
6,00	3,65		
6,40	3,58		

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
29,9	33,1

TABLE G.4

Determination of $H_2CO_3^*$alk and C_T with the aid of the First Gran Function

$NaHCO_3$ solution: 40 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,00736 mol/l

Temperature: 21°C

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,38	40,3	44,2
6,70	3,86		
7,10	3,73		
7,50	3,64		
7,90	3,57		

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,47	40,3	43,5
6,70	3,86		
7,10	3,73		
7,50	3,64		
7,90	3,57		

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,50	40,3	43,3
6,70	3,86		
7,10	3,73		
7,50	3,64		
7,90	3,57		

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,50	40,4	43,4
6,70	3,86		
7,10	3,74		
7,50	3,65		
7,90	3,57		

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
40,3	43,6

TABLE G.5

Determination of $H_2CO_3^*$alk and C_T with the aid of the First Gran Function

$NaHCO_3$ solution: 50 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,00736 mol/l

Temperature: 21°C

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,59	50,4	53,4
8,10	3,85		
8,50	3,74		
8,90	3,65		
9,30	3,57		

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,58	50,2	53,2
8,10	3,86		
8,50	3,74		
8,90	3,65		
9,30	3,58		

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,59	50,7	53,7
8,10	3,87		
8,50	3,75		
8,90	3,66		
9,40	3,58		

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
0	7,60	50,2	53,1
8,10	3,86		
8,50	3,74		
8,90	3,65		
9,30	3,57		

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	C_T mg/l as $CaCO_3$
50,4	53,4

APPENDIX H

DETERMINATION OF C_T AND H_2CO_3*ALKALINITY IN LOW ALKALINITY SOLUTIONS USING THE 4 pH POINT TITRATION METHOD

EXPERIMENTAL DATA AND RESULTS

Individual data and calculated results [H_2CO_3*alkalinity, C_T and ΔpH (delta pH)] are listed for $NaHCO_3$ solutions of 10, 20, 30, 40 and 50 mg/ℓ as $CaCO_3$ in tables designated Table H, together with the respective averaged results. (For determination of H_2CO_3*alkalinity and C_T, using the complete First Gran Function method, on the same sample, see Appendix G).

TABLE H.1

Determination of $H_2CO_3^*$alk and C_T with the aid of the 3 pH point titration method

$NaHCO_3$ solution: 10 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,00736 mol/l

Temperature: 21°C; TDS: 17 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	7,24	10,3	+ 0,01	11,7
1,24	5,48			
1,46	4,82			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,29	10,2	- 0,05	11,5
1,24	5,50			
1,46	4,83			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,28	9,8	+ 0,20	11,7
1,24	5,49			
1,46	4,81			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,27	10,4	+ 0,04	11,5
1,24	5,47			
1,46	4,81			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
10,2	no reliable estimate	11,6

Note: C_T is too small for reliable estimate of systematic pH error

TABLE H.2

Determination of $H_2CO_3^*$ alk and C_T with the aid of the 3 pH point titration method

$NaHCO_3$ solution: 20 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,00736 mol/l

Temperature: 21°C; TDS: 34 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	7,07	20,2	- 0,06	24,8
2,30	5,63			
2,74	4,93			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,20	20,3	- 0,05	23,6
2,30	5,66			
2,74	4,97			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,15	20,3	+ 0,01	23,6
2,30	5,60			
2,74	4,90			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,14	20,2	- 0,05	23,9
2,30	5,63			
2,74	4,92			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
20,3	- 0,04	24,0

TABLE H.3

Determination of $H_2CO_3^*$alk and C_T with the aid of the 3 pH point titration method

$NaHCO_3$ solution: 30 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,00736 mol/l

Temperature: 21°C; TDS: 51 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	7,33	30,3	- 0,03	33,7
3,70	5,42			
4,10	4,85			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,35	30,4	- 0,01	33,5
3,70	5,42			
4,10	4,86			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,36	30,2	- 0,04	33,5
3,70	5,43			
4,10	4,86			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,35	30,2	- 0,07	33,8
3,70	5,45			
4,10	4,87			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
30,3	- 0,04	33,6

TABLE H.4

Determination of $H_2CO_3^*$ alk and C_T with the aid of the 3 pH point titration method

$NaHCO_3$ solution: 40 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,00736 mol/l

Temperature: 21°C; TDS: 67 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	7,38	40,5	- 0,06	44,8
5,00	5,40			
5,50	4,80			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,47	40,4	- 0,06	43,9
5,00	5,40			
5,50	4,79			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,50	40,3	- 0,06	43,6
5,00	5,40			
5,50	4,78			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,50	40,7	- 0,03	43,7
5,00	5,40			
5,50	4,81			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
40,5	- 0,05	44,0

TABLE H.5

Determination of $H_2CO_3^*$alk and C_T with the aid of the 4 pH point titration method

$NaHCO_3$ solution: 50 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,00736 mol/l

Temperature: 21°C; TDS: 84 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	7,59	50,3	- 0,05	53,5
0,50	7,25			
6,20	5,43			
6,80	4,84			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,58	50,3	- 0,07	53,7
0,50	7,25			
6,20	5,44			
6,80	4,85			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,59	50,4	- 0,06	53,6
0,50	7,26			
6,20	5,45			
6,80	4,88			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,60	50,5	- 0,06	53,6
0,50	7,25			
6,20	5,44			
6,80	4,86			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
50,4	**- 0,06**	**53,6**

APPENDIX I

DETERMINATION OF C_T AND H_2CO_3*ALKALINITY IN HIGH ALKALINITY SOLUTIONS USING THE 4 pH POINT TITRATION METHOD

EXPERIMENTAL DATA AND RESULTS

Individual data and calculated results [H_2CO_3*alkalinity, C_T and ΔpH (delta pH)] are listed for $NaHCO_3$ solutions of 100, 200, 300, 400 and 500 mg/ℓ as $CaCO_3$ in tables designated Table I, together with the respective averaged results. (Calculation procedure set out in Chapter 3).

TABLE I.1

Determination of $H_2CO_3^*$alk and C_T with the
aid of the 4 pH point titration method
$NaHCO_3$ solution: 100 mg/l as $CaCO_3$
Sample size [undiluted]: 50 ml
Sample size [diluted]: 50 ml
Normality of strong acid: 0,0728 mol/l
Temperature: 21°C; TDS: 168 mg/l
Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	8,00	98	+ 0,01	100
0,36	6,79			
1,00	5,91			
1,30	5,10			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	7,99	99	- 0,03	100
0,40	6,74			
1,00	5,93			
1,30	5,12			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,01	99	- 0,03	100
0,40	6,74			
1,00	5,93			
1,30	5,11			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,00	100	- 0,04	102
0,40	6,73			
1,00	5,93			
1,30	5,11			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,01	99	- 0,01	100
0,40	6,74			
1,00	5,93			
1,30	5,16			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
99	**- 0,02**	**100**

TABLE I.2

Determination of $H_2CO_3^*$alk and C_T with the aid of the 4 pH point titration method

$NaHCO_3$ solution: 200 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 336 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	8,12	201	- 0,03	203
0,80	6,74			
2,04	5,91			
2,60	5,19			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,19	202	- 0,04	203
0,80	6,74			
2,04	5,91			
2,60	5,16			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,18	202	- 0,04	203
0,80	6,75			
2,04	5,92			
2,60	5,19			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,19	200	- 0,03	201
0,80	6,75			
2,04	5,91			
2,60	5,16			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,21	202	- 0,05	203
0,80	6,75			
2,04	5,92			
2,60	5,17			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
201	**- 0,04**	**203**

TABLE I.3

Determination of $H_2CO_3^*$alk and C_T with the aid of the 4 pH point titration method

$NaHCO_3$ solution: 300 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 504 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	8,25	298	- 0,01	298
1,14	6,77			
3,00	5,92			
3,86	5,21			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,23	300	- 0,04	301
1,14	6,77			
3,00	5,93			
3,86	5,19			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,26	301	- 0,03	301
1,14	6,77			
3,00	5,93			
3,86	5,21			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,22	300	- 0,03	301
1,14	6,77			
3,00	5,93			
3,86	5,21			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,27	298	- 0,02	298
1,14	6,77			
3,00	5,92			
3,86	5,20			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
299	**- 0,03**	**300**

TABLE I.4

Determination of $H_2CO_3^*$alk and C_T with the aid of the 4 pH point titration method

$NaHCO_3$ solution: 400 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 672 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	8,21	401	+ 0,01	401
1,34	6,79			
3,70	5,99			
5,06	5,23			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,25	398	+ 0,03	398
1,38	6,77			
3,80	5,94			
5,10	5,17			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,22	401	+ 0,02	402
1,38	6,77			
3,80	5,95			
5,12	5,17			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,25	397	+ 0,01	397
1,40	6,79			
3,84	5,95			
5,10	5,20			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,24	393	+ 0,01	393
1,40	6,81			
3,84	5,96			
5,10	5,21			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
398	+ 0,02	398

TABLE I.5

Determination of $H_2CO_3^*$alk and C_T with the aid of the 4 pH point titration method

$NaHCO_3$ solution: 500 mg/l as $CaCO_3$

Sample size [undiluted]: 50 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 840 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	8,31	502	- 0,04	502
1,90	6,77			
5,00	5,93			
6,50	5,14			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,31	498	- 0,03	497
1,90	6,77			
5,00	5,92			
6,40	5,22			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,33	503	- 0,06	502
1,90	6,78			
5,00	5,94			
6,50	5,14			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,28	497	- 0,04	497
1,90	6,78			
5,00	5,93			
6,40	5,23			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,28	502	- 0,05	502
1,90	6,77			
5,00	5,93			
6,40	5,23			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
500	**- 0,04**	**500**

APPENDIX J

INVESTIGATION INTO THE EFFECT OF INORGANIC NITROGEN ON THE DETERMINATION OF C_T USING DIFFERENT pH PAIRS

EXPERIMENTAL DATA AND RESULTS

Individual data and calculated results [H_2CO_3*alkalinity, C_T, ΔpH (delta pH), C_T corrected, C_T uncorrected, delta C_{T1} and delta C_{T2}] for $NaHCO_3$ solutions (2985 mg/ℓ as $CaCO_3$) augmented with NH_4Cl to give 0, 100, 200, 300, 400 and 500 mgN/ℓ are listed in tables designated Table J.1, together with their respective averaged results. The respective C_T values were determined with the 4 pH point titration (4 ppt) method. For the investigation into pH pair (8,0; 4,8) the symmetrical pH pair was (8,0; 4,8) and the unsymmetrical pH pair was (8,0; 5,4). For the investigation into pH pair (7,4; 5,4) the symmetrical pH pair was (7,4; 5,4) and the unsymmetrical pH pair was (7,4; 4,8). (Calculation procedure set out in Chapter 4; note that the unsymmetrical pH pair was required to facilitate the 4 pH point titration calculations with the computer program).

TABLE J.1

Influence of NH_4Cl addition on the determination of C_T with pH pairs [8,0;4,8] and [7,4; 5,4]

$NaHCO_3$: 2985 mg/l as $CaCO_3$; NH_4Cl: 0 mg/l as N

Sample size [undiluted]: 5 ml

Sample size [diluted]: 55 ml

Normality of strong acid: 0,0668 mol/l

Temperature: 20°C; TDS: 5015 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	8,26	2984	- 0,03	2992
0,40	7,37			
4,10	5,34			
4,40	4,74			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,27	3005	- 0,05	3015
0,40	7,38			
4,12	5,36			
4,40	4,83			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,34	2974	- 0,04	2972
0,40	7,39			
4,10	5,33			
4,40	4,68			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,25	2993	- 0,03	3006
0,40	7,38			
4,10	5,37			
4,40	4,80			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,30	3004	- 0,02	3006
0,40	7,38			
4,10	5,37			
4,40	4,84			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
2992	- 0,03	2998

TABLE J.2

Influence of NH_4Cl addition on the determination of C_T with pH pairs [8,0;4,8] and [7,4; 5,4]

$NaHCO_3$: 2985 mg/l as $CaCO_3$; NH_4Cl: 100 mgN/l;

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0668 mol/l

Temperature: 20°C; TDS: 5400 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,13	0			
0,38	7,38	1	0 - 3	3028	3012
4,10	5,36	2	1 - 2	3015	3011
4,40	4,78	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,15	0			
0,38	7,40	1	0 - 3	3040	3022
4,10	5,37	2	1 - 2	3008	3004
4,40	4,85	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,14	0			
0,38	7,39	1	0 - 3	3043	3027
4,10	5,38	2	1 - 2	3022	3017
4,40	4,86	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
8,4 - 4,8	**3020**	**3037**	**22**	**39**
7,3 - 5,3	**3011**	**3015**	**13**	**17**

Note: delta C_{T1} = C_T corrected - [average C_T without NH_4Cl addition];

delta C_{t2} = C_T uncorrected - [average C_T without NH_4Cl addition];

Average C_T without NH_4Cl addition = 2998 mg/l as $CaCO_3$; see Table J.1

TABLE J.3

Influence of NH_4Cl addition on the determination of C_T with pH pairs [8,0;4,8] and [7,4; 5,4]

$NaHCO_3$: 2985 mg/l as $CaCO_3$; NH_4Cl: 200 mgN/l;

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0668 mol/l

Temperature: 20°C; TDS: 5790 mg/l

Individual and averaged data and results

TEST No 1

V_X ml	pH_X	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,07	0			
0,36	7,40	1	0 - 3	3048	3017
4,06	5,41	2	1 - 2	3021	3013
4,36	4,94	3			

TEST No 2

V_X ml	pH_X	No	pH pair	$C_T$uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,08	0			
0,36	7,41	1	0 - 3	3063	3031
4,06	5,44	2	1 - 2	3037	3028
4,36	5,00	3			

TEST No 3

V_X ml	pH_X	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,08	0			
0,36	7,40	1	0 - 3	3044	3007
4,06	5,40	2	1 - 2	3014	3006
4,36	4,92	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
8,4 - 4,8	3018	3052	20	54
7,3 - 5,3	3016	3024	18	26

Note: delta C_{T1} = C_T corrected - [average C_T without NH_4Cl addition];

delta C_{t2} = C_T uncorrected - [average C_T without NH_4Cl addition];

Average C_T without NH_4Cl addition = 2998 mg/l as $CaCO_3$; see Table J.1

TABLE J.4

Influence of NH_4Cl addition on the determination of C_T with pH pairs [8,0;4,8] and [7,4; 5,4]

$NaHCO_3$: 2985 mg/l as $CaCO_3$; NH_4Cl: 300 mgN/l;

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0668 mol/l

Temperature: 20°C; TDS: 6170 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,06	0			
0,40	7,40	1	0 - 3	3060	3012
4,06	5,43	2	1 - 2	3003	2990
4,40	4,86	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,08	0			
0,40	7,42	1	0 - 3	3087	3041
4,06	5,50	2	1 - 2	3042	3029
4,42	4,94	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,05	0			
0,40	7,40	1	0 - 3	3055	3008
4,06	5,42	2	1 - 2	2995	2982
4,40	4,84	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
8,4 - 4,8	**3020**	**3067**	**22**	**69**
7,3 - 5,3	**3000**	**3013**	**2**	**15**

Note: delta C_{T1} = C_T corrected - [average C_T without NH_4Cl addition];

delta C_{t2} = C_T uncorrected - [average C_T without NH_4Cl addition];

Average C_T without NH_4Cl addition = 2998 mg/l as $CaCO_3$; see Table J.1

TABLE J.5

Influence of NH_4Cl addition on the determination of C_T with pH pairs [8,0;4,8] and [7,4; 5,4]

$NaHCO_3$: 2985 mg/l as $CaCO_3$; NH_4Cl: 400 mgN/l;

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0668 mol/l

Temperature: 20°C; TDS: 6560 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	7,99	0			
0,40	7,38	1	0 - 3	3082	3024
4,08	5,41	2	1 - 2	3019	3002
4,42	4,84	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	7,98	0			
0,40	7,38	1	0 - 3	3086	3028
4,08	5,42	2	1 - 2	3026	3009
4,42	4,84	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	7,96	0			
0,40	7,38	1	0 - 3	3091	3039
4,08	5,42	2	1 - 2	3026	3009
4,42	4,85	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
8,4 - 4,8	**3030**	**3086**	**32**	**88**
7,3 - 5,3	**3007**	**3024**	**9**	**26**

Note: delta C_{T1} = C_T corrected - [average C_T without NH_4Cl addition];

delta C_{t2} = C_T uncorrected - [average C_T without NH_4Cl addition];

Average C_T without NH_4Cl addition = 2998 mg/l as $CaCO_3$; see Table J.1

TABLE J.6

Influence of NH_4Cl addition on the determination of C_T with pH pairs [8,0;4,8] and [7,4; 5,4]

$NaHCO_3$: 2985 mg/l as $CaCO_3$; NH_4Cl: 500 mgN/l;

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0668 mol/l

Temperature: 20°C; TDS: 6940 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	7,95	0			
0,36	7,39	1	0 - 3	3103	3039
4,06	5,41	2	1 - 2	3037	3014
4,38	4,96	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	7,92	0			
0,36	7,38	1	0 - 3	3084	3020
4,06	5,39	2	1 - 2	3025	3001
4,38	4,89	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	7,93	0			
0,36	7,38	1	0 - 3	3104	3040
4,06	5,42	2	1 - 2	3050	3026
4,38	4,97	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
8,4 - 4,8	**3033**	**3097**	**35**	**99**
7,3 - 5,3	**3014**	**3037**	**16**	**39**

Note: delta C_{T1} = C_T corrected - [average C_T without NH_4Cl addition];

delta C_{t2} = C_T uncorrected - [average C_T without NH_4Cl addition];

Average C_T without NH_4Cl addition = 2998 mg/l as $CaCO_3$; see Table J.1

APPENDIX K

INVESTIGATION INTO THE EFFECT OF INORGANIC PHOSPHATE ON THE DETERMINATION OF C_T USING DIFFERENT pH PAIRS

EXPERIMENTAL DATA AND RESULTS

Individual data and calculated results may be divided into two groups:

(1) Investigation into pH pair (7,4; 5,4): Data and calculated results [H_2CO_3*alkalinity, C_T, ΔpH (delta pH), C_T corrected, C_T uncorrected, delta C_{T1} and delta C_{T2}] obtained on $NaHCO_3$ solutions (2985 mg/ℓ as $CaCO_3$) augmented with K_2HPO_4 to give 0, 16, 33, 49, 65, 82 mgP/ℓ are listed in tables designated Table K.1, together with their respective averaged results. The respective C_T values were determined with the 4 ppt method; the symmetrical pH pair was (7,4; 5,4) and the unsymmetrical pH pair was (7,4; 4,8). (Calculation procedure set out in Chapter 4; note that the unsymmetrical pH pair was required in order to facilitate the 4 pH point titration calculations with the computer program).

(2) Investigation into pH pair (6,7; 5,9): Data and calculated results [H_2CO_3*alkalinity, C_T, ΔpH (delta pH), C_T corrected, C_T uncorrected, delta C_{T1} and delta C_{T2}] obtained on $NaHCO_3$ solutions (1990 mg/ℓ as $CaCO_3$) augmented with K_2HPO_4 to give 0, 33, 65, 98 mgP/ℓ are listed in tables designated Table K.2, together with their respective averaged results. The respective C_T values were determined with the 4 pH point titration (4 ppt) method; the symmetrical pH pair was (6,7; 5,9) and the unsymmetrical pH pair was (6,7; 5,1). (Calculation procedure set out in Chapter 4).

TABLE K.1.1

Influence of K_2HPO_4 addition on determination of C_T with pH pair [7,4; 5,4]

Base $NaHCO_3$ solution: 2985 mg/l as $CaCO_3$

Sample size [undiluted]: 5 ml

Sample size [diluted]: 55 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 20°C; TDS: 5015 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	8,31	2997	- 0,01	2995
0,36	7,38			
3,50	5,47			
3,80	5,00			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,35	2986	- 0,04	2982
0,36	7,39			
3,50	5,47			
3,80	4,96			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,34	2982	- 0,05	2981
0,36	7,39			
3,50	5,47			
3,80	4,93			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,33	2975	- 0,04	2974
0,36	7,39			
3,50	5,46			
3,80	4,93			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,28	2947	- 0,02	2951
0,36	7,38			
3,50	5,42			
3,80	4,85			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
2977	- 0,03	2977

TABLE K.1.2

Influence of K_2HPO_4 addition on determination of C_T with pH pair [7,4; 5,4]

NaHCO$_3$: 2985 mg/l as CaCO$_3$; K_2HPO_4: 16 mgP/l;

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 20°C; TDS: 5100 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as CaCO$_3$	C_T corrected mg/l as CaCO$_3$
0	8,27	0	1 - 2	3022	3002
0,36	7,39	1			
3,56	5,45	2			
3,88	4,84	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as CaCO$_3$	C_T corrected mg/l as CaCO$_3$
0	8,29	0	1 - 2	3015	2995
0,36	7,38	1			
3,56	5,43	2			
3,88	4,82	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as CaCO$_3$	C_T corrected mg/l as CaCO$_3$
0	8,29	0	1 - 2	3020	2999
0,36	7,38	1			
3,56	5,43	2			
3,88	4,86	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as CaCO$_3$	C_T uncorrected mg/l as CaCO$_3$	delta C_{T1} mg/l as CaCO$_3$	delta C_{T2} mg/l as CaCO$_3$
7,3 - 5,4	**2999**	**3019**	**22**	**42**

Note: delta C_{T1} = C_T corrected - [average C_T without K_2HPO_4 addition];

delta C_{t2} = C_T uncorrected - [average C_T without K_2HPO_4 addition];

Average C_T without K_2HPO_4 addition = 2977 mg/l as CaCO$_3$; see Table K.1.1.

TABLE K.1.3

Influence of K_2HPO_4 addition on determination of C_T with pH pair [7,4; 5,4]

$NaHCO_3$: 2985 mg/l as $CaCO_3$; K_2HPO_4: 33 mgP/l;

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 20°C; TDS: 5190 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,33	0	1 - 2	3026	2984
0,38	7,39	1			
3,60	5,43	2			
3,90	4,87	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,33	0	1 - 2	3033	2991
0,38	7,39	1			
3,60	5,44	2			
3,90	4,88	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,34	0	1 - 2	3025	2984
0,38	7,39	1			
3,60	5,43	2			
3,90	4,86	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
7,3 - 5,4	2986	3028	9	51

Note: delta C_{T1} = C_T corrected - [average C_T without K_2HPO_4 addition];

delta C_{t2} = C_T uncorrected - [average C_T without K_2HPO_4 addition];

Average C_T without K_2HPO_4 addition = 2977 mg/l as $CaCO_3$; see Table K.1.1.

TABLE K.1.4

Influence of K_2HPO_4 addition on determination of C_T with pH pair [7,4; 5,4]

$NaHCO_3$: 2985 mg/l as $CaCO_3$; K_2HPO_4: 49 mgP/l;

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 20°C; TDS: 5280 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,34	0	1 - 2	3033	2971
0,40	7,39	1			
3,62	5,44	2			
3,92	4,88	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,36	0	1 - 2	3050	2989
0,40	7,39	1			
3,68	5,39	2			
3,92	4,94	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,36	0	1 - 2	3039	2978
0,40	7,39	1			
3,62	5,45	2			
3,92	4,88	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
7,3 - 5,4	**2979**	**3041**	**2**	**64**

Note: delta C_{T1} = C_T corrected - [average C_T without K_2HPO_4 addition];

delta C_{t2} = C_T uncorrected - [average C_T without K_2HPO_4 addition];

Average C_T without K_2HPO_4 addition = 2977 mg/l as $CaCO_3$; see Table K.1.1.

TABLE K.1.5

Influence of K_2HPO_4 addition on determination of C_T with pH pair [7,4; 5,4]

$NaHCO_3$: 2985 mg/l as $CaCO_3$; K_2HPO_4: 65 mgP/l;

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 20°C; TDS: 5370 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,32	0	1 - 2	3060	2981
0,42	7,36	1			
3,62	5,47	2			
3,94	4,91	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,33	0	1 - 2	3071	2991
0,42	7,37	1			
3,62	5,49	2			
3,94	4,97	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,33	0	1 - 2	3052	2972
0,42	7,36	1			
3,62	5,46	2			
3,94	4,88	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
7,3 - 5,4	**2981**	**3061**	4	84

Note: delta C_{T1} = C_T corrected - [average C_T without K_2HPO_4 addition];

delta C_{t2} = C_T uncorrected - [average C_T without K_2HPO_4 addition];

Average C_T without K_2HPO_4 addition = 2977 mg/l as $CaCO_3$; see Table K.1.1.

TABLE K.1.6

Influence of K_2HPO_4 addition on determination of C_T with pH pair [7,4; 5,4]

$NaHCO_3$: 2985 mg/l as $CaCO_3$; K_2HPO_4: 84 mgP/l;

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 20°C; TDS: 5470 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,27	0	1 - 2	3061	2957
0,44	7,34	1			
3,70	5,38	2			
3,94	4,94	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,29	0	1 - 2	3057	2954
0,44	7,35	1			
3,62	5,48	2			
3,94	4,91	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,29	0	1 - 2	3059	2950
0,44	7,35	1			
3,64	5,46	2			
3,94	4,91	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
7,3 - 5,4	2954	3059	- 23	82

Note: delta C_{T1} = C_T corrected - [average C_T without K_2HPO_4 addition];

delta C_{t2} = C_T uncorrected - [average C_T without K_2HPO_4 addition];

Average C_T without K_2HPO_4 addition = 2977 mg/l as $CaCO_3$; see Table K.1.1.

TABLE K.2.1

Influence of K_2HPO_4 addition on determination of C_T with pH pair [6,7; 5,9]

$NaHCO_3$: 1990 mg/l as $CaCO_3$; K_2HPO_4: 0 mg/l

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 22°C; TDS: 3340 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	C_T mg/l as $CaCO_3$
0	8,30	2028	- 0,05	2028
1,60	6,74			
4,00	5,94			
5,20	5,18			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,29	2028	- 0,04	2028
1,60	6,73			
4,00	5,93			
5,20	5,16			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
0	8,29	2007	- 0,03	2006
1,60	6,74			
4,00	5,93			
5,20	5,17			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	C_T mg/l as $CaCO_3$
2021	**- 0,04**	**2021**

TABLE K.2.2

Influence of K_2HPO_4 addition on determination of C_T with pH pairs [6,7; 5,9]

$NaHCO_3$: 1990 mg/l as $CaCO_3$; K_2HPO_4: 16 mgP/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 22°C; TDS: 3430 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,31	0	1 - 2	2030	2016
1,70	6,72	1			
4,20	5,88	2			
5,30	5,13	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,30	0	1 - 2	2030	2016
1,70	6,72	1			
4,20	5,88	2			
5,30	5,13	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,32	0	1 - 2	2030	2016
1,70	6,72	1			
4,20	5,88	2			
5,30	5,13	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
6,7 - 5,9	**2016**	**2030**	**- 5**	**9**

Note: delta C_{T1} = C_T corrected - [average C_T without K_2HPO_4 addition];

delta C_{t2} = C_T uncorrected - [average C_T without K_2HPO_4 addition];

Average C_T without K_2HPO_4 addition = 2021 mg/l as $CaCO_3$; see Table K.2.1.

TABLE K.2.3

Influence of K_2HPO_4 addition on determination of C_T with pH pair [6,7; 5,9]

$NaHCO_3$: 1990 mg/l as $CaCO_3$; K_2HPO_4: 33 mgP/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 22°C; TDS: 3520 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,33	0	1 - 2	2038	2006
1,74	6,73	1			
4,20	5,91	2			
5,40	5,09	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,32	0	1 - 2	2038	2006
1,74	6,73	1			
4,20	5,91	2			
5,40	5,09	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,33	0	1 - 2	2060	2031
1,74	6,72	1			
4,20	5,91	2			
5,40	5,09	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
6,7 - 5,9	**2014**	**2045**	**- 7**	**24**

Note: delta C_{T1} = C_T corrected - [average C_T without K_2HPO_4 addition];

delta C_{t2} = C_T uncorrected - [average C_T without K_2HPO_4 addition];

Average C_T without K_2HPO_4 addition = 2021 mg/l as $CaCO_3$; see Table K.2.1.

TABLE K.2.4

Influence of K_2HPO_4 addition on determination of C_T with pH pair [6,7; 5,9]

$NaHCO_3$: 1990 mg/l as $CaCO_3$; K_2HPO_4: 65 mgP/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 22°C; TDS: 3700 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,34	0	1 - 2	2071	2010
1,80	6,73	1			
4,30	5,91	2			
5,50	5,11	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,35	0	1 - 2	2069	2008
1,80	6,73	1			
4,30	5,91	2			
5,50	5,14	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,34	0	1 - 2	2069	2008
1,80	6,74	1			
4,30	5,92	2			
5,50	5,14	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
6,7 - 5,9	**2009**	**2070**	**- 12**	**49**

Note: delta C_{T1} = C_T corrected - [average C_T without K_2HPO_4 addition];

delta C_{t2} = C_T uncorrected - [average C_T without K_2HPO_4 addition];

Average C_T without K_2HPO_4 addition = 2021 mg/l as $CaCO_3$; see Table K.2.1.

TABLE K.2.5

Influence of K_2HPO_4 addition on determination of C_T with pH pair [6,7; 5,9]

$NaHCO_3$: 1990 mg/l as $CaCO_3$; K_2HPO_4: 98 mgP/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 22°C; TDS: 3880 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,37	0	1 - 2	2123	2030
1,90	6,73	1			
4,30	5,97	2			
5,60	5,19	3			

TEST No 2

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,36	0	1 - 2	2115	2022
1,90	6,73	1			
4,40	5,93	2			
5,60	5,19	3			

TEST No 3

V_x ml	pH_x	No	pH pair	C_T uncorrected mg/l as $CaCO_3$	C_T corrected mg/l as $CaCO_3$
0	8,37	0	1 - 2	2089	1996
1,90	6,73	1			
4,40	5,92	2			
5,60	5,20	3			

AVERAGED RESULTS

pH pair	C_T corrected mg/l as $CaCO_3$	C_T uncorrected mg/l as $CaCO_3$	delta C_{T1} mg/l as $CaCO_3$	delta C_{T2} mg/l as $CaCO_3$
6,7 - 5,9	**2016**	**2109**	**- 5**	**88**

Note: delta C_{T1} = C_T corrected - [average C_T without K_2HPO_4 addition];

delta C_{t2} = C_T uncorrected - [average C_T without K_2HPO_4 addition];

Average C_T without K_2HPO_4 addition = 2021 mg/l as $CaCO_3$; see Table K.2.1.

APPENDIX L:

DETERMINATION OF H_2CO_3*ALKALINITY AND SCFA OF MADE UP AQUEOUS SOLUTIONS ($NaHCO_3$ AND ACETIC ACID) USING THE 3 pH POINT TITRATION METHOD

EXPERIMENTAL DATA AND RESULTS

Individual data and calculated results [H_2CO_3*alkalinity and SCFA (A_T)] are listed in tables designated as Table L.1 to Table L.7, for different sets of $NaHCO_3$ solutions (2985 mg/ℓ as $CaCO_3$) containing additions of HAc to give 0, 100, 200, 300, 400, 500 and 600 mg/ℓ as HAc. (Calculation procedure set out in Chapter 6).

TABLE L.1

3 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 0 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 105 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS

$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA [A_T] mg/l as HAc
3038	**- 41**

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	8,44	3034	- 45
3,50	5,48		
4,10	3,94		

Test 2

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	8,36	3025	- 28
3,50	5,47		
4,10	3,95		

Test 3

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	8,38	3054	- 50
3,50	5,50		
4,10	3,99		

TABLE L.2

3 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 100 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 110 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS

$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA [A_T] mg/l as HAc
2949	**73**

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	8,06	2953	82
3,50	5,39		
4,30	3,66		

Test 2

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,91	2942	68
3,30	5,57		
4,10	3,92		

Test 3

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,90	2952	68
3,30	5,58		
4,10	3,95		

TABLE L.3

3 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 200 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 110 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS

$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA [A_T] mg/l as HAc
2883	**161**

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,67	mg/l as $CaCO_3$	mg/l as $CaCO_3$
3,30	5,53		
4,30	3,68	2899	169

Test 2

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,63	mg/l as $CaCO_3$	mg/l as $CaCO_3$
3,20	5,59		
4,30	3,64	2875	166

Test 3

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,62	mg/l as $CaCO_3$	mg/l as $CaCO_3$
3,30	5,50		
4,10	3,90	2876	148

TABLE L.4

3 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 300 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 110 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS

$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA [A_T] mg/l as HAc
2784	**256**

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,45	mg/l as $CaCO_3$	mg/l as $CaCO_3$
3,10	5,58		
4,30	3,60	2777	257

Test 2

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,48	mg/l as $CaCO_3$	mg/l as $CaCO_3$
3,10	5,59		
4,10	3,87	2786	255

Test 3

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,43	mg/l as $CaCO_3$	mg/l as $CaCO_3$
3,10	5,59		
4,10	3,88	2790	255

TABLE L.5

3 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 400 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 110 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS	
$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA $[A_T]$ mg/l as HAc
2699	357

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,33		
3,10	5,51		
4,30	3,60	2703	352

Test 2

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,34		
3,10	5,51		
4,10	3,85	2701	357

Test 3

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,31		
3,10	5,50		
4,10	3,84	2694	361

TABLE L.6

3 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 500 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 110 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS	
$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA $[A_T]$ mg/l as HAc
2611	462

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,22		
3,10	5,42		
4,30	3,59	2614	457

Test 2

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,23		
3,10	5,42		
4,10	3,82	2613	456

Test 3

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,19		
3,10	5,41		
4,10	3,83	2606	474

TABLE L.7

3 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 600 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 110 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS

$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA [A_T] mg/l as HAc
2547	555

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,14		
3,10	5,36		
4,30	3,60	2557	543

Test 2

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,14		
3,10	5,34		
4,10	3,82	2537	561

Test 3

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,12		
3,10	5,35		
4,10	3,84	2547	562

APPENDIX M

DETERMINATION OF H_2CO_3*ALKALINITY AND SCFA OF MADE UP AQUEOUS SOLUTIONS ($NaHCO_3$ AND ACETIC ACID) USING THE 4 pH POINT TITRATION METHOD

EXPERIMENTAL DATA AND RESULTS

Individual data and calculated results [H_2CO_3*alkalinity and SCFA (A_T)] are listed in tables designated as Table M.1 to Table M.7, for different sets of $NaHCO_3$ solutions (2985 mg/ℓ as $CaCO_3$) containing additions of HAc to give 0, 100, 200, 300, 400, 500 and 600 mg/ℓ as HAc. (Calculation procedure set out in Chapter 6).

TABLE M.1

4 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 0 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 55 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS

$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA [A_T] mg/l as HAc
2974	**- 44**

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	8,39		
0,50	7,24	2988	- 57
3,40	5,56		
4,00	3,95		

Test 2

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	8,28		
0,50	7,21	2962	- 30
3,40	5,53		
4,00	3,90		

Test 3

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	8,36		
0,40	7,35	2971	- 45
3,54	5,39		
4,00	3,89		

TABLE M.2

4 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 100 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS

$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA [A_T] mg/l as HAc
2892	**58**

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,88		
0,28	7,35	2890	63
3,44	5,39		
3,94	4,06		

Test 2

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,87		
0,28	7,34	2888	57
3,44	5,38		
4,00	3,82		

Test 3

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,88		
0,28	7,35	2899	55
3,44	5,40		
3,96	4,00		

TABLE M.3

4 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 200 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS

$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA $[A_T]$ mg/l as HAc
2812	**153**

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,59	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,59	2812	151
3,30	5,41		
3,98	3,77		

Test 2

V_x	pH_x	H_2CO_3*alk	A_T
0	7,58	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,58	2811	158
3,30	5,41		
4,06	3,62		

Test 3

V_x	pH_x	H_2CO_3*alk	A_T
0	7,59	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,59	2812	151
3,30	5,41		
3,92	3,93		

TABLE M.4

4 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 300 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS

$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA [A_T] mg/l as HAc
2741	**251**

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,45		
0	7,45	2743	257
3,24	5,40		
3,94	3,90		

Test 2

V_x	pH_x	H_2CO_3*alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,46		
0	7,46	2737	238
3,24	5,39		
3,88	4,00		

Test 3

V_x	pH_x	H_2CO_3*alk mg/l as $CaCO_3$	A_T mg/l as $CaCO_3$
0	7,46		
0	7,46	2742	258
3,24	5,40		
3,96	3,85		

TABLE M.5

4 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 400 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS

$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA [A_T] mg/l as HAc
2686	356

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,34	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,34	2695	351
3,10	5,49		
4,00	3,82		

Test 2

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,33	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,33	2686	354
3,10	5,48		
4,00	3,80		

Test 3

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,33	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,33	2678	363
3,06	5,51		
3,96	3,89		

TABLE M.6

4 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 500 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS	
$H_2CO_3^*$alk	SCFA [A_T]
mg/l as $CaCO_3$	mg/l as HAc
2584	**470**

TEST No 1			
V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,21	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,21	2584	482
2,98	5,49		
4,00	3,78		

Test 2			
V_x	pH_x	H_2CO_3*alk	A_T
0	7,21	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,21	2573	471
3,10	5,36		
4,00	3,73		

Test 3			
V_x	pH_x	H_2CO_3*alk	A_T
0	7,21	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,21	2596	458
3,24	5,23		
4,04	3,69		

TABLE M.7

4 pH point titration method

$NaHCO_3$: 2985 mg/l as $CaCO_3$; HAc: 600 mg/l

Sample size [undiluted]: 5 ml

Sample size [diluted]: 60 ml

Normality of strong acid: 0,0763 mol/l

Temperature: 21°C

TDS: 5015 mg/l

Individual and averaged data and results

AVERAGED RESULTS

$H_2CO_3^*$alk mg/l as $CaCO_3$	SCFA [A_T] mg/l as HAc
2509	560

TEST No 1

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,10	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,10	2529	552
3,00	5,41		
3,90	3,98		

Test 2

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,10	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,10	2500	563
3,00	5,38		
3,90	3,92		

Test 3

V_x	pH_x	$H_2CO_3^*$alk	A_T
0	7,11	mg/l as $CaCO_3$	mg/l as $CaCO_3$
0	7,11	2498	565
3,00	5,38		
3,90	3,92		

APPENDIX N

DETERMINATION OF H_2CO_3*ALKALINITY AND SCFA OF MADE UP AQUEOUS SOLUTIONS ($NaHCO_3$ AND ACETIC ACID) USING THE 5 pH POINT TITRATION METHOD

EXPERIMENTAL DATA RESULTS

The individual data and calculated results [H_2CO_3*alkalinity, SCFA (A_T) and ΔpH (delta pH)] may be divided into two groups:

(1) Sets of $NaHCO_3$ solutions (1990 mg/ℓ as $CaCO_3$) containing additions of HAc (A_T) to give 0, 100, 200, 300, 400 and 500 mg/ℓ as HAc. The individual data and calculated results are listed in tables designated as Table N.1 to Table N.6.

(2) Sets of $NaHCO_3$ solutions (2488 mg/ℓ as $CaCO_3$) containing additions of HAc (A_T) to give 600, 700, 800, 900 and 1000 mg/ℓ as HAc. The individual data and calculated results are listed in tables designated as Table N.7 to Table N.11. (Calculation procedure set out in Chapter 6).

TABLE N.1

5 pH point titration method

$NaHCO_3$: 1990 mg/l as $CaCO_3$; Hac: 0 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 22°C; TDS: 3340 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
0	8,30	2029	- 0,05	- 2
1,60	6,74			
4,00	5,94			
5,20	5,18			
5,54	4,28			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	8,29	2028	- 0,04	- 1
1,60	6,73			
4,00	5,93			
5,20	5,16			
5,54	4,24			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	8,29	2007	- 0,03	- 4
1,60	6,74			
4,00	5,93			
5,20	5,17			
5,54	4,27			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
2021	**- 0,04**	**- 2**

TABLE N.2

5 pH point titration method

$NaHCO_3$: 1990 mg/l as $CaCO_3$; Hac: 100 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 3340 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
0	7,67	1948	- 0,03	97
1,34	6,74			
3,76	5,94			
5,04	5,16			
5,50	4,21			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,66	1930	- 0,03	102
1,40	6,72			
3,80	5,92			
5,04	5,15			
5,46	4,32			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,67	1937	- 0,01	82
1,40	6,72			
3,80	5,92			
5,04	5,18			
5,46	4,37			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	8,00	1929	- 0,05	112
1,40	6,73			
3,80	5,93			
5,04	5,15			
5,46	4,32			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,66	1935	- 0,01	95
1,40	6,71			
3,80	5,91			
5,04	5,15			
5,46	4,33			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
1936	**- 0,03**	**98**

TABLE N.3

5 pH point titration method

$NaHCO_3$: 1990 mg/l as $CaCO_3$; Hac: 200 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 3340 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
0	7,36	1844	- 0,03	199
1,06	6,76			
3,50	5,95			
4,84	5,18			
5,40	4,29			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,36	1841	- 0,05	212
1,10	6,75			
3,10	5,92			
4,84	5,18			
5,40	4,30			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,37	1860	- 0,03	198
1,20	6,70			
3,60	5,91			
4,90	5,12			
5,40	4,30			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,36	1852	- 0,04	211
1,20	6,70			
3,60	5,91			
4,90	5,11			
5,40	4,30			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,36	1844	- 0,03	208
1,16	6,72			
3,60	5,91			
4,90	5,11			
5,40	4,30			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
1848	**- 0,04**	**206**

TABLE N.4

5 pH point titration method

$NaHCO_3$: 1990 mg/l as $CaCO_3$; Hac: 300 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 3340 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
0	7,16	1758	- 0,04	300
0,80	6,77			
3,40	5,91			
4,70	5,15			
5,36	4,24			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,15	1766	+ 0,01	283
0.90	6,72			
3,40	5,89			
4,70	5,14			
5,34	4,27			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,14	1758	- 0,03	297
0,90	6,72			
3,40	5,90			
4,70	5,14			
5,30	4,34			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,17	1766	- 0,01	285
0,90	6,73			
3,40	5,90			
4,70	5,15			
5,30	4,35			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,16	1749	- 0,03	296
0,90	6,74			
3,40	5,91			
4,70	5,16			
5,30	4,37			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
1759	**- 0,02**	**292**

TABLE N.5

5 pH point titration method

$NaHCO_3$: 1990 mg/l as $CaCO_3$; Hac: 400 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 3340 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
0	7,02	1663	- 0,02	397
0,60	6,76			
3,10	5,93			
4,50	5,17			
5,26	4,30			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,03	1678	- 0,03	401
0,60	6,76			
3,28	5,87			
4,50	5,18			
5,26	4,32			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,01	1656	- 0,02	397
0,60	6,76			
3,10	5,93			
4,50	5,17			
5,26	4,30			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,02	1671	- 0,01	387
0,64	6,75			
3,14	5,92			
4,50	5,18			
5,26	4,31			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,02	1662	- 0,02	398
0,64	6,75			
3,14	5,92			
4,50	5,18			
5,26	4,32			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
1666	**- 0,02**	**396**

TABLE N.6

5 pH point titration method

$NaHCO_3$: 1990 mg/l as $CaCO_3$; Hac: 500 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 3340 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
0	6,93	1581	- 0,08	492
0,50	6,74			
3,00	5,93			
4,36	5,18			
5,22	4,28			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,90	1578	- 0,03	498
0,50	6,71			
3,00	5,89			
4,36	5,14			
5,20	4,28			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,90	1578	- 0,03	498
0,50	6,71			
3,00	5,89			
4,36	5,14			
5,20	4,28			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,89	1570	- 0,03	498
0,50	6,71			
3,00	5,89			
4,36	5,14			
5,20	4,28			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,90	1578	- 0,03	498
0,50	6,71			
3,00	5,89			
4,36	5,14			
5,20	4,28			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
1577	**- 0,04**	**497**

TABLE N.7

5 pH point titration method

$NaHCO_3$: 2488 mg/l as $CaCO_3$; Hac: 600 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 4180 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
0	6,92	1994	- 0,04	609
0,50	6,76			
3,60	5,95			
5,50	5,14			
6,56	4,24			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,92	2007	- 0,05	595
0,50	6,76			
3,60	5,96			
5,50	5,15			
6,54	4,26			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,92	1994	- 0,04	606
0,50	6,76			
3,60	5,95			
5,50	5,14			
6,54	4,26			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,93	2015	- 0,03	601
0,50	6,76			
3,60	5,95			
5,50	5,15			
6,54	4,28			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,93	2006	- 0,04	601
0,50	6,77			
3,60	5,96			
5,50	5,16			
6,54	4,29			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
2003	**- 0,04**	**602**

TABLE N.8

5 pH point titration method

$NaHCO_3$: 2488 mg/l as $CaCO_3$; Hac: 700 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 4180 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
0	6,83	1917	- 0,02	705
0,30	6,75			
3,40	5,94			
5,40	5,10			
6,54	4,21			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,84	1918	- 0,03	693
0,30	6,76			
3,40	5,95			
5,40	5,11			
6,50	4,25			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,84	1917	- 0,03	703
0,30	6,76			
3,40	5,95			
5,40	5,11			
6,50	4,26			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,84	1902	- 0,06	722
0,30	6,76			
3,40	5,96			
5,40	5,12			
6,50	4,28			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,84	1934	- 0,03	693
0,34	6,74			
3,40	5,95			
5,40	5,12			
6,50	4,27			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
1918	**- 0,03**	**703**

TABLE N.9

5 pH point titration method

$NaHCO_3$: 2488 mg/l as $CaCO_3$; Hac: 800 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 4180 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
0	6,76	1851	- 0,04	799
0	6,76			
3,10	5,97			
5,10	5,19			
6,44	4,26			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,77	1846	- 0,05	809
0	6,77			
3,20	5,95			
5,10	5,20			
6,44	4,28			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,77	1839	- 0,04	810
0	6,77			
3,20	5,94			
5,10	5,18			
6,44	4,25			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,77	1838	- 0,04	819
0	6,77			
3,20	5,94			
5,10	5,18			
6,44	4,26			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	6,76	1820	- 0,06	827
0	6,76			
3,20	5,94			
5,20	5,17			
6,44	4,24			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
1839	**- 0,05**	**813**

TABLE N.10

5 pH point titration method

$NaHCO_3$: 2488 mg/l as $CaCO_3$; Hac: 900 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 4180 mg/l

Individual and averaged data and results

TEST No 1

V_x	pH_x	$H_2CO_3^*$ alk	Systmatic	A_T
ml		mg/l as $CaCO_3$	pH error	mg/l as HAc
0	6,70	1749	- 0,05	919
0	6,70			
2,70	6,02			
4,94	5,17			
6,40	4,23			

TEST No 2

V_x	pH_x	$H_2CO_3^*$ alk	Systematic	A_T
ml		mg/l as $CaCO_3$	pH error	mg/l as HAc
0	6,68	1785	- 0,03	890
0	6,68			
2,90	5,96			
4,94	5,19			
6,36	4,29			

TEST No 3

V_x	pH_x	$H_2CO_3^*$ alk	Systematic	A_T
ml		mg/l as $CaCO_3$	pH error	mg/l as HAc
0	6,68	1763	- 0,06	907
0	6,68			
3,00	5,94			
4,94	5,19			
6,36	4,29			

TEST No 4

V_x	pH_x	$H_2CO_3^*$ alk	Systematic	A_T
ml		mg/l as $CaCO_3$	pH error	mg/l as HAc
0	6,70	1779	- 0,02	888
0	6,70			
2,90	5,96			
4,94	5,18			
6,36	4,27			

TEST No 5

V_x	pH_x	$H_2CO_3^*$ alk	Systematic	A_T
ml		mg/l as $CaCO_3$	pH error	mg/l as HAc
0	6,70	1769	- 0,04	914
0	6,70			
3,00	5,94			
4,94	5,19			
6,36	4,30			

AVERAGED RESULTS

$H_2CO_3^*$ alk	Systematic	A_T
mg/l as $CaCO_3$	pH error	mg/l as HAc
1769	**- 0,04**	**904**

TABLE N.11

5 pH point titration method

NaHCO$_3$: 2488 mg/l as CaCO$_3$; Hac: 1000 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 4180 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as CaCO$_3$	Systmatic pH error	A_T mg/l as HAc
0	6,64	1678	- 0,05	1007
0	6,64			
2,50	6,02			
4,84	5,15			
6,30	4,28			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as CaCO$_3$	Systematic pH error	A_T mg/l as HAc
0	6,63	1692	- 0,05	983
0	6,63			
2,50	6,02			
4,84	5,16			
6,30	4,28			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as CaCO$_3$	Systematic pH error	A_T mg/l as HAc
0	6,64	1707	- 0,03	975
0	6,64			
2,50	6,02			
4,84	5,16			
6,30	4,28			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as CaCO$_3$	Systematic pH error	A_T mg/l as HAc
0	6,63	1650	- 0,08	1029
0	6,63			
2,50	6,02			
4,84	5,14			
6,30	4,27			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as CaCO$_3$	Systematic pH error	A_T mg/l as HAc
0	6,61	1678	- 0,06	1003
0	6,61			
2,50	6,01			
4,84	5,15			
6,30	4,28			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as CaCO$_3$	Systematic pH error	A_T mg/l as HAc
1681	**- 0,05**	**999**

APPENDIX O

INVESTIGATION INTO CORRECTION FOR SYSTEMATIC pH ERROR BY THE COMPUTER PROGRAM

EXPERIMENTAL DATA AND RESULTS

Individual data and calculated results [H_2CO_3*alkalinity, A_T and ΔpH (delta pH)] for the different stages of the investigation are listed in Table O.1 (stage 1), Table O.2 (stage 2) and Table O.3 (stage 3).

TABLE 0.1

STAGE 1 : ZERO CALIBRATION ERROR

pH buffer 1: 7,02; Calibration to 7,02

pH buffer 2: 4,00; Calibration to 4,00

$NaHCO_3$: 1990 mg/l as $CaCO_3$; Hac: 300 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 3340 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
	7,18	1743	- 0,06	298
0,90	6,77			
3,40	5,94			
4,70	5,18			
5,34	4,31			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,20	1754	- 0,06	298
0,90	6,77			
3,40	5,94			
4,70	5,19			
5,34	4,33			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,21	1760	- 0,06	293
0,90	6,77			
3,40	5,94			
4,70	5,18			
5,34	4,30			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,21	1754	- 0,07	308
0,90	6,77			
3,40	5,94			
4,70	5,18			
5,34	4,32			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,20	1777	- 0,09	297
0,90	6,77			
3,40	5,96			
4,70	5,21			
5,34	4,35			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
1756	**- 0,07**	**299**

TABLE 0.2

STAGE 2 : CALIBRATION ERROR: + 0,10

pH buffer 1: 7,02; Calibration to 7,12

pH buffer 2: 4,00; Calibration to 4,10

$NaHCO_3$: 1990 mg/l as $CaCO_3$; Hac: 300 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 3340 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
0	7,31	1762	- 0,18	303
1,20	6,77			
3,70	5,93			
5,00	4,97			
5,44	4,25			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,31	1766	- 0,19	313
1,20	6,76			
3,70	5,92			
4,90	5,06			
5,40	4,29			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,28	1771	- 0,19	310
1,20	6,75			
3,70	5,92			
4,84	5,14			
5,40	4,31			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,30	1746	- 0,16	308
1,20	6,76			
3,70	5,91			
4,84	5,13			
5,40	4,30			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,32	1769	- 0,18	296
1,20	6,77			
3,70	5,93			
4,84	5,15			
5,40	4,30			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
1763	**- 0,18**	**306**

TABLE 0.3

STAGE 3 : CALIBRATION ERROR: - 0,10

pH buffer 1: 7,02; Calibration to 6,92

pH buffer 2 : 4,00; Calibration to 3,90

$NaHCO_3$: 1990 mg/l as $CaCO_3$; Hac: 300 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 3340 mg/l

Individual and averaged data and results

TEST No 1

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systmatic pH error	A_T mg/l as HAc
0	7,10	1770	+ 0,06	290
0,60	6,78			
3,10	5,94			
4,60	5,16			
5,30	4,27			

TEST No 2

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,11	1765	+ 0,05	296
0,70	6,75			
3,10	5,95			
4,60	5,17			
5,30	4,29			

TEST No 3

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,11	1776	+ 0,05	291
0,70	6,75			
3,10	5,95			
4,60	5,18			
5,30	4,30			

TEST No 4

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,11	1757	+ 0,04	298
0,70	6,75			
3,10	5,95			
4,6	5,16			
5,30	4,26			

TEST No 5

V_x ml	pH_x	$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	7,11	1776	+ 0,05	291
0,70	6,75			
3,10	5,95			
4,60	5,18			
5,30	4,30			

AVERAGED RESULTS

$H_2CO_3^*$ alk mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
1769	**+ 0,05**	**293**

APPENDIX P

INVESTIGATION INTO THE EFFECT OF INORGANIC NITROGEN ON THE DETERMINATION OF C_T AND SCFA WITH THE 5 pH POINT TITRATION METHOD

EXPERIMENTAL DATA AND RESULTS

An example is presented which is based on a 5 pH point titration (5 ppt) performed on a sample containing only $NaHCO_3$ (1990 mg/ℓ as $CaCO_3$), i.e. SCFA (represented as A_T) equals zero. The effect of inorganic nitrogen on the determination of C_T (and hence H_2CO_3*alkalinity) and SCFA is demonstrated by calculating C_T and A_T for two cases:

(1) Zero inorganic nitrogen present, and,

(2) 500 mgN/ℓ present.

The titration data and calculated results [C_T, SCFA (A_T) and ΔpH (delta pH)] for both cases are listed in Table P.1. (Calculation procedure set out in Chapter 6).

TABLE P.1

INFLUENCE OF AMMONIUM SUBSYSTEM ON C_T AND A_T ESTIMATES FROM 5 pH POINT TITRATION METHOD

$NaHCO_3$: 1990 mg/l as $CaCO_3$; HAc: 0 mg/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; TDS: 3340 mg/l

Zero N				
V_X ml	pH_X	C_T mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	8,30	**2029**	**- 0,05**	**- 2**
1,60	6,74			
4,00	5,94			
5,20	5,18			
5,54	4,28			

N error: + 500 mgN/l				
V_X ml	pH_X	C_T mg/l as $CaCO_3$	Systematic pH error	A_T mg/l as HAc
0	8,30	**2019**	**- 0,04**	**- 6**
1,60	6,74			
4,00	5,94			
5,20	5,18			
5,54	4,28			

APPENDIX Q

INVESTIGATION INTO THE EFFECT OF INORGANIC PHOSPHATE ON THE DETERMINATION OF C_T AND SCFA WITH THE 5 pH POINT TITRATION METHOD

EXPERIMENTAL DATA AND RESULTS

Data and calculated results [H_2CO_3*alkalinity, A_T, C_T, ΔpH (delta pH), A_T corrected, A_T uncorrected, C_T corrected, C_T uncorrected, delta A_{T1}, delta A_{T2}, delta C_{T1} and delta C_{T2}] obtained on $NaHCO_3$ solutions (1990 mg/ℓ as $CaCO_3$) augmented with K_2HPO_4 to give 0, 33, 65, 98 mgP/ℓ are listed in tables designated Table Q.2, together with their respective averaged results. Note that the SCFA (A_T) concentrations in all these made up solutions equal zero. (Calculation procedure set out in Chapter 6).

TABLE Q.1

INFLUENCE OF K_2HPO_4 ADDITION ON ESTIMATES OF C_T AND A_T FROM 5 pH POINT TITRATION METHOD

$NaHCO_3$: 1990 mg/l as $CaCO_3$; HAc: 0 mg/l as HAc

K_2HPO_4: 0 mgP/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 22°C; TDS: 3340 mg/l

Individual and averaged data and results

TEST No 1

V_x	pH_x	A_T	C_T	$H_2CO_3^*$ alk	Systmatic
ml		mg/l	mg/l as $CaCO_3$		pH error
0	8,30	- 2	2029	2029	- 0,05
1,60	6,74				
4,00	5,94				
5,20	5,18				
5,54	4,28				

TEST No 2

V_x	pH_x	A_T	C_T	$H_2CO_3^*$ alk	Systematic
ml		mg/l	mg/l as $CaCO_3$		pH error
0	8,29	- 1	2029	2028	- 0,04
1,60	6,73				
4,00	5,93				
5,20	5,16				
5,54	4,24				

TEST No 3

V_x	pH_x	A_T	C_T	$H_2CO_3^*$ alk	Systematic
ml		mg/l	mg/l as $CaCO_3$		pH error
0	8,29	- 4	2006	2007	- 0,03
1,60	6,74				
4,00	5,93				
5,20	5,17				
5,54	4,27				

AVERAGED RESULTS

A_T	C_T	$H_2CO_3^*$ alk	Systematic
mg/l	mg/l as $CaCO_3$		pH error
- 2	2021	2021	- 0,04

TABLE Q.2

Influence of K_2HPO_4 addition on determination of C_T with 5 pH point titration method

$NaHCO_3$: 1990 mg/l as $CaCO_3$; HAc: 0 mg/l;

K_2HPO_4: 33 mgP/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 22°C; TDS: 3520 mg/l

Individual and averaged data and results

TEST No 1

V_x	pH_x	A_T corrected	A_T uncorrected	C_T corrected	C_T uncorrected
ml		mg/l		mg/l as $CaCO_3$	
0	8,33	6	7	2006	2037
1,74	6,73				
4,20	5,91				
5,40	5,09				
5,70	4,23				

TEST No 2

V_x	pH_x	A_T corrected	A_T uncorrected	C_T corrected	C_T uncorr.
ml		mg/l		mg/l as $CaCO_3$	
0	8,32	- 7	- 9	2007	2037
1,74	6,73				
4,20	5,91				
5,40	5,09				
5,74	4,01				

TEST No 3

V_x	pH_x	A_T corrected	A_T uncorrected	C_T corrected	C_T uncorr.
ml		mg/l		mg/l as $CaCO_3$	
0	8,33	0	- 2	2031	2061
1,74	6,72				
4,20	5,91				
5,40	5,09				
5,70	4,20				

AVERAGED RESULTS

A_T corrected	A_T uncorrected	C_T corrected	C_T uncorrected	delta A_{T1}	delta A_{T2}	delta C_{T1}	delta C_{T2}
mg/l		mg/l as $CaCO_3$		mg/l		mg/l as $CaCO_3$	
0	- 1	2015	2045	2	1	- 6	24

Note: delta C_{T1} = C_T corrected - (average C_T without K_2HPO_4 addition);

delta C_{t2} = C_T uncorrected - (average C_T without K_2HPO_4 addition);

Average C_T without K_2HPO_4 addition = 2021 mg/l as $CaCO_3$; see Table Q.1.

Analogueously calculate delta A_{T1} and delta A_{T2}.

TABLE Q.3

Influence of K_2HPO_4 addition on determination of C_T with 5 pH point titration method

$NaHCO_3$: 1990 mg/l as $CaCO_3$; HAc: 0 mg/l;

K_2HPO_4: 65 mgP/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 22°C; TDS: 3700 mg/l

Individual and averaged data and results

TEST No 1

V_X	pH_X	A_T corrected	A_T uncorrected	C_T corrected	C_T uncorrected
ml		mg/l		mg/l as $CaCO_3$	
0	8,34	3	3	2009	2070
1,80	6,73				
4,30	5,91				
5,50	5,11				
5,80	4,29				

TEST No 2

V_X	pH_X	A_T corrected	A_T uncorrected	C_T corrected	C_T uncorr.
ml		mg/l		mg/l as $CaCO_3$	
0	8,35	2	1	2008	2069
1,80	6,73				
4,30	5,91				
5,50	5,14				
5,84	4,22				

TEST No 3

V_X	pH_X	A_T corrected	A_T uncorrected	C_T corrected	C_T uncorr.
ml		mg/l		mg/l as $CaCO_3$	
0	8,34	6	6	2007	2068
1,80	6,74				
4,30	5,92				
5,50	5,14				
5,84	4,22				

AVERAGED RESULTS

A_T corrected	A_T uncorrected	C_T corrected	C_T uncorrected	delta A_{T1}	delta A_{T2}	delta C_{T1}	delta C_{T2}
mg/l		mg/l as $CaCO_3$		mg/l		mg/l as $CaCO_3$	
4	3	2008	2069	6	5	- 13	47

Note: delta C_{T1} = C_T corrected - {average C_T without K_2HPO_4 addition};

delta C_{t2} = C_T uncorrected - {average C_T without K_2HPO_4 addition};

Average C_T without K_2HPO_4 addition = 2021 mg/l as $CaCO_3$; see Table Q.1.

Analogueously calculate delta A_{T1} and delta A_{T2}.

TABLE Q.4

Influence of K_2HPO_4 addition on determination of C_T with 5 pH point titration method

$NaHCO_3$: 1990 mg/l as $CaCO_3$; HAc: 0 mg/l;

K_2HPO_4: 98 mgP/l;

Sample size [undiluted]: 10 ml

Sample size [diluted]: 50 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 22°C; TDS: 3880 mg/l

Individual and averaged data and results

TEST No 1

V_x	pH_x	A_T corrected	A_T uncorrected	C_T corrected	C_T uncorrected
ml		mg/l		mg/l as $CaCO_3$	
0	8,37	6	7	2029	2122
1,90	6,73				
4,30	5,97				
5,60	5,19				
6,00	4,13				

TEST No 2

V_x	pH_x	A_T corrected	A_T uncorrected	C_T corrected	C_T uncorr.
ml		mg/l		mg/l as $CaCO_3$	
0	8,36	7	4	2024	2115
1,90	6,73				
4,40	5,93				
5,60	5,19				
5,96	4,30				

TEST No 3

V_x	pH_x	A_T corrected	A_T uncorrected	C_T corrected	C_T uncorr.
ml		mg/l		mg/l as $CaCO_3$	
0	8,37	0	- 4	1996	2090
1,90	6,73				
4,40	5,92				
5,60	5,20				
5,96	4,36				

AVERAGED RESULTS

A_T corrected	A_T uncorrected	C_T corrected	C_T uncorrected	delta A_{T1}	delta A_{T2}	delta C_{T1}	delta C_{T2}
mg/l		mg/l as $CaCO_3$		mg/l		mg/l as $CaCO_3$	
4	**2**	**2016**	**2109**	**6**	**4**	**- 5**	**88**

Note: delta C_{T1} = C_T corrected - {average C_T without K_2HPO_4 addition};

delta C_{t2} = C_T uncorrected - {average C_T without K_2HPO_4 addition};

Average C_T without K_2HPO_4 addition = 2021 mg/l as $CaCO_3$; see Table Q.1.

Analogueously calculate delta A_{T1} and delta A_{T2}.

APPENDIX R

DETERMINATION OF H_2CO_3*ALKALINITY AND SCFA WITH THE 5 pH POINT TITRATION METHOD IN TREATED (IN UASB REACTOR) WINE DISTILLERY AND LAUTER TUN (BREWERY) WASTES AUGMENTED WITH ACETIC ACID

EXPERIMENTAL DATA AND RESULTS

The individual data and results [H_2CO_3*alkalinity, SCFA (A_T) and ΔpH (delta pH)] may be divided into two groups:

(1) Treated lauter tun waste samples augmented with HAc (A_T) to give HAc concentrations in the augmented sample of: HAc originally contained in the treated lauter tun waste plus 0, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mg/ℓ as HAc. These data and calculated results are listed in tables designated Table R.1.

(2) Treated wine distillery waste samples augmented with HAc (A_T) to give HAc concentrations in the augmented sample of: HAc originally contained in the treated wine distillery waste plus 0, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mg/ℓ as HAc. These data and calculated results are listed in tables designated Table R.2. (Calculation procedure set out in Chapter 6).

Table R.1.1

5 pH point titration method

Treated lauter tun effluent augmented with acetic acid: 100 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 20°C; SC: 420 mS/m

P_T: 55 mgP/l; N_T: 20 mgN/l;

0 mgHAc/l added

V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	7,83	1318	6	- 0,08
0,60	6,72			
1,40	5,95			
1,80	5,12			
1,94	4,19			
Sample size [diluted]: 55 ml				

Test 1: 100 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,52	1210	100	- 0,04
0,54	6,69			
1,30	5,93			
1,66	5,29			
1,90	4,22			
Sample size [diluted]: 60 ml				

Test 2: 100 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,50	1194	111	- 0,04
0,54	6,68			
1,30	5,91			
1,66	5,24			
1,90	4,17			
Sample size [diluted]: 60 ml				

Test 3: 100 mgHAc/l added

V_x	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,51	1208	107	- 0,06
0,54	6,69			
1,30	5,93			
1,66	5,27			
1,90	4,20			
Sample size [diluted]: 60				

Test 4: 100 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,52	1213	98	- 0,05
0,54	6,68			
1,30	5,92			
1,66	5,25			
1,90	4,15			
Sample size [diluted]: 60 ml				

Test 5: 100 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,53	1198	103	- 0,04
0,54	6,69			
1,30	5,92			
1,66	5,25			
1,90	4,16			
Sample size [diluted]: 60 ml				

AVERAGED RESULTS

Alk mg/l	SCFA mg/l	pH error
Samples with HAc add.		
1205	**104**	**- 0,05**
Sample without HAc addition		
1318	**6**	**- 0,08**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.1.2

5 pH point titration method

Treated lauter tun effluent augmented with acetic acid: 200 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 20°C; SC: 420 mS/m

P_T: 55 mgP/l; N_T: 20 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	7,58	734	4	- 0,02
0,30	6,76			
0,80	5,94			
1,02	5,29			
1,16	4,14			
Sample size [diluted]: 55 ml				

Test 1: 200 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,89	620	171	+ 0,05
0,10	6,72			
0,60	5,92			
0,90	5,12			
1,14	4,03			
Sample size [diluted]: 60 ml				

Test 2: 200 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,91	612	190	+ 0,03
0,10	6,72			
0,60	5,91			
0,86	5,24			
1,10	4,20			
Sample size [diluted]: 60 ml				

Test 3: 200 mgHAc/l added				
V_x	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,92	609	187	+ 0,01
0,10	6,73			
0,60	5,92			
0,86	5,24			
1,10	4,19			
Sample size [diluted]: 60				

Test 4: 200 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,94	619	181	+ 0,05
0,10	6,74			
0,60	5,92			
0,86	5,26			
1,10	4,20			
Sample size [diluted]: 60 ml				

Test 5: 200 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,95	611	187	+ 0,04
0,10	6,75			
0,60	5,92			
0,86	5,25			
1,10	4,20			
Sample size [diluted]: 60				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
614	**183**	**+ 0,04**
Sample without HAc addition		
734	**4**	**- 0,02**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.1.3

5 pH point titration method

Treated lauter tun effluent augmented with acetic acid: 300 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 20°C; SC: 420 mS/m

P_T: 55 mgP/l; N_T: 20 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	7,64	845	29	- 0,07
0,40	6,73			
1,00	5,84			
1,20	5,22			
1,36	4,10			
Sample size [diluted]: 55 ml				

Test 1: 300 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,84	663	276	- 0,07
0,10	6,70			
0,70	5,86			
1,00	5,12			
1,30	4,08			
Sample size [diluted]: 60 ml				

Test 2: 300 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,87	670	272	- 0,14
0,10	6,72			
0,70	5,90			
1,00	5,16			
1,26	4,25			
Sample size [diluted]: 60 ml				

Test 3: 300 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,85	651	285	- 0,10
0,10	6,71			
0,70	5,86			
0,96	5,23			
1,26	4,21			
Sample size [diluted]: 60				

Test 4: 300 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,87	656	281	- 0,08
0,10	6,72			
0,30	5,86			
0,96	5,23			
1,26	4,20			
Sample size [diluted]: 60 ml				

Test 5: 300 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,87	659	276	- 0,07
0,10	6,72			
0,70	5,86			
0,96	5,23			
1,26	4,19			
Sample size [diluted]: 60				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
660	278	- 0,09
Sample without HAc addition		
845	29	- 0,07

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.1.4

5 pH point titration method

Treated lauter tun effluent augmented with acetic acid: 400 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 20°C; SC: 420 mS/m

P_T: 55 mgP/l; N_T: 20 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	7,64	947	0	- 0,06
0,40	6,76			
1,00	5,82			
1,30	5,26			
1,46	4,09			
Sample size [diluted]: 55 ml				

Test 1: 400 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,73	668	375	- 0,08
0	6,73			
0,66	5,90			
1,00	5,20			
1,36	4,18			
Sample size [diluted]: 60 ml				

Test 2: 400 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,73	672	382	- 0,04
0	6,73			
0,66	5,88			
1,00	5,18			
1,36	4,17			
Sample size [diluted]: 60 ml				

Test 3: 400 mgHAc/l added				
V_x	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,75	660	383	- 0,13
0	6,75			
0,66	5,92			
1,00	5,21			
1,36	4,20			
Sample size [diluted]: 60				

Test 4: 400 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,74	675	379	- 0,08
0	6,74			
0,66	5,91			
1,00	5,22			
1,36	4,21			
Sample size [diluted]: 60 ml				

Test 5: 400 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,74	662	398	- 0,13
0	6,74			
0,66	5,92			
1,00	5,23			
1,36	4,25			
Sample size [diluted]: 60				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
667	383	- 0,09
Sample without HAc addition		
947	0	- 0,06

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.1.5

5 pH point titration method

Treated lauter tun effluent augmented with acetic acid: 500 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 420 mS/m

P_T: 50 mgP/l; N_T: 20 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,13	1819	2	- 0,05
0,84	6,74			
1,94	5,95			
2,46	5,24			
2,68	4,14			
Sample size [diluted]: 55 ml				

Test 1: 500 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,99	1476	482	- 0,03
0,30	6,74			
1,46	5,92			
2,06	5,23			
2,56	4,21			
Sample size [diluted]: 60 ml				

Test 2: 500 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,99	1466	492	- 0,05
0,30	6,73			
1,46	5,91			
2,06	5,20			
2,56	4,17			
Sample size [diluted]: 60 ml				

Test 3: 500 mgHAc/l added				
V_x	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,00	1465	492	- 0,03
0,30	6,74			
1,46	5,91			
2,06	5,21			
2,56	4,19			
Sample size [diluted]: 60				

Test 4: 500 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,98	1456	499	- 0,05
0,30	6,73			
1,46	5,91			
2,06	5,20			
2,56	4,18			
Sample size [diluted]: 60 ml				

Test 5: 500 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,01	1459	513	- 0,08
0,30	6,75			
1,46	5,93			
2,06	5,22			
2,56	4,21			
Sample size [diluted]: 60				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
1464	**495**	**- 0,05**
Sample without HAc addition		
1819	**2**	**- 0,05**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.1.6

5 pH point titration method

Treated lauter tun effluent augmented with acetic acid: 600 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 420 mS/m

P_T: 50 mgP/l; N_T: 20 mgN/l;

0 mgHAc/l added

V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,42	2138	- 15	- 0,04
1,10	6,70			
2,40	5,88			
3,00	5,00			
3,14	4,21			

Sample size [diluted]: 55 ml

Test 1: 600 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,03	1743	574	- 0,05
0,60	6,61			
1,80	5,88			
2,40	5,28			
3,04	4,15			

Sample size [diluted]: 60 ml

Test 2: 600 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,03	1742	585	- 0,06
0,50	6,67			
1,80	5,88			
2,44	5,22			
3,00	4,24			

Sample size [diluted]: 60 ml

Test 3: 600 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,02	1720	586	- 0,07
0,54	6,65			
1,80	5,88			
2,44	5,21			
3,00	4,22			

Sample size [diluted]: 60

Test 4: 600 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,02	1713	590	- 0,06
0,46	6,68			
1,80	5,85			
2,44	5,16			
3,00	4,15			

Sample size [diluted]: 60 ml

Test 5: 600 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,03	1721	586	- 0,05
0,46	6,69			
1,80	5,86			
2,44	5,18			
3,00	4,18			

Sample size [diluted]: 60

AVERAGED RESULTS

Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
1728	**584**	**- 0,06**
Sample without HAc addition		
2138	**- 15**	**- 0,04**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.1.7

5 pH point titration method

Treated lauter tun effluent augmented with acetic acid: 700 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 420 mS/m

P_T: 50 mgP/l; N_T: 20 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,67	2715	10	- 0,05
1,30	6,75			
3,00	5,89			
3,70	5,14			
4,04	3,81			
Sample size [diluted]: 55 ml				

Test 1: 700 mgHAc/l added					Test 2: 700 mgHAc/l added					Test 3: 700 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error	V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error	V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,09	2209	704	- 0,09	0	7,10	2228	696	- 0,07	0	7,10	2235	685	- 0,06
0,60	6,72				0,60	6,72				0,60	6,72			
2,26	5,91				2,26	5,91				2,26	5,91			
3,10	5,20				3,10	5,21				3,10	5,22			
3,80	4,13				3,80	4,15				3,80	4,16			
Sample size [diluted]: 60 ml					Sample size [diluted]: 60 ml					Sample size [diluted]: 60				

Test 4: 700 mgHAc/l added					Test 5: 700 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error	V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,08	2207	695	- 0,04	0	7,09	2224	702	- 0,06
0,60	6,71				0,60	6,72			
2,26	5,89				2,26	5,91			
3,10	5,19				3,10	5,22			
3,80	4,13				3,80	4,18			
Sample size [diluted]: 60 ml					Sample size [diluted]: 60				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2221	696	- 0,06
Sample without HAc addition		
2715	10	- 0,05

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.1.8

5 pH point titration method

Treated lauter tun effluent augmented with acetic acid: 800 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 24°C; SC: 420 mS/m

P_T: 50 mgP/l; N_T: 20 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,79	2957	3	- 0,05
1,40	6,75			
3,20	5,91			
3,98	5,20			
4,26	4,21			
Sample size [diluted]: 55 ml				

Test 1: 800 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,06	2379	796	- 0,08
0,60	6,72			
2,40	5,91			
3,30	5,24			
4,10	4,17			
Sample size [diluted]: 60 ml				

Test 2: 800 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,06	2367	794	- 0,06
0,60	6,72			
2,40	5,90			
3,30	5,23			
4,10	4,16			
Sample size [diluted]: 60 ml				

Test 3: 800 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,07	2388	796	- 0,08
0,60	6,72			
2,40	5,91			
3,30	5,24			
4,10	4,17			
Sample size [diluted]: 60				

Test 4: 800 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,08	2376	794	- 0,07
0,60	6,73			
2,40	5,91			
3,30	5,24			
4,10	4,17			
Sample size [diluted]: 60 ml				

Test 5: 800 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,07	2252	813	- 0,09
0,60	6,73			
2,40	5,91			
3,30	5,23			
4,10	4,16			
Sample size [diluted]: 60				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2372	799	- 0,08
Sample without HAc addition		
2957	3	- 0,05

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.1.9

5 pH point titration method

Treated lauter tun effluent augmented with acetic acid: 900 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 26°C; SC: 420 mS/m

P_T: 50 mgP/l; N_T: 20 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,77	3451	5	- 0,01
1,40	6,81			
3,60	5,92			
4,56	5,25			
4,96	4,12			
Sample size [diluted]: 55 ml				

Test 1: 900 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,02	2800	898	- 0,03
0,54	6,74			
2,60	5,95			
3,84	5,21			
4,76	4,14			
Sample size [diluted]: 60 ml				

Test 2: 900 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,02	2811	897	- 0,03
0,54	6,74			
2,70	5,91			
3,84	5,22			
4,76	4,16			
Sample size [diluted]: 60 ml				

Test 3: 900 mgHAc/l added				
V_x	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,02	2791	901	- 0,02
0,54	6,74			
2,70	5,90			
3,84	5,20			
4,76	4,13			
Sample size [diluted]: 60				

Test 4: 900 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,03	2808	879	+ 0,01
0,54	6,74			
2,70	5,89			
3,84	5,19			
4,76	4,11			
Sample size [diluted]: 60 ml				

Test 5: 900 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,03	2785	887	- 0,01
0,54	6,75			
2,70	5,90			
3,84	5,20			
4,76	4,12			
Sample size [diluted]: 60				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2799	**892**	**- 0,02**
Sample without HAc addition		
3451	**5**	**- 0,01**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.1.10

5 pH point titration method

Treated lauter tun effluent augmented with acetic acid: 1000 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 25°C; SC: 420 mS/m

P_T: 50 mgP/l; N_T: 20 mgN/l;

0 mgHAc/l added

V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,83	3806	- 18	- 0,05
1,70	6,75			
4,00	5,91			
5,00	5,20			
5,38	4,02			

Sample size [diluted]: 55 ml

Test 1: 1000 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,03	3014	959	- 0,02
0,60	6,75			
2,90	5,92			
4,20	5,17			
5,10	4,19			

Sample size [diluted]: 60 ml

Test 2: 1000 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,03	3002	959	- 0,03
0,60	6,76			
2,90	5,93			
4,20	5,18			
5,10	4,20			

Sample size [diluted]: 60 ml

Test 3: 1000 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,04	3021	977	- 0,05
0,60	6,76			
2,90	5,94			
4,20	5,20			
5,10	4,24			

Sample size [diluted]: 60

Test 4: 1000 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,04	3067	934	+ 0,01
0,60	6,75			
2,90	5,92			
4,20	5,19			
5,10	4,23			

Sample size [diluted]: 60 ml

Test 5: 1000 mgHAc/l added

V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,04	3061	948	- 0,02
0,60	6,75			
2,90	5,93			
4,20	5,20			
5,10	4,24			

Sample size [diluted]: 60

AVERAGED RESULTS

Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
3033	**955**	**- 0,02**
Sample without HAc addition		
3806	**- 18**	**- 0,05**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.2.1

5 pH point titration method

Treated wine distillery effluent augmented with acetic acid: 100 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 20°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,46	2960	52	- 0,01
1,50	6,71			
3,20	5,95			
4,10	5,21			
4,44	4,14			
Sample size [diluted]: 55 ml				

Test 1: 100 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	8,18	2946	134	- 0,01
1,40	6,71			
3,10	5,96			
4,04	5,21			
4,44	4,13			
Sample size [diluted]: 60 ml				

Test 2: 100 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	8,18	2918	156	- 0,02
1,40	6,69			
3,10	5,93			
4,00	5,16			
4,40	4,05			
Sample size [diluted]: 60 ml				

Test 3: 100 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	8,19	2913	146	+ 0,01
1,40	6,70			
3,10	5,94			
4,00	5,22			
4,40	4,20			
Sample size [diluted]: 60				

Test 4: 100 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	8,23	2921	112	+ 0,02
1,40	6,71			
3,10	5,95			
4,00	5,26			
4,40	4,25			
Sample size [diluted]: 60 ml				

Test 5: 100 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	8,21	2916	161	- 0,01
1,40	6,70			
3,10	5,94			
4,00	5,21			
4,40	4,18			
Sample size [diluted]: 60 ml				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2923	**142**	**0**
Sample without HAc addition		
2960	**52**	**- 0,01**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.2.2

5 pH point titration method

Treated wine distillery effluent augmented with acetic acid: 200 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,44	2994	36	- 0,02
1,50	6,71			
3,20	5,96			
4,10	5,24			
4,44	4,19			
Sample size [diluted]: 55 ml				

Test 1: 200 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,87	2940	250	- 0,05
1,20	6,75			
3,00	5,97			
3,96	5,22			
4,40	4,23			
Sample size [diluted]: 60 ml				

Test 2: 200 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,87	2908	239	- 0,04
1,20	6,75			
3,00	5,96			
3,96	5,19			
4,40	4,15			
Sample size [diluted]: 60 ml				

Test 3: 200 mgHAc/l added				
V_x	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,89	2909	255	- 0,05
1,20	6,76			
3,00	5,97			
3,96	5,21			
4,40	4,21			
Sample size [diluted]: 60				

Test 4: 200 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,88	2911	238	- 0,03
1,20	6,75			
3,00	5,96			
3,96	5,20			
4,40	4,18			
Sample size [diluted]: 60 ml				

Test 5: 200 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,94	2920	244	- 0,04
1,20	6,77			
3,00	5,98			
3,96	5,25			
4,40	4,29			
Sample size [diluted]: 60 ml				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2918	**245**	**- 0,04**
Sample without HAc addition		
2994	**36**	**- 0,02**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.2.3

5 pH point titration method

Treated wine distillery effluent augmented with acetic acid: 300 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,44	3067	32	- 0,03
1,50	6,72			
3,30	5,94			
4,20	5,19			
4,50	4,23			
Sample size [diluted]: 55 ml				

Test 1: 300 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,70	2961	333	- 0,07
1,20	6,73			
3,10	5,92			
4,04	5,13			
4,50	4,13			
Sample size [diluted]: 60 ml				

Test 2: 300 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,70	2867	330	- 0,01
1,20	6,73			
3,10	5,89			
4,04	5,10			
4,46	4,21			
Sample size [diluted]: 60 ml				

Test 3: 300 mgHAc/l added				
V_x	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,72	2900	291	- 0,05
1,20	6,75			
3,10	5,92			
4,00	5,18			
4,46	4,16			
Sample size [diluted]: 60				

Test 4: 300 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,73	2909	349	- 0,04
1,20	6,72			
3,10	5,89			
4,00	5,14			
4,44	4,24			
Sample size [diluted]: 60 ml				

Test 5: 300 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,72	2876	344	- 0,03
1,20	6,72			
3,10	5,88			
4,00	5,11			
4,44	4,18			
Sample size [diluted]: 60 ml				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2903	**329**	**- 0,04**
Sample without HAc addition		
3067	**32**	**- 0,03**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.2.4

5 pH point titration method

Treated wine distillery effluent augmented with acetic acid: 400 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 20°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,42	3061	40	- 0,04
1,50	6,74			
3,34	5,94			
4,20	5,22			
4,52	4,21			
Sample size [diluted]: 55 ml				

Test 1: 400 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,49	2859	424	- 0,04
1,04	6,74			
2,90	5,95			
3,90	5,19			
4,44	4,19			
Sample size [diluted]: 60 ml				

Test 2: 400 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,48	2843	464	- 0,07
1,04	6,75			
2,94	5,94			
3,90	5,19			
4,44	4,22			
Sample size [diluted]: 60 ml				

Test 3: 400 mgHAc/l added				
V_x	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,49	2808	439	- 0,02
1,04	6,74			
3,00	5,88			
3,90	5,16			
4,44	4,16			
Sample size [diluted]: 60				

Test 4: 400 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,50	2866	436	- 0,05
1,04	6,74			
3,00	5,90			
3,90	5,18			
4,44	4,18			
Sample size [diluted]: 60 ml				

Test 5: 400 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,50	2807	446	- 0,03
1,04	6,75			
3,00	5,89			
3,90	5,17			
4,44	4,18			
Sample size [diluted]: 60 ml				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2837	**442**	**- 0,04**
Sample without HAc addition		
3061	**40**	**- 0,04**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.2.5

5 pH point titration method

Treated wine distillery effluent augmented with acetic acid: 500 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,41	3127	26	- 0,04
1,50	6,74			
3,34	5,96			
4,24	5,26			
4,58	4,24			
Sample size [diluted]: 55 ml				

Test 1: 500 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,36	2806	539	- 0,06
1,00	6,73			
2,86	5,95			
3,86	5,22			
4,50	4,17			
Sample size [diluted]: 60 ml				

Test 2: 500 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,36	2809	551	- 0,06
1,00	6,72			
2,90	5,92			
3,86	5,20			
4,50	4,15			
Sample size [diluted]: 60 ml				

Test 3: 500 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,37	2893	576	- 0,14
1,00	6,73			
2,90	5,96			
3,86	5,24			
4,50	4,21			
Sample size [diluted]: 60				

Test 4: 500 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,40	2823	550	- 0,09
1,00	6,75			
3,00	5,90			
3,86	5,23			
4,50	4,18			
Sample size [diluted]: 60 ml				

Test 5: 500 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,40	2855	560	- 0,10
1,00	6,74			
3,00	5,90			
3,86	5,24			
4,50	4,21			
Sample size [diluted]: 60 ml				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2837	**556**	**- 0,09**
Sample without HAc addition		
3127	**26**	**- 0,04**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.2.6

5 pH point titration method

Treated wine distillery effluent augmented with acetic acid: 600 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,34	3120	49	- 0,04
1,50	6,73			
3,40	5,92			
4,26	5,21			
4,60	4,16			
Sample size [diluted]: 55 ml				

Test 1: 600 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,24	2766	633	- 0,07
0,86	6,73			
2,80	5,93			
3,80	5,20			
4,48	4,17			
Sample size [diluted]: 60 ml				

Test 2: 600 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,24	2725	637	- 0,03
0,86	6,73			
2,80	5,91			
3,80	5,18			
4,48	4,16			
Sample size [diluted]: 60 ml				

Test 3: 600 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,24	2775	630	- 0,05
0,86	6,73			
2,80	5,93			
3,80	5,22			
4,48	4,22			
Sample size [diluted]: 60				

Test 4: 600 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,23	2714	626	- 0,04
0,86	6,73			
2,80	5,91			
3,80	5,17			
4,48	4,12			
Sample size [diluted]: 60 ml				

Test 5: 600 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,24	2766	633	- 0,07
0,86	6,73			
2,80	5,93			
3,80	5,20			
4,48	4,17			
Sample size [diluted]: 60 ml				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2749	**632**	**- 0,05**
Sample without HAc addition		
3120	**49**	**- 0,04**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.2.7

5 pH point titration method

Treated wine distillery effluent augmented with acetic acid: 700 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,54	3150	35	- 0,06
1,56	6,75			
3,46	5,94			
4,36	5,17			
4,68	4,08			
Sample size [diluted]: 55 ml				

Test 1: 700 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,22	2691	742	- 0,08
0,80	6,77			
2,80	5,93			
3,80	5,20			
4,50	4,24			
Sample size [diluted]: 60 ml				

Test 2: 700 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,21	2670	737	- 0,07
0,84	6,74			
2,80	5,91			
3,80	5,16			
4,50	4,17			
Sample size [diluted]: 60 ml				

Test 3: 700 mgHAc/l added				
V_x	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,23	2700	742	- 0,08
0,80	6,77			
2,80	5,93			
3,80	5,20			
4,50	4,24			
Sample size [diluted]: 60				

Test 4: 700 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,21	2668	742	- 0,07
0,80	6,75			
2,80	5,90			
3,80	5,14			
4,50	4,14			
Sample size [diluted]: 60 ml				

Test 5: 700 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,23	2702	723	- 0,08
0,80	6,77			
2,80	5,93			
3,80	5,20			
4,50	4,22			
Sample size [diluted]: 60 ml				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2686	737	- 0,08
Sample without HAc addition		
3150	35	- 0,06

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.2.8

5 pH point titration method

Treated wine distillery effluent augmented with acetic acid: 800 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,35	3117	20	- 0,03
1,50	6,75			
3,44	5,92			
4,30	5,22			
4,66	4,04			
Sample size [diluted]: 55 ml				

Test 1: 800 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,07	2613	828	- 0,09
0,70	6,71			
2,70	5,89			
3,66	5,20			
4,44	4,19			
Sample size [diluted]: 60 ml				

Test 2: 800 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,07	2603	830	- 0,07
0,70	6,70			
2,70	5,87			
3,66	5,17			
4,44	4,15			
Sample size [diluted]: 60 ml				

Test 3: 800 mgHAc/l added				
V_x	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,07	2609	825	- 0,05
0,70	6,71			
2,70	5,88			
3,66	5,20			
4,44	4,21			
Sample size [diluted]: 60				

Test 4: 800 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,06	2573	856	- 0,09
0,70	6,71			
2,70	5,88			
3,66	5,18			
4,44	4,18			
Sample size [diluted]: 60 ml				

Test 5: 800 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,08	2622	869	- 0,15
0,70	6,71			
2,70	5,90			
3,66	5,19			
4,44	4,18			
Sample size [diluted]: 60 ml				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2604	**842**	**- 0,09**
Sample without HAc addition		
3117	**20**	**- 0,03**

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.2.9

5 pH point titration method

Treated wine distillery effluent augmented with acetic acid: 900 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 20°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,43	3093	51	- 0,03
1,50	6,76			
3,44	5,92			
4,30	5,21			
4,62	4,24			
Sample size [diluted]: 55 ml				

Test 1: 900 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,02	2525	921	- 0,04
0,90	6,59			
2,60	5,88			
3,54	5,23			
4,40	4,22			
Sample size [diluted]: 60 ml				

Test 2: 900 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,02	2521	953	- 0,07
0,60	6,72			
2,60	5,89			
3,54	5,24			
4,40	4,25			
Sample size [diluted]: 60 ml				

Test 3: 900 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,02	2508	922	- 0,05
0,60	6,73			
2,60	5,89			
3,54	5,24			
4,40	4,23			
Sample size [diluted]: 60				

Test 4: 900 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,03	2539	909	- 0,06
0,60	6,73			
2,60	5,90			
3,54	5,26			
4,40	4,25			
Sample size [diluted]: 60 ml				

Test 5: 900 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	7,04	2510	940	- 0,07
0,60	6,74			
2,60	5,90			
3,54	5,25			
4,40	4,25			
Sample size [diluted]: 60 ml				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2521	929	- 0,06
Sample without HAc addition		
3093	51	- 0,03

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

Table R.2.10

5 pH point titration method

Treated wine distillery effluent augmented with acetic acid: 1000 mg/l

Sample size [undiluted]: 5 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

0 mgHAc/l added				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,40	3290	50	- 0,06
1,54	6,76			
3,60	5,92			
4,46	5,24			
4,84	4,10			
Sample size [diluted]: 55 ml				

Test 1: 1000 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,97	2552	1036	- 0,07
0,50	6,74			
2,60	5,90			
3,60	5,25			
4,56	4,21			
Sample size [diluted]: 60 ml				

Test 2: 1000 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,98	2569	1046	- 0,09
0,50	6,75			
2,60	5,92			
3,60	5,28			
4,56	4,26			
Sample size [diluted]: 60 ml				

Test 3: 1000 mgHAc/l added				
V_x	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,98	2564	1048	- 0,07
0,50	6,74			
2,60	5,90			
3,60	5,25			
4,56	4,22			
Sample size [diluted]: 60				

Test 4: 1000 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,97	2575	991	- 0,05
0,50	6,74			
2,60	5,90			
3,60	5,26			
4,56	4,20			
Sample size [diluted]: 60 ml				

Test 5: 1000 mgHAc/l added				
V_x ml	pH_x	Alk mg/l	SCFA mg/l	pH error
0	6,98	2564	1057	- 0,10
0,50	6,74			
2,60	5,91			
3,60	5,26			
4,58	4,20			
Sample size [diluted]: 60 ml				

AVERAGED RESULTS		
Alk mg/l	SCFA mg/l	pH error
Samples with HAc addition		
2565	1035	- 0,08
Sample without HAc addition		
3290	50	- 0,06

Note: SCFA: mg/l as HAc.

Alk = $H_2CO_3^*$alk: mg/l as $CaCO_3$

APPENDIX S

COMPARISON BETWEEN SCFA RESULTS FROM 5 pH POINT TITRATION METHOD AND WET CHEMICAL METHOD, MEASURED IN TREATED (IN UASB REACTOR) WINE DISTILLERY AND LAUTER TUN (BREWERY) WASTES

EXPERIMENTAL DATA AND RESULTS

For the treated lauter tun and wine distillery waste only; 3 typical titration examples (out of a total of 30 on each waste) are listed in tables designated as Table S.1 and Table S.2 respectively as illustration.

Table S.1.1

5 pH point method vs Montgomery et al.'s method

Treated lauter tun waste

Sample size [undiluted]: 5 ml

Sample size [diluted]: 55 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 420 mS/m

P_T: 50 mgP/l; N_T: 50 mgN/l;

5 pH point method				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,17	1868	- 4	- 0,03
0,90	6,71			
2,00	5,94			
2,54	5,22			
2,76	4,12			
Montgomery et al.'method			2	

Table S.1.2

5 pH point method vs Montgomery et al.'s method

Treated lauter tun waste

Sample size [undiluted]: 5 ml

Sample size [diluted]: 55 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 420 mS/m

P_T: 50 mgP/l; N_T: 50 mgN/l;

5 pH point method				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	7,97	1353	42	- 0,04
0,90	6,47			
1,60	5,76			
1,86	5,22			
2,06	4,15			
Montgomery et al.'method			30	

Table S.1.3

5 pH point method vs Montgomery et al.'s method

Treated lauter tun waste

Sample size [undiluted]: 5 ml

Sample size [diluted]: 55 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 21°C; SC: 420 mS/m

P_T: 50 mgP/l; N_T: 50 mgN/l;

5 pH point method				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,45	2363	15	- 0,04
1,10	6,74			
2,50	5,95			
3,20	5,18			
3,44	4,17			
Montgomery et al.'method			12	

Table S.2.1

5 pH point method vs Montgomery et al.'s method

Treated wine distillery waste

Sample size [undiluted]: 5 ml

Sample size [diluted]: 55 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 24°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

5 pH point method				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,33	3181	41	- 0,04
1,50	6,74			
3,50	5,90			
4,36	5,21			
4,70	4,20			
Montgomery et al.'method			30	

Table S.2.2

5 pH point method vs Montgomery et al.'s method

Treated wine distillery waste

Sample size [undiluted]: 5 ml

Sample size [diluted]: 55 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 24°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

5 pH point method				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,10	2870	458	- 0,06
1,36	6,72			
3,10	5,94			
4,00	5,25			
4,60	4,18			
Montgomery et al.'method			440	

Table S.2.3

5 pH point method vs Montgomery et al.'s method

Treated wine distillery waste

Sample size [undiluted]: 5 ml

Sample size [diluted]: 55 ml

Normality of strong acid: 0,0728 mol/l

Temperature: 24°C; SC: 440 mS/m

P_T: 70 mgP/l; N_T: 150 mgN/l;

5 pH point method				
V_x ml	pH_x	Alk mg/l as $CaCO_3$	SCFA mg/l as HAc	systematic pH error
0	8,51	2730	789	- 0,06
1,40	6,73			
3,10	5,92			
4,00	5,23			
4,76	4,20			
Montgomery et al.'method			760	

APPENDIX T

4 pH POINT TITRATION METHOD FOR THE DETERMINATION OF H_2CO_3*ALKALINITY AND TOTAL CARBONATE SPECIES CONCENTRATION IN AQUEOUS SOLUTIONS CONTAINING KNOWN CONCENTRATIONS OF INORGANIC NITROGEN AND PHOSPHATE

Introduction

The testing procedure for the 4 pH point titration (4 ppt) method is set out for the 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 and inorganic phosphate.

Principle

The sample is titrated from its initial pH to 3 further pH points. Knowing the concentrations of inorganic phosphate and free and saline ammonia, 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 inserted in a personal computer program (see Appendix U) to facilitate the necessary calculations.

Apparatus

The apparatus required is set out in Appendix V under section " Apparatus".

Chemicals

Chemicals required are set out in Appendix V under section "Chemicals".

Sample preparation

A choice has to be made with regard to:

(1) Sample size (ml) undiluted.

(2) Sample size (ml) diluted.

Sample size (undiluted): The choice of undiluted sample volume is determined by (1) the dilution ratio required and (2) 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 excessive CO_2 loss during titration, (2) to reduce the total dissolved solids concentration to < 2500 mg/ℓ to allow calculation of the activity coefficients according to the Davies Equation (see Appendix A). The dilution ratio is kept low to avoid multiplication effects of titration errors: C_T, H_2CO_3*alkalinity are determined for the *diluted* sample by titration; 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 pH's 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, with the Radiometer probe, the tip and porous pin were 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.

4 pH point titration procedure

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

(1) Pipette 50 mℓ of sample into a 100 mℓ Erlenmeyer flask (diluted or undiluted). The requirements are that C_T is below about 500 mg/ℓ as $CaCO_3$, and TDS below about 2500 mg/ℓ.

(2) Insert thermometer and pH probe, stir gently for 15 seconds (s), take temperature reading, remove thermometer and stop stirring.

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

(4) Switch on stirrer and titrate sample from initial pH 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 initial pH to pH_1 and take pH_1 reading about 30 s after termination of stirring. The volume of titrant added to titrate from pH initial to pH_1 is designated V_{x1}.

(5) Repeat step (4) 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 to reach the respective lower pH points.

If the initial pH of the diluted sample is below 6,7, the initial pH is recorded; strong base is added to raise the pH to $pH_1 + 6,7$ ± 0,1. The volume of strong base added is ignored (V_{x1} at pH_1 is set to zero 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 strong acid volumes added to reach pH_2 and pH_3 from the starting pH point, pH_1.

If the initial pH of the diluted sample is 6,7 ± 0,1 the initial pH 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_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_{x2} : pH_2 (5,90 ± 0,1)
V_{x3} : pH_3 (5,20 ± 0,1)

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

V_x : **pH_x**
0 : initial diluted sample pH (pH_0)
$V_{x1} = 0$: pH_1 (after adding of strong base or if initial pH = 6,70 ± 0,1)
V_{x2} : pH_2 (5,90 ± 0,1)
V_{x3} : pH_3 (5,20 ± 0,1)

The pH values located within the ± 0,1 limit ideally should be aimed for (and are 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 tolerance 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 its ideal value. If the sample is being "under titrated", step (4) 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 its ideal pH value.

Ancillary measurements

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 ammonium/ammonia total species concentration can be measured according to Standard Methods (1989). 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 in Chapter 4.

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, which can be measured according to Standard Methods (1989). 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 also presented in Chapter 4.

Total dissolved solids, TDS, or specific conductivity, SC, of undiluted sample

To calculate the dissociation constants of the different weak acid/bases (carbonate, free and saline ammonia and inorganic phosphate) 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 (see Appendix A). The measurement of one of these parameters means additional experimental effort which may not be justified seeing that the algorithm employed to determine the C_T and H_2CO_3*alkalinity is not very sensitive to variations in TDS or SC (see Appendix V). Hence approximation of these latter two parameters may be justified in many cases. This decision must be taken against the background of the accuracy desired for the determination of SCFA and H_2CO_3*alkalinity.

Standardisation of strong acid

The standardisation procedure for a strong acid (hydrochloric) is set out in Appendix V under section "Standardisation of strong acid".

Input data table for computer program

H_2CO_3*alkalinity and C_T are calculated using a personal computer program, (the program source code is listed in Appendix U; a floppy disk with source code file and an executable file of the program is attached to the inside of the thesis cover).

The input data for the computer program is 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)
V_{x2} (mℓ)
V_{x3} (mℓ)
Normality of strong acid (mol/ℓ)
Sample size (undiluted) (mℓ)
Sample size (diluted) (mℓ)
Temperature (deg Celsius)
TDS (mg/ℓ)
SC (mS/m)
N_T (total species con. of free and saline ammonia, mg/ℓ as N)
P_T (total species con. of inorganic phosphate, mg/ℓ as P)

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.

Output data table of computer program

(1) H_2CO_3*alkalinity of undiluted sample (mg/ℓ as $CaCO_3$)
(2) Total carbonate species concentration (mg/ℓ as $CaCO_3$)
(3) Correction for systematic pH error

Note: (1) The correction for systematic pH error is subject to the condition that the carbonate weak acid/base dominates [i.e. $C_T > 2 \cdot (N_T + P_T)$] in the sample.

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 was encountered with the diluted sample having a TDS < 2500 mg/l. 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.

(2) 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 to be obtained, 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 Chapter 2.

<u>Example:</u>

The following example demonstrates the data input and output (for the computer program listed in Appendix U) for a pure aqueous carbonate solution, made up from 0,168 $gNaHCO_3/\ell$ (100 mg/ℓ as $CaCO_3$).

Data input screen:

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})....	5,11
V_{x1} (mℓ)....	0,40
V_{x2} (mℓ)....	1,00
V_{x3} (mℓ)....	1,30
Normality of strong acid (mol/ℓ)....	0,0728
Sample size (undiluted) (mℓ)....	50
Sample size (diluted) (mℓ)....	50
Temperature (deg Celsius).....	21
TDS (mg/ℓ)....	168
SC (mS/m) ...	
N_T (total species con. of inorganic nitrogen, mg/ℓ as N)....	0
P_T (total species con. of inorganic phosphate, mg/ℓ as P)....	0

Data output screen:

H_2CO_3*alkalinity of undiluted sample
(mg/ℓ as $CaCO_3$)....................................100

Total carbonate species con. of undiluted sample
(mg/ℓ as $CaCO_3$)....................................102

systematic pH error.............................– 0,04

APPENDIX U

SOURCE CODE LISTING OF PERSONAL COMPUTER PROGRAM FOR 4 pH POINT TITRATION METHOD

This appendix contains the listing of the source code for the source code file: 4ppt.pas. This file is available on the floppy disk which is attached to the inside of the thesis cover. The program is coded using Turbo Pascal Ver 4.0. It allows the calculation of H_2CO_3*alkalinity, C_T and systematic pH measurement error from the data collected in the 4 pH point titration procedure. (For 4 pH point titration procedure, see Appendix T).

```
  program ct;

                  { 4 pH POINT TITRATION METHOD}

 {This program calculates the H2CO3*alkalinity and total carbonate species concentration in aqueous solutions
containing the carbonate, ammonium and phosphate subsystems; the total species concentrations of the ammonium
and phosphate subsystems need to be entered into the program.  The sample is titrated from the initial sample
pH to 3 further pH values measured in the pH region: 6.7, 5.9, 5.2. The program provides an estimate of a
possible systematic pH measurement error.}


 {PROGRAM START}


  uses  crt;

  type phstr= string[50];

  var  pH0, pH1, pH2, pH3, pH4, delph, pHcorr,
       MCt1, MCt2, Ct2, Ct1, Ctcomp,
       dil, vsdil, vsundil, vx, vx1, vx2, vx3,  vxfi, vxs, ca, temp, ktemp, TDS,
       logf1, logf2, pK1, pK11, pK2, pK22, pKn, pKnn, Nt,
       pKp, pKpp, Pt,
       MH2CO3alksam, H2CO3alksam, Mcarb01, Mcarb02,
       counter, ionstr, number :real;

       again, selection, move,
       intro : char;
  labels: array[1..16] of phstr;
  value: array[1..16] of real;
  I,II,posy: Integer;




  function log(x:real):real;
   begin
    log:=ln(x)/2.302585093;
   end;

  function tento(y:real):real;
   begin
    tento:=exp(y*ln(10));
   end;

  function mue (TDS,dil:real):real;
   begin
    mue:= 0.000025*(TDS/dil-20);
   end;

  function logf (mue,ktemp:real):real;
   begin
    logf:=    -    1.825*1000000*exp(-1.5*ln(78.3*ktemp))*
                  (sqrt(mue)/(1+sqrt(mue))-0.3*mue);
   end;

  function perH2CO3 (ph:real):real;
   begin
    perH2CO3:= 1/(1+tento(-pk11)/tento(-ph)+tento(-pk11)
                  *tento (-pk22)/tento(-2*ph));
   end;

  function perHCO3 (ph:real):real;
```

```
 begin
  perHCO3:=
         1/(tento(-ph)/tento(-pk11)+1+tento(-pk22)/tento(-ph));
 end;

function perCO3 (ph:real):real;
 begin
  perCO3:=1/(tento(-2*ph)/(tento(-pk11)*tento(-pk22))+tento
            (-ph)/tento(-pk22) + 1);
 end;

function per(ph,pkk:real):real;
 begin
  per:=tento(-pkk)/(tento(-pkk)+tento(-ph));
 end;

function dH2CO3alk(pHf,pHs: real): real;
 begin
  dH2CO3alk:= perHCO3(pHf)-perHCO3(pHs)+2*(perCO3(pHf)-perCO3(pHs));
 end;

function MH2O (vxfi,vxs,pHfi,pHs: real):real;
 begin
  MH2O:= (vsdil+vxs)*tento(-pHs)/tento(logf1) -
      (vsdil+vxfi)*tento(-pHfi)/tento(logf1)
      +vsdil+vxfi)*tento((pHfi-14))-(vsdil+vxs)* tento((pHs-14));
 end;

function MNH3(pHf,pHs:real):real;
 begin
  MNH3:= Nt/(14000*dil)*vsdil*(per(pHf,pKnn) - per(pHs,pKnn));
 end;

function MHPO4(pHf,pHs:real):real;
 begin
  MHPO4:= Pt/(31000*dil)*vsdil*(per(pHf,pKpp)-per(pHs,pKpp))   end;



procedure mark;
 begin
  textbackground(white);
  textcolor(black);
 end;

procedure unmark;
 begin
  textbackground(black);
  textcolor(white);
 end;

procedure box(x1,y1,x2,y2,a:integer);
 var
  II:integer;
 begin
  a:= x2-x1-1;
   FOR II:=1 to a DO        {draw the horizontal lines}
    begin
     GOTOXY(x1+1,y1);
     writeln(chr(196));
     GOTOXY(x1+1,y2);
     writeln(chr(196));
     x1:=x1+1;
    end;
  x1:=x1-a;
  a:=y2-y1-1;
   FOR II:=1 to a DO        {draw the vertical lines}
    begin
```

```
     GOTOXY(x1,y1+1);
     writeln(chr(179));
     GOTOXY(x2,y1+1);
     writeln(chr(179));
     y1:=y1+1;
    end;
  y1:=y1-a;
  GOTOXY(x1,y1);           {draw the corners}
  writeln(chr(218));
  GOTOXY(x1,y2);
  writeln(chr(192));
  GOTOXY(x2,y1);
  writeln(chr(191));
  GOTOXY(x2,y2);
  writeln(chr(217));
 end; {procedure box}

procedure introscreen;
 begin
  clrscr; mark;
  box(10,3,70,20,1); unmark;
  box(24,6,56,8,1);box(22,5,58,9,1);
  box(12,10,68,16,1);
  GOTOXY(25,7); highvideo;
  write('FOUR pH POINT TITRATION METHOD');normvideo;
  GOTOXY(28,11);
  write('FOR DETERMINATION OF:');
  GOTOXY(18,13);
  write('(1) H2CO3*ALKALINITY');
  GOTOXY(18,14);
  write('(2) TOTAL CARBONATE SPECIES CONCENTRATION (CT)');
  GOTOXY(11,16);
  GOTOXY(12,18);
  write('Copyright: UCT');
  box(10,22,41,24,1);
  GOTOXY(12,23);
  write('Press any letter to continue');
  intro := readkey;
 end; {procedure introscreen}

procedure initlabel;
 begin
  labels[1]:='pHo (initial pH)................';
  labels[2]:='pH1 (after adding Vx1)..........';
  labels[3]:='pH2 (after adding Vx2)..........';
  labels[4]:='pH3 (after adding Vx3)..........';
  labels[5]:='   Vx1 (ml).....................';
  labels[6]:='   Vx2 (ml).....................';
  labels[7]:='   Vx3 (ml).....................';
  labels[8]:='Normality of titrant (mols/l)...';
  labels[9]:='Sample size (undiluted) (ml)....';
  labels[10]:='Sample size (diluted) (ml)......';
  labels[11]:='Temperature (Celsius)...........';
  labels[12]:='TDS (mg/l)......................';
  labels[13]:='Ionic strength (mS/m)...........';
  labels[14]:='Inorganic Nitrogen (mgN/l)......';
  labels[15]:='Inorganic Phosphorus (mgP/l)....';
 end;  {procedure initlabel}

procedure default_values;
 begin
  value[1]:= 8.00;
  value[2]:= 6.73;
  value[3]:= 5.93;
  value[4]:= 5.12;
  value[5]:= 0.40;
  value[6]:= 1.00;
  value[7]:= 1.30;
  value[8]:= 0.0728;
```

```
  value[9]:= 50;
  value[10]:=50;
  value[11]:= 21;
  value[12]:= 160;
  value[13]:= 16;
  value[14]:= 0;
  value[15]:= 0;
 end; {procedure default_values}

procedure allocate_data;
 begin
  pH0:= value[1];
  pH1:= value[2];
  pH2:= value[3];
  pH3:= value[4];
  vx1:= value[5];
  vx2:= value[6];
  vx3:= value[7];
  ca:= value[8];
  vsundil:= value[9];
  vsdil:= value[10];
  temp:= value[11];
  TDS:= value[12];
  ionstr:= value[13];
  Nt:= value[14];
  Pt:= value[15];
 end;  {procedure allocate_data}

procedure write_value;
 begin
  GOTOXY(37,2+posy);
   case posy of
          1,2,3,4,5,6,7: begin
                          writeln(value[posy]:2:2);
                         end;
                      8: begin
                          write(value[posy]:1:4);
                         end;
    9,10,11,12,13,14,15: begin
                          write(value[posy]:1:0);
                         end;
                         else
                         end;
 end; {procedure write_value}

procedure screen;
 begin
  mark; box(50,2,79,8,1); unmark;
  box(50,10,79,19,1);
  box(50,10,59,19,1);
  box(50,10,79,13,1);
  GOTOXY(52,4);
  write(' 4 pH POINT TITRATION ');
  GOTOXY(52,6);
  write(' TITRATION INPUT DATA');
  GOTOXY(52,12);
  writeln('  KEY      FUNCTION');
  GOTOXY(52,14);
  writeln('   ',CHR(24),CHR(25),'    SELECT PARAMETER');
  GOTOXY(52,15);
  writeln('<enter>  ERASE VALUE');
  GOTOXY(52,16);
  writeln('<enter>  INSERT NEW VALUE');
  GOTOXY(52,17);
  writeln('   C     CALCULATION');
  GOTOXY(52,18);
  writeln('   Q     QUIT');
 end; {procedure screen}
```

```
procedure display;
 begin
  clrscr; screen;
  mark; box(1,1,47,19,1); unmark;
   FOR I:= 1 to 15 Do
    begin
    if I=1 then mark;
    GOTOXY(3,2+I);
    writeln(labels[I]);
    GOTOXY(37,2+I);
     if I < 8 then
      begin
       writeln(value[I]:1:2);
      end;
     if I = 8 then
      begin
       write(value[I]:1:4);
      end;
     if I > 8 then
      begin
       write(value[I]:1:0);
      end;
    if I=1 then unmark;
   end; {FOR}
  posy:=1;
   REPEAT
    REPEAT move := READKEY UNTIL (UPCASE(move) IN ['C','Q']) OR
               (ORD(move) IN [72,80,13]);
    case ORD(move) of
     80:  begin
           GOTOXY(3,2+posy);
           writeln(labels[posy]);
           write_value;
           posy:=posy+1;
           if posy=16 then posy:=1;
           GOTOXY(3,2+posy);
           mark; writeln(labels[posy]); write_value; unmark;
          end;

    72:   begin
           GOTOXY(3,2+posy);
           writeln(labels[posy]);
           write_value;
           posy:=posy-1;
           if posy=0 then posy:=15;
           GOTOXY(3,2+posy);
           mark; writeln(labels[posy]); write_value; unmark;
          end;

   13:   begin
          repeat
           GOTOXY(37,2+posy);
           mark;
           write('       ');
           GOTOXY(37,2+posy);
           {$I-} read(number) {$I+}
          until ioresult = 0;
          value[posy]:= number; unmark;
          GOTOXY(37,2+posy);
          write('       ');
          write_value;
           case posy of
            12: begin
                 value[posy+1]:= 0.1488*(value[posy]-20);
                 if value[posy+1] < 0 then value[posy+1]:= 0;
                 GOTOXY(37,posy+3);
                 write('       ');
                 GOTOXY(37,posy+3);
                 write(value[posy+1]:1:0);
```

```
                 end;
             13: begin
                  value[posy-1]:= 6.72*value[posy]+20;
                  GOTOXY(37,posy+1);
                  write('      ');
                  GOTOXY(37,posy+1);
                  write(value[posy-1]:1:0);
                 end;
                 else
                 end; {case of}
           end;
           else
           end;  {case of}
   until upcase(move) in ['C','Q'];
  clrscr; writeln('Calculating, Please wait');
 end;  {procedure display}


procedure pK ;
 begin
  ktemp:= 273 + temp;
  if TDS < 20 then TDS:= 21;
  logf1:= logf(mue(TDS,dil),ktemp);
  logf2:= 4*logf1;
  pK1:= -1*(-356.3094 - 0.06091964*ktemp + 21834.37/ktemp +
                126.8339 *log(ktemp) - 1684915/(ktemp*ktemp));
  pK11:= pK1 + logf1;
  pK2:= -1*(-107.8871 - 0.03252849*ktemp + 5151.79/ktemp +
                38.92561*log(ktemp) - 563713.9/(ktemp*ktemp));
  pK22:= pK2 - logf1 + logf2 ;
  pKn:= 2835.8/ktemp -0.6322 + 0.00123 * ktemp;
  pKnn:= pKn + logf1 ;
  pKp:= 1979.5/ktemp - 5.3541 + 0.01984 * ktemp;
  pKpp:= pKp - logf1 + logf2 ;
 end; {procedure pK}

procedure deltapH;
 begin
  pH0:= pH0 + pHcorr;  pH1:= pH1 + pHcorr;  pH2:= pH2 + pHcorr;
  pH3:= pH3 + pHcorr;
 end;

procedure ctcalculation;
 begin
  Mcarb01:= (vx2-vx1)*ca - MH2O(vx1,vx2,pH1,pH2) - MNH3(pH1,pH2) - MHPO4(pH1,pH2);
  Mcarb02:= (vx3-vx1)*ca - MH2O(vx1,vx3,pH1,pH3) - MNH3(pH1,pH3)  - MHPO4(pH1,pH3);
  MCt1:= Mcarb01 / dH2CO3alk(pH1,pH2);
  MCt2:= Mcarb02 / dH2CO3alk(pH1,pH3);
  Ct1:= MCt1/vsdil*50000*dil; Ct2:= MCt2/vsdil*50000*dil;
  Ctcomp:= Ct1 - Ct2;
 end;

procedure carbsysonly;
 begin
  dil:= vsdil/vsundil;
  pK; delpH:= 0; pHcorr:=0; counter := 0; ctcalculation;
  if (Ctcomp < 0) or (Ctcomp > 0) then
  begin
  if Ctcomp > 0 then
   begin
    pHcorr:= -0.01;
     repeat
      delpH:= delpH - 0.01;
      deltapH; counter:= counter + 1;
      ctcalculation;
     until (Ctcomp < 0) or (counter > 19);
   end
   else
   begin
```

```
    pHcorr:= 0.01;
     repeat
      delpH:= delpH + 0.01;
      deltapH; counter:= counter + 1;
      ctcalculation;
     until (Ctcomp > 0) or (counter > 19);
   end;
   end;
  MH2CO3alksam:= MCt1 * (perHCO3(pH0) + 2 * perCO3(pH0));
  H2CO3alksam:= MH2CO3alksam / vsdil * dil * 50000 + (tento((pH0-14))
                - tento(-pH0)/tento(logf1)) * 50000;
 end;  {procedure carbsysonly}

procedure output;
 begin
  clrscr;
  mark; box(10,2,50,4,1); unmark;
  box(2,6,63,9,1); box(50,6,63,9,1);
  box(2,10,63,13,1);box(50,10,63,13,1);
  box(2,14,63,17,1);box(50,14,63,17,1);
  GOTOXY(22,3);
  highvideo; write('TABLE OF RESULTS '); normvideo;
  GOTOXY(4,7);
  write('H2CO3*alkalinity (undiluted sample)');
  GOTOXY(54,7);
  write(H2CO3alksam:3:0);
  GOTOXY(4,8);
  write('(mg/l as CaCO3)');
  GOTOXY(4,11);
  write('Total carbonate species (undiluted sample)');
  GOTOXY(54,11);
  write(Ct1:3:0);
  GOTOXY(4,12);
  write('(mg/l as CaCO3)');
  GOTOXY(4,16);
  writeln('Estimate of systematic pH error');
  GOTOXY(54,16);
  write(delpH:1:2);
  if counter = 20 then
   begin
    GOTOXY(4,15);
    write('The titration data indicate a systematic pH');
    GOTOXY(4,16);
    write('error > 0,2; please check pH probe calibration');
    GOTOXY(54,16);
    write('      ');
   end;
 end;  {procedure output}

procedure exitbox;
 begin
  repeat
   box(5,20,60,22,1); box(50,20,60,22,1);
   box(5,22,60,24,1); box(50,22,60,24,1);
   GOTOXY(7,21);
   write('Do you wish to do a further calculation ?');
   GOTOXY(53,21);
   highvideo; write('Y'); normvideo; write('/'); highvideo; write('N');
   normvideo;
   GOTOXY(7,23);
   write('Do you wish to quit the program ?');
   GOTOXY(54,23);
   highvideo; write('Q'); normvideo;
   again:= readkey; again:=upcase(again);
  until again in ['Y','N','Q']; clrscr;
 end;  {procedure exitbox}
```

```
begin                {of main program}

 introscreen;
 again:= 'Y';
 default_values;

 repeat
  clrscr;
  initlabel;
  display;
  if upcase(move) in ['C'] then
   begin
    allocate_data;
    carbsysonly; output; exitbox;
   end
   else
   begin clrscr; again:= 'N';
  end;
 until again in ['N','Q'];

end. {of main program}

{PROGRAM END.}
```

APPENDIX V

5 pH POINT TITRATION METHOD FOR THE DETERMINATION OF H_2CO_3*ALKALINITY AND SCFA IN AQUEOUS SOLUTIONS CONTAINING KNOWN CONCENTRATIONS OF INORGANIC NITROGEN AND PHOSPHATE

Introduction

The testing procedure for the 5 pH point titration method is set out for the 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 the ammonium and phosphate weak acid/bases, e.g. anaerobic digester liquid. It was developed for appliCation in monitoring anaerobic fermentation systems. The theory of the method is set out in Chapter 5.

Principle

The sample is titrated from its initial pH to 4 further pH points. Knowing the concentrations of inorganic nitrogen (NH_3/NH_4^+) and phosphate 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 inserted in a personal computer program to facilitate the necessary calculations (see Appendix W).

Apparatus

The following apparatus is required (for details see Appendix B):

- 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 ≃ 25 mm),
- thermometer accurate to ± 0,5 degC,
- 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), and,
- mass scale accurate to ± 1 mg,
- stop watch.

Chemicals

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

The hydrochloric acid requires accurate standardisation, see section "Standardization of strong acid". With the sample volumes (for anaerobic digester samples), suggested in the testing procedure below, standardisation of the strong acid to about 0,08 N is recommended, using high purity sodium carbonate. The strong base solution (if required), e.g. sodium hydroxide, should be made up to approximately the same normality as the hydrochloric acid e.g. 0,08 to 0,1 N; standardisation 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 NBS standard buffer solutions, (1) 0,05 M potassium hydrogen 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).

Sample preparation

A choice has to be made with regard to:

(1) Sample size (ml) undiluted.

(2) Sample size (ml) diluted.

Sample size (undiluted): The undiluted sample has to be representative of the liquid to be tested. With an anaerobic reactor liquid usually a sufficiently large liquid volume is available for testing purpose. Filter the sample prior to the titration to (1) separate the solid from the liquid phase and (2) expel CO_2 from the sample (this has the important effect in that it raises 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). From the filtered undiluted sample a volume needs to be selected for titration.

The choice of undiluted sample volume is determined by (1) the dilution ratio required and (2) 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 excessive CO_2 loss during titration, (2) to reduce the total dissolved solids concentration to < 2500 mg/ℓ to allow calculation of the activity coefficients according to the Davies Equation (see Appendix A) and, (3) to reduce the temperature of the diluted sample to about 20 – 25°C. For anaerobic reactor liquids, generally the above conditions will be satisfied using a dilution ratio of 1:4. Normally a diluted sample volume of 50 mℓ is adequate (see below); this implies an undiluted sample volume of 10 mℓ. The dilution ratio is kept low to avoid multiplication effects of titration errors: C_T, H_2CO_3*alkalinity and SCFA are determined for the *diluted* sample by titration; 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 pH's 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, with the Radiometer probe, the tip and porous pin were 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.

5 pH point titration procedure

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

(1) Pipette 10 mℓ of the filtered sample into a 100 mℓ Erlenmeyer flask and pipette 40 mℓ distilled water to give a dilution of 1:4. The requirement 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 digestor 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).

(2) Insert thermometer and pH probe, stir gently for 15 seconds (s), take temperature reading, remove thermometer and stop stirring.

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

(4) Switch on stirrer and titrate sample from initial pH 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 initial pH to pH_1 and take pH_1

reading about 30 s after termination of stirring. The volume of titrant added to titrate from pH initial to pH_1 is designated V_{x1}.

(5) Repeat step (4) 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 to reach the respective lower pH points.

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

If the initial pH of the diluted sample is 6,7 ± 0,1 the initial pH 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_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_{x2} : pH_2 (5,90 ± 0,1)
V_{x3} : pH_3 (5,20 ± 0,1)
V_{x4} : pH_4 (4,30 ± 0,1)

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

$\mathbf{V_x}$: $\mathbf{pH_x}$
0 : initial diluted sample pH (pH_0)
$V_{x1} = 0$: pH_1 (after adding of strong base or if initial pH = 6,70 ± 0,1)
V_{x2} : pH_2 (5,90 ± 0,1)
V_{x3} : pH_3 (5,20 ± 0,1)
V_{x4} : pH_4 (4,30 ± 0,1)

The pH values located within the ± 0,1 limit ideally should be aimed for (and are 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 tolerance 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 its ideal value. If the sample is being "under titrated", step (4) 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 its ideal pH value.

Ancillary measurements

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 inorganic nitrogen total species concentration can be measured according to Standard Methods (1989), (for reference see Chapter 9). 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 in Chapter 4.

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, which can be measured according to Standard Methods (1989). 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 also presented in Chapter 4.

Total dissolved solids, TDS, or specific conductivity, SC, of undiluted sample

To calculate the dissociation constants of the different weak acid/bases (carbonate, SCFA, free and saline ammonia and inorganic phosphate) 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 (see Appendix A). The measurement of one of these parameters means additional experimental effort which may not be justified seeing that the algorithm employed to determine the SCFA and H_2CO_3*alkalinity is not very sensitive to variations in TDS or SC. Hence approximation of these latter two parameters may be justified in many cases. Accordingly measurement of TDS or SC may not be necessary for each filtered sample but done only daily or weekly, depending on the expected variations of the operating conditions of the reactor. This decision must be taken against the background of 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 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), 21°C (after dilution) and $N_T = P_T = 0$ mg/ℓ; Calculate SCFA and H_2CO_3*alkalinity values using various hypothetical values for TDS ranging from 1000 to 7000 mg/ℓ (in the undiluted sample). The results for these calculations are shown plotted in Fig V.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, equivalently SC).

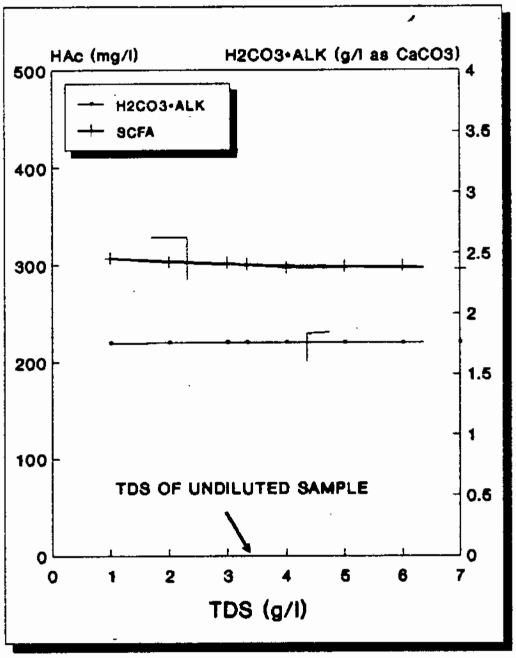


Fig V.1: Influence of changes in the total dissolved solids concentration (TDS) on the determination of SCFA and H_2CO_3*alkalinity with the aid of the 5 pH point titration method: SCFA and H_2CO_3*alkalinity values for a sample containing 300 mg/ℓ of HAc and 1740 mg/ℓ as $CaCO_3$ of H_2CO_3*alkalinity are calculated with hypothetical TDS concentrations ranging from 1000 to 7000 mg/ℓ.

Standardisation of strong acid

To obtain accurate results from the 5 pH point titration method it is of great importance to determine the normality (concentration of H^+ ions) of the strong acid titrant accurately. The standardisation method (used in developing the 5 pH point method) is based on the theory of the 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 standardised. From the mass 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.
In Chapter 2 the difficulties in identifying the H_2CO_3*equivalence point were highlighted and it was suggested to use the method developed by Gran (1952), (for reference see Chapter 3) to overcome the problems associated with this endpoint. The theory of Gran's method, more specifically the First Gran Function, was discussed in detail by Loewenthal et al. (1989), (for reference see Chapter 3) 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 standardisation of the strong acid involves the following steps: (1) preparation of strong acid, (2) Gran titration of carbonate solution, (3) application of the First Gran Function, (4) calculation of normality of strong acid.

Preparation of strong acid: In preparing the strong acid the following two aspects must be kept in mind (1) volume of undiluted sample and (2) the alkalinity of the undiluted sample. Both these factors influence the mass of strong acid required to titrate the sample from the initial pH to pH_4 (in the 5 pH point titration): If the normality is high small quantities of strong acid addition will cause great 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 a volume of 10 mℓ of an undiluted sample of a typical anaerobic digester a 0,08 N strong acid is recommended; to approximate this value one may dilute 35 mℓ of 33 percent hydrochloric acid with 5 ℓ of CO_2 free distilled water. This strong acid solution needs to be standardised using the Gran method.

Gran titration of carbonate solution: To standardise the above strong acid, a carbonate solution of known H_2CO_3*alkalinity is made up from CO_2 free distilled water and anhydrous Na_2CO_3: add 5,300 g $NaCO_3$ to 5 ℓ of CO_2 free distilled water; take 50 mℓ of this and perform a Gran titration, as follows: Titrate the sample with the made up strong acid to a pH of about 3,9 and record pH value 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 the 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_{x1}, for each of the V_x, pH_x pairs from,

$$F_{x1} = 10^{-pH_x} (V_s + V_x) \qquad (V.1)$$

where: F_{x1} = First Gran Function value,
pH_x = pH reading in pH region 3,9 to 3,4,
V_x = volume of strong acid required (mℓ) to titrate to pH_x,
V_s = initial sample volume (mℓ).

This gives the following F_{x1}, V_x pairs:

V_x	:	F_{x1}
13,32	:	0,0080
13,34	:	0,0100
13,37	:	0,0126
13,40	:	0,0159
13,44	:	0,0201

Plot F_{x1} 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_{x0}, (i.e. F_{x1} = 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_{x0} can be determined by applying a linear regression to the data set V_x vs F_{x1}; from the linear equation V_{x0} is calculated for $F_{x1} = 0$. Linear regression programs are readily available on many calculators and PC software; in the example presented here this approach was selected and V_{x0} was found to be 13,24 mℓ. With the volume of strong acid known that is required to titrate the carbonate solution of known H_2CO_3*alkalinity, 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 equals the mass of strong acid required to titrate to the H_2CO_3*equivalence point:

$$Ca \cdot V_{x0} = m \cdot V_s \tag{V.2}$$

where Ca = normality of strong acid (mol/ℓ),
V_{x0} = volume of strong acid required 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 (V.2):

$$Ca = m \cdot \frac{V_s}{V_{x0}} \tag{V.3}$$

For the above example of 5,300 $gNa_2CO_3/(5\ \ell$ distilled water), initial sample size 50 mℓ and V_{x0} = 13,24 mℓ, Ca can be calculated as follows:

$$Ca = 2 \cdot \frac{\begin{bmatrix}\text{mass of } Na_2CO_3 \\ (5{,}3\ g)\end{bmatrix}}{\begin{bmatrix}\text{Volume of dist.} \\ \text{water } (5\ \ell)\end{bmatrix}\begin{bmatrix}\text{molecular weight} \\ \text{of } Na_2CO_3\ (106\ g/mol)\end{bmatrix}} \cdot \frac{V_s}{V_{x0}}$$

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

Input data table for computer program

The H_2CO_3*alkalinity and SCFA of the undiluted sample is calculated from the titration and ancillary data obtained on the diluted sample (except for TDS and SC which are measured in the undiluted sample); a personal computer program is used for the calculations (The program source code is listed in Appendix W; a floppy disk with the source code and the executable file for the program is attached to the inside cover of the thesis).

The input data 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)
V_{x2} (mℓ)
V_{x3} (mℓ)
V_{x4} (mℓ)
Normality of strong acid (mol/ℓ)
Sample size (undiluted) (mℓ)
Sample size (diluted) (mℓ)
Temperature (deg Celsius)
TDS (mg/ℓ)
SC (mS/m)
N_T (total species con. of free and saline ammonia, mg/ℓ as N)
P_T (total species con. of inorganic phosphate, mg/ℓ as P)

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.

Output data table of computer program

(1) H_2CO_3*alkalinity of undiluted sample (mg/ℓ as $CaCO_3$)
(2) SCFA of undiluted sample (mg/ℓ as acetic acid)
(3) Correction for systematic pH error

Note: (1) 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 · C_T (mg/ℓ as $CaCO_3$), see Chapter 5. 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 digestor is showing signs of failure, in which event accuracy of SCFA and H_2CO_3*alkalinity no longer is a prime requirement).

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 was 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.

(2) The H_2CO_3*alkalinity and SCFA are the concentrations present in the undiluted sample and these are also 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 to be obtained, 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 Chapter 2.

Example

The following example demonstrates the data input and data output (after calculation of H_2CO_3*alkalinity, SCFA and the systematic pH error with the aid of the computer program) for data measured on a UASB reactor effluent treating lauter tun (brewery) waste.

Data input screen:

---

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
Sample size (undiluted) (mℓ).....	10
Sample size (diluted) (mℓ).....	50
Temperature (deg Celsius).....	24
TDS (mg/ℓ).....	
SC (mS/m).....	380
N_T (total species con. of free and saline ammonia, mg/ℓ as N).....	30
P_T (total species con. of inorganic phosphate, mg/ℓ as P).....	25

Data output screen:

H_2CO_3*alkalinity of undiluted sample
(mg/ℓ as $CaCO_3$)....................................1741

SCFA of undiluted sample
(mg/ℓ as acetic acid)................................6

systematic pH error............................– 0,02

APPENDIX W

SOURCE CODE LISTING OF PERSONAL COMPUTER PROGRAM FOR 5 pH POINT TITRATION METHOD

This appendix contains the listing of the source code for the source code file: 5ppt.pas. This file is available on the floppy disk which is attached to the inside of the thesis cover. The program is coded using Turbo Pascal Ver 4.0. It allows the calculation of H_2CO_3*alkalinity, SCFA (as A_T) and systematic pH measurement error from the data collected in the 5 pH point titration procedure. (For 5 pH point titration procedure, see Appendix V).

```
  program atct;

                         {5 pH POINT TITRATION PROGRAM}

  {This program calculates H2CO3-alkalinity and short-chain fatty acid
   concentrations in aqueous solutions containing the carbonate, SCFA,
   ammonium and phosphate subsystems. The total species concentrations
   of the ammonium and phosphate subsystems need to be entered into the
   computer program. The sample is titrated from its initial pH to four
   further pH values measured in the pH region:  6.7, 5.9, 5.2, 4.3. The
   program provides an estimate of a possible systematic pH measurement
   error in the event that the carbonate system dominates
   over the remaining weak acid/base subsystems.}

{PROGRAM START:}


 uses  crt;


 type phstr= string[50];


 var  pH0, pH1, pH2, pH3, pH4, delph, pHcorr,
      A1, B1, A2, B2,
      MCt1, MCt2, Ct2, Ct1, Ctcomp, MAt1, MAt2, At1, At2, CtAtratio,
      dil, vx1, vx2, vx3, vx4, vxfi, vxs, ca, temp, ktemp, TDS,
      logf1, logf2, pK1, pK11, pK2, pK22, pKn, pKnn, Nt,
      pKp, pKpp, Pt, pKa, pKaa, At,
      MH2CO3alksam, H2CO3alksam, Mcarb01, Mcarb02,
      counter, ionstr, number, vsdil, vsundil :real;

     again, move,intro, x, y, a, b, c, d : char;
     labels: array[1..18] of phstr;
     value: array[1..18] of real;
     I,II,posy: Integer;



 function log(x:real):real;
  begin
   log:=ln(x)/2.302585093;
  end;

 function tento(y:real):real;
  begin
   tento:=exp(y*ln(10));
  end;

 function mue (TDS,dil:real):real;
  begin
   mue:= 0.000025* (TDS/dil-20);
  end;

 function logf (mue,ktemp:real):real;
  begin
   logf:= - 1.825 * 1000000 * exp(-1.5*ln(78.3*ktemp)) * (sqrt(mue)/(1+
         sqrt(mue)) - 0.3*mue);
  end;

 function perH2CO3 (ph:real):real;
  begin
```

```
  perH2CO3:= 1/(1 + tento(-pk11)/tento(-ph) + tento(-pk11) * tento
               (-pk22)/tento(-2*ph));
 end;

function perHCO3 (ph:real):real;
 begin
  perHCO3:= 1/(tento(-ph)/tento(-pk11) + 1 + tento(-pk22)/tento
             (-ph));
 end;

function perCO3 (ph:real):real;
 begin
  perCO3:=1/(tento(-2*ph)/(tento(-pk11)*tento(-pk22)) + tento
             (-ph)/tento(-pk22) + 1);
 end;

function per(ph,pkk:real):real;
 begin
  per:=tento(-pkk)/(tento(-pkk)+tento(-ph));
 end;

function dH2CO3alk(pHf,pHs: real): real;
 begin
  dH2CO3alk:= perHCO3(pHf)-perHCO3(pHs) + 2 * (perCO3(pHf)-perCO3(pHs));
 end;

function dHAcalk(pHf,pHs: real): real;
 begin
  dHAcalk:= per(pHf,pkaa) - per(pHs,pkaa);
 end;

function MH2O (vxfi,vxs,pHfi,pHs: real):real;
 begin
  MH2O:= (vsdil+vxs)*tento(-pHs)/tento(logf1) - (vsdil+vxfi)*tento(-pHfi)/
         tento(logf1) + (vsdil+vxfi)*tento((pHfi-14)) - (vsdil+vxs)*
         tento((pHs-14));
 end;

function MNH3(pHf,pHs:real):real;
 begin
  MNH3:= Nt/(14000*dil) * vsdil * (per(pHf,pKnn) - per(pHs,pKnn));
 end;

function MHPO4(pHf,pHs:real):real;
 begin
   MHPO4:= Pt/(31000*dil) * vsdil * (per(pHf,pKpp) - per(pHs,pKpp))
 end;



procedure mark;
 begin
  textbackground(white);
  textcolor(black);
 end;

procedure unmark;
 begin
  textbackground(black);
  textcolor(white);
 end;

procedure box(x1,y1,x2,y2,a:integer);
 var
  II:integer;
 begin
  a:= x2-x1-1;
   FOR II:=1 to a DO         {draw the horizontal lines}
```

```
    begin
     GOTOXY(x1+1,y1);
     writeln(chr(196));
     GOTOXY(x1+1,y2);
     writeln(chr(196));
     x1:=x1+1;
    end;
  x1:=x1-a;
  a:=y2-y1-1;
   FOR II:=1 to a DO         {draw the vertical lines}
    begin
     GOTOXY(x1,y1+1);
     writeln(chr(179));
     GOTOXY(x2,y1+1);
     writeln(chr(179));
     y1:=y1+1;
    end;
  y1:=y1-a;
  GOTOXY(x1,y1);           {draw the corners}
  writeln(chr(218));
  GOTOXY(x1,y2);
  writeln(chr(192));
  GOTOXY(x2,y1);
  writeln(chr(191));
  GOTOXY(x2,y2);
  writeln(chr(217));
end; {procedure box}

procedure introscreen;
 begin
  clrscr; mark;
  box(10,3,70,20,1); unmark;
  box(24,6,56,8,1);box(22,5,58,9,1);
  box(26,10,55,16,1);
  GOTOXY(25,7); highvideo;
  write('FIVE pH POINT TITRATION METHOD');normvideo;
  GOTOXY(28,11);
  write('FOR DETERMINATION OF:');
  GOTOXY(28,13);
  write('(1) SHORT-CHAIN FATTY ACIDS');
  GOTOXY(28,15);
  write('(2) H2CO3*ALKALINITY');
  GOTOXY(11,16);
  GOTOXY(12,18);
  write('Copyright: UCT');
  box(10,22,41,24,1);
  GOTOXY(12,23);
  write('Press any letter to continue');
  intro := readkey;
 end;  {procedure introscreen}

procedure initlabel;
 begin
  labels[1]:='pHo (initial pH)................';
  labels[2]:='pH1 (after adding Vx1)..........';
  labels[3]:='pH2 (after adding Vx2)..........';
  labels[4]:='pH3 (after adding Vx3)..........';
  labels[5]:='pH4 (after adding Vx4)..........';
  labels[6]:='   Vx1 (ml).....................';
  labels[7]:='   Vx2 (ml).....................';
  labels[8]:='   Vx3 (ml).....................';
  labels[9]:='   Vx4 (ml).....................';
  labels[10]:='Normality of titrant (mol/l)....';
  labels[11]:='Sample size: undiluted (ml).....';
  labels[12]:='Sample size: diluted (ml).......';
  labels[13]:='Temperature (Celsius)...........';
  labels[14]:='TDS (mg/l)......................';
  labels[15]:='Specific Conductivity (mS/m)....';
  labels[16]:='Inorganic Nitrogen (mgN/l)......';
```

```
  labels[17]:='Inorganic Phosphorus (mgP/l)....';
 end;  {procedure initlabel}

procedure default_values;
 begin
  value[1]:= 7.36;
  value[2]:= 6.75;
  value[3]:= 5.95;
  value[4]:= 5.18;
  value[5]:= 4.29;
  value[6]:= 1.06;
  value[7]:= 3.50;
  value[8]:= 4.84;
  value[9]:= 5.40;
  value[10]:= 0.0728;
  value[11]:= 10;
  value[12]:= 50;
  value[13]:= 21;
  value[14]:= 3300;
  value[15]:= 488;
  value[16]:= 0;
  value[17]:= 0;
 end;  {procedure default_values}

procedure allocate_data;
 begin
  pH0:= value[1];
  pH1:= value[2];
  pH2:= value[3];
  pH3:= value[4];
  pH4:= value[5];
  vx1:= value[6];
  vx2:= value[7];
  vx3:= value[8];
  vx4:= value[9];
  ca:= value[10];
  vsundil:= value[11];
  vsdil:= value[12];
  temp:= value[13];
  TDS:= value[14];
  ionstr:= value[15];
  Nt:= value[16];
  Pt:= value[17];
 end;  {allocate_data}

procedure write_value;
 begin
  GOTOXY(37,2+posy);
   case posy of
          1,2,3,4,5,6,7,8,9: begin
                               writeln(value[posy]:1:2);
                             end;
                         10: begin
                              writeln(value[posy]:1:4);
                             end;
    11,12,13,14,15,16,17,18: begin
                              writeln(value[posy]:1:0);
                             end;
                             else
                             end;
 end;   {procedure write_value}

procedure screen;
 begin
  mark; box(50,2,79,8,1); unmark;
  box(50,10,79,19,1);
  box(50,10,59,19,1);
  box(50,10,79,13,1);
  GOTOXY(52,4);
```

```
  write(' 5 pH POINT TITRATION ');
  GOTOXY(52,6);
  write(' TITRATION INPUT DATA');
  GOTOXY(52,12);
  writeln('  KEY      FUNCTION');
  GOTOXY(52,14);
  writeln('   ',CHR(24),CHR(25),'    SELECT PARAMETER');
  GOTOXY(52,15);
  writeln('<enter>  ERASE VALUE');
  GOTOXY(52,16);
  writeln('<enter>  INSERT NEW VALUE');
  GOTOXY(52,17);
  writeln('   C     CALCULATION');
  GOTOXY(52,18);
  writeln('   Q     QUIT');
 end; {procedure sreeen}

procedure restore;
 begin
  clrscr;
  screen;
  mark; box(1,1,47,22,1); unmark;
   FOR I:= 1 to 17 Do
    begin
     GOTOXY(3,2+I);
     writeln(labels[I]);
     GOTOXY(37,2+I);
      case I of
             1,2,3,4,5,6,7,8,9: begin
                                 writeln(value[I]:1:2);
                                end;
                            10: begin
                                 writeln(value[I]:1:4);
                                end;
       11,12,13,14,15,16,17,18: begin
                                 writeln(value[I]:1:0);
                                end;

       else
       end;
    end;  {FOR}
  GOTOXY(3,2+posy);
  mark;
  write(labels[posy]);
  write_value;
  unmark;
 end;

procedure display;
 begin
  clrscr;
  screen;
  mark; box(1,1,47,21,1); unmark;
  FOR I:= 1 to 17 Do
   begin
    if I=1 then mark;
    GOTOXY(3,2+I);
    writeln(labels[I]);
    GOTOXY(37,2+I);
   case I of
          1,2,3,4,5,6,7,8,9: begin
                              writeln(value[I]:1:2);
                             end;
                         10: begin
                              writeln(value[I]:1:4);
                             end;
    11,12,13,14,15,16,17,18: begin
                              writeln(value[I]:1:0);
                             end;
   else
```

```
  end;
  if I=1 then unmark;
 end;
posy:=1;
REPEAT
repeat move := readkey until (upcase(move) in ['C','Q']) or (ORD(move)
                                           in [72,80,13]);
 case ORD(move) of
  80: begin
       GOTOXY(3,2+posy);
       writeln(labels[posy]);
       write_value;
       posy:=posy+1;
       if posy=18 then posy:=1;
       GOTOXY(3,2+posy);
       mark; writeln(labels[posy]); write_value; unmark;
      end;
  72: begin
       GOTOXY(3,2+posy);
       writeln(labels[posy]);
       write_value;
       posy:=posy-1;
       if posy=0 then posy:=17;
       GOTOXY(3,2+posy);
       mark; writeln(labels[posy]); write_value; unmark;
      end;
  13: begin
       repeat
        GOTOXY(37,2+posy);
        mark;
        writeln('        ');
        GOTOXY(37,2+posy);
        {$I-} read(number) {$I+}
       until ioresult = 0;
       value[posy]:= number;
       GOTOXY(37,2+posy);
       unmark;
       writeln('        ');
       write_value;
       case posy of
         14: begin
              value[posy+1]:= 0.1488*(value[posy]-20);
              if value[posy+1] < 0 then value[posy+1]:= 0;
              GOTOXY(37,posy+3);
              write('        ');
              GOTOXY(37,posy+3);
              write(value[posy+1]:1:0);
             end;
        15: begin
             value[posy-1]:= 6.72*value[posy]+20;
             GOTOXY(37,posy+1);
             write('        ');
             GOTOXY(37,posy+1);
             write(value[posy-1]:1:0);
            end;
       else
       end;
      end;
 else
 end;

 until upcase(move) in ['C','Q'];
 clrscr; writeln('Calculating, please wait');
end;  {procedure display}


procedure pK ;
 begin
  ktemp:= 273 + temp;
```

```
  if TDS < 20 then TDS:= 21;
  logf1:= logf(mue(TDS,dil),ktemp);
  logf2:= 4*logf1;
  pK1:= -1*(-356.3094 - 0.06091964*ktemp + 21834.37/ktemp + 126.8339
        *log(ktemp) - 1684915/(ktemp*ktemp));
  pK11:= pK1 + logf1;
  pK2:= -1*(-107.8871 - 0.03252849*ktemp + 5151.79/ktemp + 38.92561
        *log(ktemp) - 563713.9/(ktemp*ktemp));
  pK22:= pK2 - logf1 + logf2 ;
  pKa:= 1170.5/ktemp - 3.165 + 0.0134 * ktemp;
  pKaa:= pKa + logf1;
  pKn:= 2835.8/ktemp -0.6322 + 0.00123 * ktemp;
  pKnn:= pKn + logf1 ;
  pKp:= 1979.5/ktemp - 5.3541 + 0.01984 * ktemp;
  pKpp:= pKp - logf1 + logf2 ;
 end;  {procedure pK}

procedure deltapH;
 begin
  pH0:= pH0 + pHcorr;  pH1:= pH1 + pHcorr;  pH2:= pH2 + pHcorr;
  pH3:= pH3 + pHcorr;  pH4:= pH4 + pHcorr;
 end;

procedure atctcalculation;
 begin
  A1:= (vx2-vx1)*ca - MH2O(vx1,vx2,pH1,pH2) - MNH3(pH1,pH2) -
       MHPO4(pH1,pH2) + dHAcalk(pH1,pH2)/dHAcalk(pH3,pH4) *
       (MH2O(vx3,vx4,pH3,pH4) + MNH3(pH3,pH4) + MHPO4(pH3,pH4) -
       (vx4-vx3)*ca);
  B1:= dH2CO3alk(pH1,pH2) - dHAcalk(pH1,pH2)/dHAcalk(pH3,pH4) *
       dH2CO3alk(pH3,pH4);

  A2:= (vx4-vx1)*ca - MH2O(vx1,vx4,pH1,pH4) - MNH3(pH1,pH4) -
       MHPO4(pH1,pH4) + dHAcalk(pH1,pH4)/dHAcalk(pH3,pH4) *
       (MH2O(vx3,vx4,pH3,pH4) + MNH3(pH3,pH4) + MHPO4(pH3,pH4) -
       (vx4-vx3)*ca);
  B2:= dH2CO3alk(pH1,pH4) - dHAcalk(pH1,pH4)/dHAcalk(pH3,pH4) *
       dH2CO3alk(pH3,pH4);

 Ct1:= (A1/B1)/vsdil * 50000 * dil;           {using pH: 1-2; 3-4}
 Ct2:= (A2/B2)/vsdil * 50000 * dil;           {using pH: 1-4; 3-4}
 MCt1:= A1/B1;
 Ctcomp:= Ct1 - Ct2 ;
end;  {procedure atctcalculation}

procedure atct1;
 begin
  dil:= vsdil/vsundil;
  pK; delpH:= 0; pHcorr:=0; atctcalculation; counter:= 0;
  MAt1:= 1/dHAcalk(pH3,pH4) * ((vx4-vx3)*ca-MCt1*dH2CO3alk(pH3,pH4) -
  MNH3(pH3,pH4) - MHPO4(pH3,pH4) - MH2O(vx3,vx4,pH3,pH4));
  At1:= MAt1/vsdil * 60000 * dil;
  CtAtratio:= At1/Ct1;
  if Ctcomp = 0 then x:= 'd';
  if Ctcomp > 0 then x:= 'a';
  if Ctcomp < 0 then x:= 'b';
  if CtAtratio > 0.5 then x:= 'c';
   case x of
     'a': begin
           pHcorr:= -0.01;
            repeat
             delpH:= delpH - 0.01;
             deltapH; counter:= counter + 1;
             atctcalculation;
            until (Ctcomp < 0) or (counter > 19);
          end;
     'b': begin
           pHcorr:= 0.01;
            repeat
```

```
            delpH:= delpH + 0.01;
            deltapH; counter:= counter + 1;
            atctcalculation;
           until (Ctcomp > 0) or (counter > 19);
         end;
    else
    end;

  MAt1:= 1/dHAcalk(pH3,pH4) * ((vx4-vx3)*ca-MCt1*dH2CO3alk(pH3,pH4) -
         MNH3(pH3,pH4) - MHPO4(pH3,pH4) - MH2O(vx3,vx4,pH3,pH4));
  At1:= MAt1/vsdil * 60000 * dil;

  MAt2:= 1/dHAcalk(pH1,pH4) * ((vx4-vx1)*ca-MCt1*dH2CO3alk(pH1,pH4) -
         MNH3(pH1,pH4) - MHPO4(pH1,pH4) - MH2O(vx1,vx4,pH1,pH4));
  At2:= MAt2/vsdil * 60000 * dil;

  MH2CO3alksam:= MCt1 * (perHCO3(pH0) + 2 * perCO3(pH0));
  H2CO3alksam:= MH2CO3alksam / vsdil * dil * 50000 + (tento((pH0-14)) -
                tento(-pH0)/tento(logf1)) * 50000;
 end;  {procedure atct1}

procedure output;
 begin
  clrscr;
  mark; box(10,2,60,4,1);unmark;
  box(2,7,73,10,1); box(49,7,73,10,1);
  box(2,11,73,14,1);  box(49,11,73,14,1);
  box(2,15,73,18,1); box(49,15,73,18,1);
  GOTOXY(26,3);
  highvideo; write('OUTPUT DATA '); normvideo;
  GOTOXY(5,8);
  write('H2CO3*alkalinity (undiluted sample)');
  GOTOXY(58,8);
  highvideo; write(H2CO3alksam:3:0); normvideo;
  GOTOXY(5,9);
  write('(mg/l as CaCO3)');
  GOTOXY(5,12);
  write('Short-chain fatty acids (undiluted sample)');
  GOTOXY(58,12);
  if At1 > 0 then
   begin
    highvideo; write(At1:3:0); normvideo;
   end
   else
   begin
    highvideo; write('0 ');normvideo;
   end;
  GOTOXY(5,13);
  write('(mg/l as acetic acid)');
  GOTOXY(5,17);
  write('Systematic pH error');
  GOTOXY(58,17);
  highvideo; write(delpH:1:2); normvideo;
  if counter = 20 then
   begin
    GOTOXY(5,16);
    write('The titration data indicate a systematic');
    GOTOXY(5,17);
    write('pH error > 0.2; Check pH probe calibration');
    GOTOXY(58,17);
    write('      ');
   end;
  if x = 'c' then
   begin
    GOTOXY(5,16);
    write('Correction for systematic pH error');
    GOTOXY(5,17);
    write('is not possible for this titration');
    GOTOXY(60,17);
```

```
     write('      ');
    end;
  end; {procedure output}

 procedure exitbox;
  begin
   repeat;
    box(5,20,60,24,1); box(49,20,60,22,1);
    box(5,22,60,24,1); box(49,22,60,24,1);
    GOTOXY(7,21);
    write('Do you wish to do a further calculation ?');
    GOTOXY(53,21);
    highvideo; write('Y'); normvideo; write('/'); highvideo; write ('N');
    normvideo;
    GOTOXY(7,23);
    write('Do you wish to quit the program ?');
    GOTOXY(54,23);
    highvideo; write('Q'); normvideo;
    again:=readkey; again:=upcase(again);
   until again in ['Y','N','Q'];
   clrscr;
  end;  {procedure exitbox}



  begin                 { of main program}

    introscreen;
    again:= 'Y';
    default_values;

    repeat; clrscr; initlabel; display;
     if upcase(move) in ['C'] then
      begin
       allocate_data; atct1; output; exitbox;
      end
      else
      begin
       clrscr; again:= 'N';
      end;
    until again in ['N','Q'];

 end.   {of main program}

{PROGRAM END.}
```

APPENDIX X

INSTRUCTIONS TO RUN THE EXECUTABLE FILES OF 4 AND 5 pH POINT TITRATION PERSONAL COMPUTER PROGRAMS

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 disk attached to the inside of the thesis cover
- To initiate the execution of the program for the ***4 pH point titration***, at the DOS prompt A:> the user must type

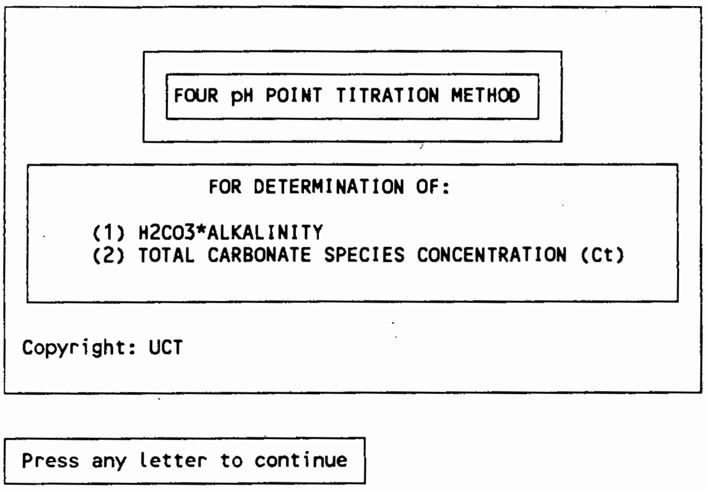
  4ppt.exe

  and then press the carriage return key (**<RETURN>**, **<C/R>**, **<ENTER>** key on different keyboards).
- To initiate the execution of the program for the ***5 pH point titration***, at the DOS prompt A:> the user must type

  5ppt.exe

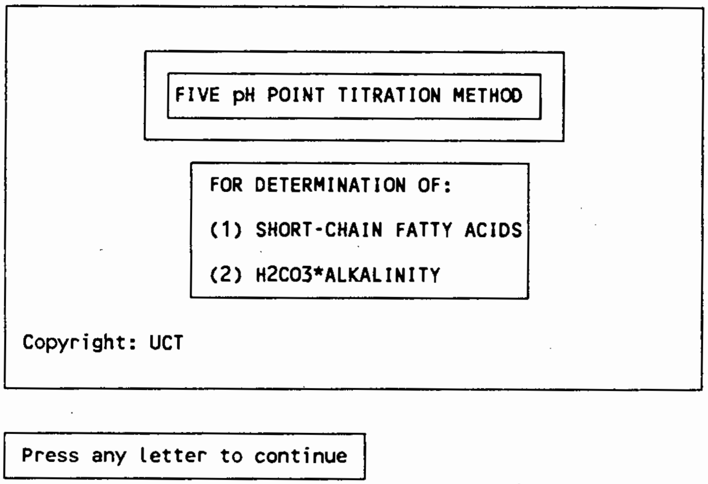
  and then press the carriage return key.
- The program will be loaded into memory from disk. Depending on the choice of programs one of the title pages shown in Table X.1 and Table X.2 respectively, will appear on the screen:

Table X.1: Title page for the 4 pH point titration method:



```
FOUR pH POINT TITRATION METHOD

FOR DETERMINATION OF:

(1) H2CO3*ALKALINITY
(2) TOTAL CARBONATE SPECIES CONCENTRATION (Ct)

Copyright: UCT

Press any letter to continue
```

Table X.2: Title page for the 5 pH point titration method:



```
FIVE pH POINT TITRATION METHOD

FOR DETERMINATION OF:

(1) SHORT-CHAIN FATTY ACIDS

(2) H2CO3*ALKALINITY

Copyright: UCT

Press any letter to continue
```

Hard disk system:

- Boot up the system from the hard disk
- To initiate the execution of the program for the ***4 pH point titration***, at the DOS prompt C:> the user must type

  a:4ppt.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:> the user must type

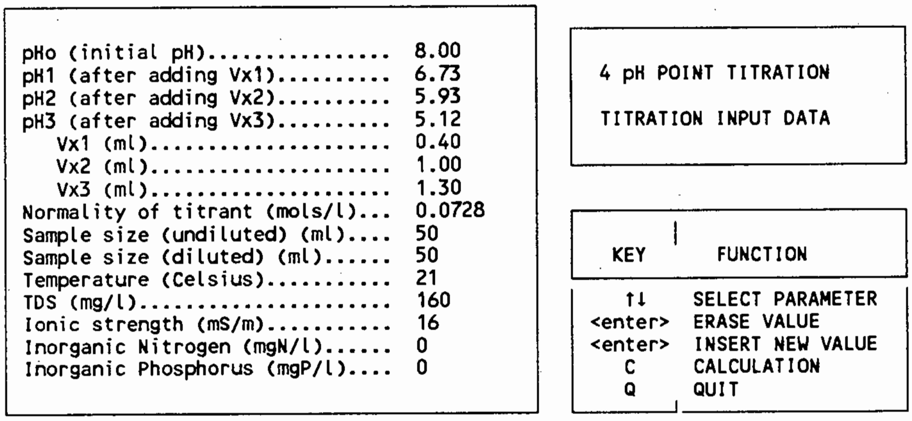
  a:5ppt.exe

  and then press the carriage return key.
- The program will be loaded into memory from disk. Depending on the choice of programs one of the above title pages will appear on the screen.

Data input by the user

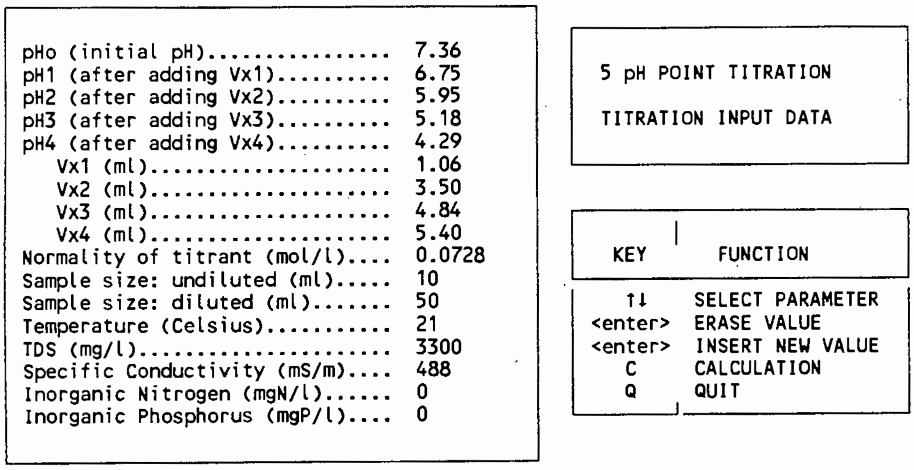
With the title page present on the screen a data input table will appear on the screen if any letter on the keyboard is being pressed. For the 4 pH point titration program the data input table shown in Table X.3 will appear on the screen. For the 5 pH point titration program the input data table shown in Table X.4 will appear.

Table X.3: Data input table for 4 pH point titration method.



```
pHo (initial pH)................  8.00          4 pH POINT TITRATION
pH1 (after adding Vx1)..........  6.73
pH2 (after adding Vx2)..........  5.93          TITRATION INPUT DATA
pH3 (after adding Vx3)..........  5.12
   Vx1 (ml).....................  0.40
   Vx2 (ml).....................  1.00
   Vx3 (ml).....................  1.30
Normality of titrant (mols/l)...  0.0728
Sample size (undiluted) (ml)....  50
Sample size (diluted) (ml)......  50             KEY     FUNCTION
Temperature (Celsius)...........  21
TDS (mg/l)......................  160            ↑↓     SELECT PARAMETER
Ionic strength (mS/m)...........  16           <enter>  ERASE VALUE
Inorganic Nitrogen (mgN/l)......  0            <enter>  INSERT NEW VALUE
Inorganic Phosphorus (mgP/l)....  0               C     CALCULATION
                                                  Q     QUIT
```

Table X.4: Data input table for 5 pH point titration method.



```
pHo (initial pH)................ 7.36
pH1 (after adding Vx1).......... 6.75
pH2 (after adding Vx2).......... 5.95
pH3 (after adding Vx3).......... 5.18
pH4 (after adding Vx4).......... 4.29
   Vx1 (ml)..................... 1.06
   Vx2 (ml)..................... 3.50
   Vx3 (ml)..................... 4.84
   Vx4 (ml)..................... 5.40
Normality of titrant (mol/l).... 0.0728
Sample size: undiluted (ml)..... 10
Sample size: diluted (ml)....... 50
Temperature (Celsius)........... 21
TDS (mg/l)...................... 3300
Specific Conductivity (mS/m).... 488
Inorganic Nitrogen (mgN/l)...... 0
Inorganic Phosphorus (mgP/l).... 0
```

```
5 pH POINT TITRATION

TITRATION INPUT DATA
```

```
  KEY       FUNCTION

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

Both data input tables contain 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 (1) press the carriage return key to erase the existing value, (2) type in the new value, and (3) 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. In order to invoke the calculation part of the program the user must type the letter **C**. After termination of the calculations the output data table (table of result) will appear on the screen.

For the 4 pH point titration program two different output tables may be obtained depending on the magnitude of the systematic pH error: if the systematic pH error is smaller than 0,2 the output table shown in Table X.5 will appear. If the systematic pH error is greater than 0,2 the output table shown in Table X.6 will appear.

Table 5: Output data table for 4 pH point titration program with a systematic pH error smaller than 0,2.

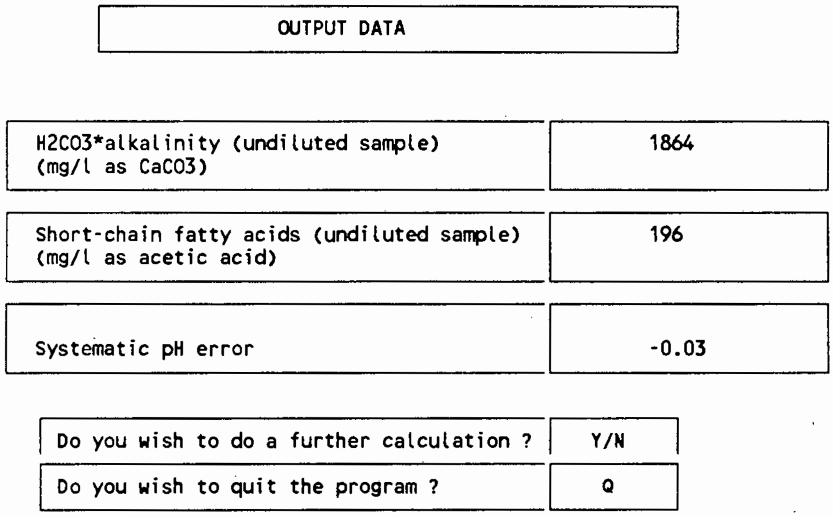
```
TABLE OF RESULTS

H2CO3*alkalinity (undiluted sample)          100
(mg/l as CaCO3)

Total carbonate species (undiluted sample)   102
(mg/l as CaCO3)

Estimate of systematic pH error              -0.03

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

Table 6: Output data table for 4 pH point titration program with a systematic pH error greater than 0,2.

```
TABLE OF RESULTS

H2CO3*alkalinity (undiluted sample)
(mg/l as CaCO3)

Total carbonate species (undiluted sample)
(mg/l as CaCO3)

The titration data indicate a systematic pH
error > 0,2; please check pH probe calibration

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

Similarly, for the 5 pH point titration program two different output tables will be obtained: if the systematic pH error is smaller than 0,2 the output table shown in Table X.7 will appear. If the systematic pH error is greater than 0,2 the output table shown in Table X.8 will appear.

Table 7: Output data table for 5 pH point titration program with a systematic pH error smaller than 0,2.



```
                 OUTPUT DATA

H2CO3*alkalinity (undiluted sample)          1864
(mg/l as CaCO3)

Short-chain fatty acids (undiluted sample)   196
(mg/l as acetic acid)

Systematic pH error                          -0.03

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

Table 8: 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)

Short-chain fatty acids (undiluted sample)
(mg/l as acetic acid)

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
```

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