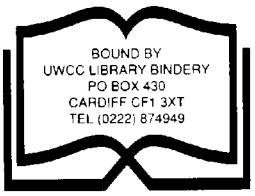
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Monitoring the Stability of Anaerobic Digestion Using a Novel On-line Bicarbonate Alkalinity Monitor.

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A dissertation submitted to the University of Glamorgan
in part fulfilment for degree of Doctor of Philosophy.

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ABSTRACT.

In many biological reactors' bicarbonate ions are the major species determining pH buffering capacity, or alkalinity. In anaerobic digesters the bicarbonate levels should be within 10 to 50mM to ensure stable operation. Bicarbonate concentration in wastewater treatment processes is routinely measured off-line by titration with standard acid to a set pH value. However along with the bicarbonate/carbonate system, the phosphate, ammonia, sulphides and volatile fatty acids systems are present in anaerobic process. These systems can exert a significant influence on the accuracy of bicarbonate titration's to a set pH.

An overload of 4.7 to 13.6 $kgCODm^{-3}d^{-1}$ administered to a $5m^3$ pilot scale anaerobic filter reactor showed that bicarbonate alkalinity, measured off-line by titration responded rapidly to the organic overload, decreasing by 10% after only 1 hour of the overload initiation. The propionic acid concentration (often regarded as the best indicator of instability in anaerobic digestion) increased from 170ppm to 190 ppm in the same period, which corresponds to an increase of 12%.

At present the use of anaerobic digestion as a waste treatment method is partly limited because of the lack of reliable control procedures. This thesis introduces a simple on-line instrument for direct determination of bicarbonate concentration especially for automatic control of anaerobic digesters. The proposed method is based on a continuous flow rate measurement of carbon dioxide evolved from a continuous stream of sampled ($<15cm^3min^{-1}$) solution after saturation with gaseous CO_2 and subsequent acidification with excess acid. Measurement of bicarbonate in this way eliminates the interferences of the phosphate, ammonia, sulphides and volatile fatty acids systems and removes the need for a pH probe which are subject to fouling.

The BA monitor was calibrated using sodium bicarbonate solutions (0.01-0.065M) and was shown to have an accuracy of ±5%. The device was also tested on effluent from an anaerobic digester operating on ice-cream waste supplemented with sodium bicarbonate in the range 0.02-0.04moll^{-1}. The results compared favourably with titrimetric measurements extensively used to determine bicarbonate alkalinity with an accuracy of ±95%. At this stage of development of the BA monitor the evolved CO_2 was measured manually using a digital bubble meter.

An on-line high precision low flow gas meter is also introduced in this thesis. The meter used a highly sensitive pressure transducer that meant the meter could operate with a small back pressure. Calibration of the gas meter showed an accuracy better than ±95% in the range 0.1 to 14cm^3 min^{-1}. The newly developed gas meter was built into the on-line BA monitor so that the CO_2 evolved from the acidification chamber of the BA monitor could be measured accurately on-line. The signals from the gas meter and the temperature sensor in the BA monitor were interfaced with a data acquisition program (MAC, University of Glamorgan UK) which was written specifically for work presented in this thesis.

The BA monitor was further developed, using the same principles of operation as the first device. A continuous stream (15cm^3 min^{-1}) of effluent to be monitored was saturated with gaseous CO_2, acidified by the addition of excess acid in a separate chamber, and the rate of CO_2 evolution was continuously measured by the developed sensitive on-line gas meter. The performance of the BA monitor was satisfactory for wastewater treatment process control applications, with linearity in the range 5-50 mM HCO_3^-, a response time in the order of 30 minutes, and accuracy of the order of 7% in the concentration range 5 to 50 mM sodium bicarbonate. The prototype BA monitor gave results which was at best 99.8% of the expected influent (with standard bicarbonate of 1500 mg$CaCO_3$l^{-1} in the

influent) and at worst 90.4% with standard bicarbonate of 400mg$CaCO_3l^{-1}$, acetate 300mg$l^{-1}$and propionic acid 300mgl^{-1}.

Using a 10 litre anaerobic filter digester operating on ice-cream wastewater with a COD of around 4500mgl^{-1}, on-line measurements were made of bicarbonate alkalinity, pH, gas production and $\%CO_2$ and hydrogen concentration in the biogas during periods of organic overload. The anaerobic filter was operated routinely at a volumetric organic loading rate B_V = 5 to 6 kgCOD$m^{-3}d^{-1}$, (influent flow rate 10 cm^3min^{-1}, hydraulic retention time 0.7 days). Treatment efficiency measured as COD destruction averaged 73%, with a biogas yield between 0.24 - 0.33m^3kg^{-1}COD added. A series of organic overloads was applied to the filter, doubling or trebling the feed concentration of the feed for 8 hours and keeping all the other parameters constant. The bicarbonate alkalinity monitor was shown to be an effective instrument for monitoring instability of anaerobic digestion, and a useful tool for early warning of overloading. The change in the bicarbonate alkalinity measured before the overload and during overload/recovery ($\Delta BA = BA_{steady\ state} - BA_{transient}$) was plotted against figures for the increase in volatile fatty acids measured ($\Delta VFA = VFA_{transient} - VFA_{steady\ state}$) to show the change in bicarbonate alkalinity was equivalent to the change in volatile fatty acid concentration, on a molar basis. To test the validity of this correlation, data for three overloads were compared.

So, in digesters fed with wastewaters containing low potential alkalinity, the BA monitor allows indirect on-line determination of variations in volatile fatty acid concentration. Finally, used in conjunction with a sensor that measures CO_2 in the gas, it allows an indirect but accurate determination of pH in those solutions where fouling of electrodes is severe.

ABBREVIATIONS.

AF	Anaerobic filter.
$Alk_{5.75}$	Bicarbonate alkalinity measured by titration with acid to pH 5.75.
ASCS	Automatic sample collection system.
BOD	Biological oxygen demand.
COD	Chemical oxygen demand.
CSTR	Continuously stirrer tank reactor.
EGM	Electrode gas meter.
FAS	Ferrous ammonium sulphate.
GLC	Gas liquid chromotography.
GMS	Gas metering system.
HPLC	High performance liquid chromotography.
IA	Intermediate alkalinity (alkalinity measured by titration with acid from pH 5.75 to pH 4.3).
IC	Inorganic carbon.
PA	Partial alkalinity (alkalinity measured by titration with acid to pH 5.75).
PID	Proportional intergral differential.
RA	Residual alkalinity
SV	Solenoid valve.
TA	Total alkalinity measured by titration with acid to pH 4.3.
TBA	True bicarbonate alkalinity.
TOC	Total organic carbon.
TVFA	Total volatile fatty acid.
UASB	Upflow anaerobic sludge blanket.
uVFA	Undissociated volatile fatty acid.
VFA	Volatile fatty acid.
DAS	Data acquisition system.
HRT	Hydraulic retention time.
LR	Loading rate.

1. INTRODUCTION.

The treatment of industrial and municipal wastes by anaerobic digestion has experienced a revitalisation in the last 15 years. The anaerobic process is increasingly viewed as a practical and economical wastewater process which can reduce dependence on aerobic treatment, land filling and incineration. This renewed interest in the anaerobic process is a result of a number of technical and economic factors described below.

A greater understanding of the mass transfer in the anaerobic system led to the introduction of a new generation of reactors, the high rate anaerobic reactors. The design of these reactors enabled considerable reduction in the hydraulic retention times, without the associated loss of biomass concentration from the reactor (bacterial wash-out), a problem associated with conventional continuously stirrer anaerobic digesters. The most common types of high rate reactor design are the upflow anaerobic sludge blanket (UASB), the anaerobic filter (AF) reactor and the expanded/fluidised bed (EB/FB) reactors. The importance of the choice of reactor systems should not be understated, as the reactor configuration can have a profound effect on the treatment efficiency. The arrival of this new generation of high rate reactors was the catalyst for much of the renewed interest in anaerobic digestion as an effective alternative to aerobic treatment. The advantages and disadvantages of the different reactor configurations are reviewed by van den Berg and Kennedy (1983), Hickey *et al.* (1990), and Weiland and Rozzi (1990).

There are two important economic advantages that arise as a result of the reduction in size on the treatment plant. Firstly the initial capital outlay for the construction of the treatment plant can be reduced significantly reducing the pay back time. Secondly less space is required, which is important because space at industrial complexes is usually appropriated for increase in the production rather than waste treatment. So the cost of treatment has to be competitive both with the increased revenue that can be generated from the expansion of production and the off-site treatment of waste.

One of the most important factors in the choice of any wastewater treatment process is the running costs. The running cost for high rate anaerobic process can be significantly less than an activated sludge process. A high percentage, up to 66%, of the total running cost of an activated sludge process arises from the production of large quantities of biomass sludge. Major savings in the handling, transport and treatment cost can be made by removal of the water in the sludge. There are variety of ways in which water can be removed including, clarifiers, lagoons, vacuum filters and centrifuges. Typically however sludge settlement using a clarifier and then the remaining water is removed either by pressing using a belt press or drying in sludge pits. The sludge is then ready for disposal either by injection into or spreading on land in accordance with regulations, dumping to landfill, or treatment using anaerobic digestion and in some cases incinerated. Anaerobic bacteria however are much less efficient at utilising their substrate for cell growth and therefore problem of sludge production is much less.

However in an efficiently operating anaerobic digester available energy is produced as an end product in the form of methane gas. Methane, a high energy fuel is produced proportionately to the organic load destroyed by anaerobic bacteria. This provides a renewable source of energy that can be used on-site, for example to generate heat or electricity. The production of methane can be the primary objective in countries where electricity or natural gas is unavailable or too expensive. In most developed countries where electricity is cheap, the energy that can be produced from biogas has no practical value, so biogas is often just flared off. However the utilisation of the energy from wastes is becoming increasingly more popular with heightened sensitivity to global environmental problems. For example the Brazilian government has legislated against the use of fossil fuels in harvesting and transport of sugar cane, therefore the industry uses biogas (methane) from the anaerobic digestion of the sugar cane husks.

With advances in the anaerobic process the full potential of anaerobic digestion is beginning to be realised. Research involving the expertise of microbiologists, engineers and mathematicians world-wide has resulted in the continued updating of process

fundamentals and greater appreciation of the complexity and diversity of the process. However considering the advantages of anaerobic digestion, anaerobic industrial waste water treatment is less widespread than would be expected. Reluctance of industrialists to change from well-established ways of wastewater treatment, such as aerobic treatment, has been common in the past and partly responsible for slow implementation of anaerobic digesters for industrial waste water treatment. This problem is especially severe in the United Kingdom. A large proportion of the blame can be attributed to the unsolved problem of process stability and control in anaerobic digestion. Although the complexities and capacities of anaerobes are largely understood, and improved reactor design has lead to more economic and higher performance anaerobic reactors, there are still few reliable techniques for monitoring and controlling the unique capabilities of anaerobic digestion. The anaerobic digestion process is still thought of as an unstable and an unreliable waste treatment process.

The stability of the process is dependant on the critical balance that exists between the symbiotic growth rates of the principal metabolic groups of bacteria i.e. acid forming bacteria, obligate hydrogen producing acetogens and methanogens. Instability may result from a variety of environmental perturbations, such as increases in the organic loading rate, addition of toxic chemicals and changes from the optimum operating temperature are some of the common causes of process inhibition in anaerobic digestion.

In the event of an organic overload, (a common cause of instability in industrial waste water anaerobic treatment) the slow growing methanogens and obligate hydrogen producing acetogens become less able to utilise the volatile fatty acids (VFA) produced by acidogenesis. As the VFA concentration increases in the reactor the pH begins to fall, subsequently the methanogens are inhibited further as they only function in the pH range of 6.5-7.5. If this situation is allowed to continue without corrective action the process eventually fails completely resulting in a 'sour' reactor.

The digesters' alkalinity buffers against changes in pH and plays a vital role in the stabilisation of biotechnological processes providing the necessary environment for bacterial reproduction and conversion of the organic waste. Mono-hydrogen carbonate concentration (bicarbonate alkalinity) is the main contributor to the buffering capacity in the pH range of 6.5-7.5. Bicarbonate alkalinity is typically determined by acid titration to a set pH endpoint. However VFAs such as acetic and propionic acid contribute to the buffering capacity in the pH range close to their pK values, 3.5 to 5.7 and 3.9 to 5.9 respectively. Under stable anaerobic digestion conditions there is no additional contribution to the buffering capacity from VFAs. Hence determination of bicarbonate alkalinity of anaerobic effluents using pH end point titration which are below 5.9 will be subject to interferences from VFAs with an over estimation of bicarbonate alkalinity. For more explanation about the problems of set point bicarbonate determinations and a review of appropriate techniques and instrumentation for monitoring bicarbonate alkalinity in anaerobic digestion see section 2.3.2.

If there is insufficient buffering capacity within an anaerobic reactor, the anaerobic process can be de-stabilised by organic overload or other disturbances resulting eventually in a 'sour' digester. Restoration of the normal operation from a 'sour' reactor condition is time consuming and expensive. Production can be interrupted if the waste is unable to be stored or treated elsewhere and the economic consequences are clearly damaging. It is therefore vital that the inherent instability of the anaerobic process should be controlled during organic overloading if the anaerobic digestion process is to be competitive in the industrial market place.

Even with the scientific advances in the field of anaerobic digestion, it is common for industrial scale reactors to be operating well within their optimum organic loading limits. Often far larger digesters are constructed than necessary to reduce the effect of overloading. This misguided solution to instability in anaerobic digestion is due to a general lack of confidence in the reliability and stability of the process and the absence of an adequate control system. Consequently the initial financial outlay can be as much as

ten times greater than for a smaller controlled digester treating the same quantity of waste but operating at a higher loading rate. Hence there is a distinct need for a control system for anaerobic digestion incorporating an instrument that is capable of monitoring a parameter which is sensitive to process instability.

Identification of kinetic parameters sensitive to changes in stability and the production of well-defined mathematical model controllers have been investigated in recent years. However less work has been concerned with the on-line or automated monitoring of such parameters. There are even fewer documented cases of successful on-line monitoring and control systems for full scale anaerobic digesters operating on industrial wastewaters. Implementation of on-line data acquisition and control systems to the anacrobic process has been impeded by the lack of sensors for on-line measurement of instability and control variables of the anaerobic process. Therefore precise determination of the causes of instability of anaerobic digestion has been difficult during operation. A control system requires on-line monitoring of a good control variable, preferably one in the environment in which the anaerobic micro-organisms are contained, i.e. the liquid phase (Graef and Andrews 1974).

On-line gas composition measurement involves relatively straight forward techniques and the hardware to measure the methane, carbon dioxide, hydrogen and carbon monoxide content have been available for some time. However, although these gaseous parameters are related to the stability of the anaerobic bacteria, they are an effect of instability and not the cause, therefore the bacteria may have already been inhibited before any significant change has occurred in the gas composition. The build up of undissociated volatile fatty acids (uVFA's) in the liquor phase has been established to be responsible for the inhibition of the methanogenic bacteria and the whole process. Sophisticated automated gas chromatography equipment does exist which could be used to monitor individual VFA concentration, but it is expensive and operation requires frequent maintenance and sample preparation (e.g. fine filtration or extraction).

The importance of bicarbonate concentration to the stability of the anaerobic process was identified early in the development of anaerobic waste treatment by McCarty (1964), Pohland and Engstrom (1964) and Andrews (1969). More recently Rozzi *et al.* (1985) and van Breusegen *et al.* (1990) reported that bicarbonate alkalinity could be used to great effect as a process control variable. The concentration of bicarbonate alkalinity is inversely proportional to the VFA concentration, so the bicarbonate alkalinity present in an anaerobic digester effectively neutralises the inhibitory effect of the VFAs. An on-line bicarbonate monitor would be a useful laboratory research tool as well as an invaluable instrument for controlling industrial size anaerobic digesters. Prototypes of semi-automatic devices have been constructed and run for a short period of time on 'synthetic' wastes containing low fat and suspended solids concentrations. On-line monitoring of alkalinity has not been successful using real anaerobic digester liquors.

Therefore the aims of this thesis are to construct an inexpensive, robust on-line instrument and establish its use for monitoring the bicarbonate alkalinity of anaerobic effluent.

The design requirements of the bicarbonate monitor are;

1) The response time of the BA monitor should be of the order of the bicarbonate alkalinity changes occurring in the digester during organic overloading.

2) The instrument should be reliable and accurate enough for implementation in a control system.

The BA monitor will be used to show that changes in bicarbonate alkalinity are a useful indicator an anaerobic digester stability during overload in comparison with other instability parameters already mentioned above.

2. LITERATURE REVIEW.

2.1. MICROBIOLOGY AND BIOCHEMISTRY OF ANAEROBIC DIGESTION.

The success of anaerobic digestion is reliant on the complex co-ordinated metabolic activities of the different populations of micro-organisms in the process.

Pioneering research into the biochemical and microbiological characteristics of anaerobic bacteria has enabled a more accurate idea of how the process can be controlled. The different populations of anaerobic bacteria can be thought of as a consortium that exercises a degree of self regulation, a function of the complex interdependency that exists within the consortium. However the self regulation of the process stability is easily disrupted by a variety of physical and chemical factors.

The process of anaerobic digestion can be thought of as six metabolic stages as outlined below:

1. HYDROLYSIS OF POLYMERS.
    a) Proteins.
    b) Carbohydrates.
    c) Lipids.
2. FERMENTATION OF AMINO ACIDS AND SUGARS.
3. ANAEROBIC OXIDATION OF LONG CHAIN FATTY ACIDS.
4. ANAEROBIC OXIDATION OF INTERMEDIATE PRODUCTS SUCH AS VOLATILE FATTY ACIDS (EXCEPT ACETATE).
5. CONVERSION OF ACETATE TO METHANE.
6. CONVERSION OF HYDROGEN AND CARBON DIOXIDE TO METHANE.

The process can be simplified further into four main bio-conversions; hydrolysis, acidogenesis, acetogenesis and methanogenesis. The interactions of these four bio-

conversions involved in the conversion of glucose to methane and carbon dioxide are illustrated in a schematic diagram taken from Mosey 1983 (see Figure 2.1).

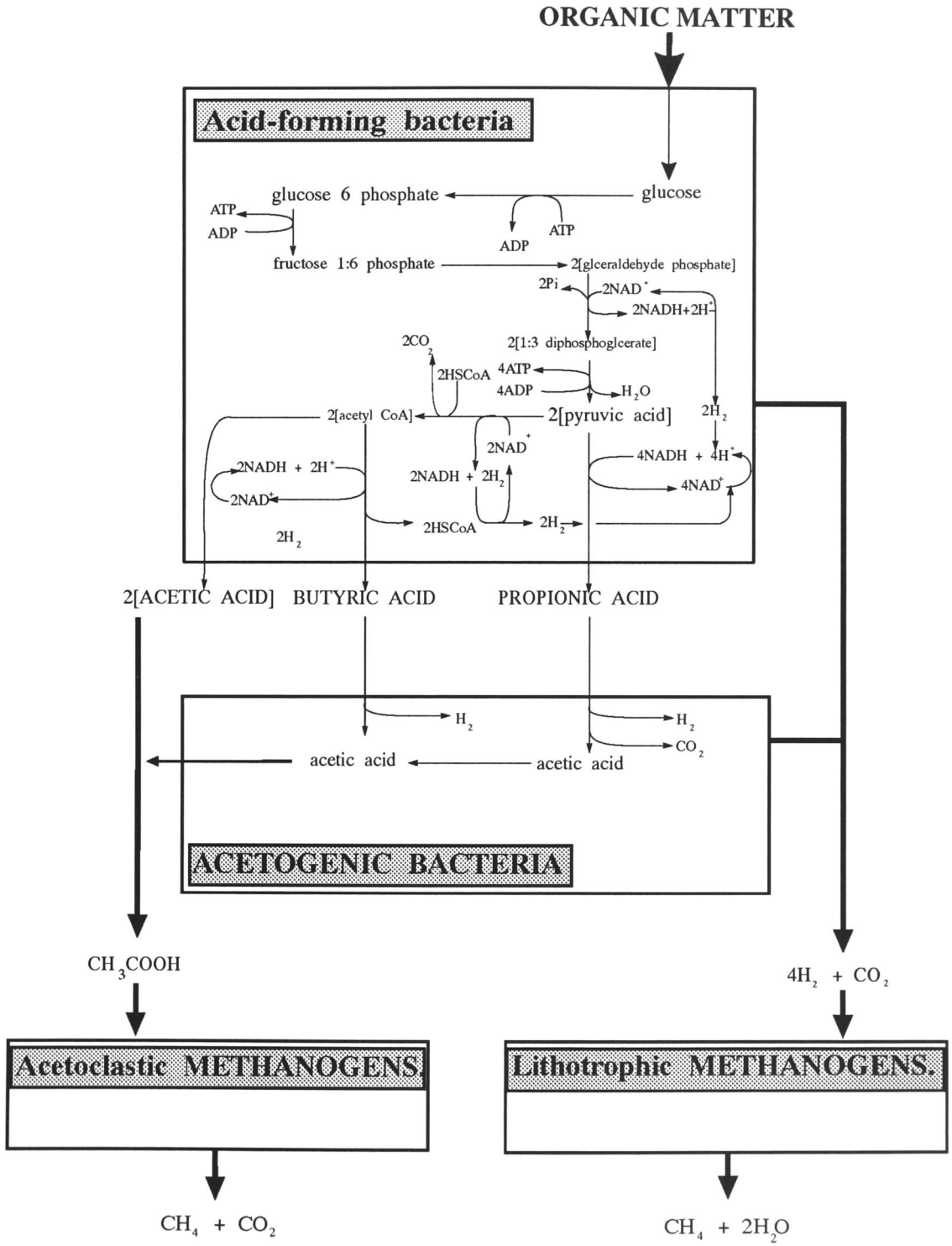


Figure 2.1 The metabolic pathways of anaerobic digestion (taken from Mosey 1983).

The role of the main bacteria groups in the complex interdependent anaerobic process is described in the following sections.

2.1.1 Acid forming bacteria.

The acid-forming bacteria consist of the hydrolytic and acidogenic bacteria which are a complex and versatile group within the anaerobic consortium. Before microbial assimilation can occur exo-enzymes such as proteases, lipases, amylases, cellulases and pectinases have respectively to break down proteins, lipids, homo and hetero-polysaccharides in the waste. The products of hydrolysis are sugars, amino acids and carboxylic acids. Substrate molecules produced in hydrolysis are rapidly fermented, e.g. via the Embden Meyernoff pathway. Hobson *et al.* (1980) suggested that hydrolysis was unlikely to be a rate-limiting step of the whole anaerobic process. However the rate of hydrolysis is first order, so it is proportional to the substrate concentration. Therefore if hydrolysis is inhibited then the bacteria that utilise the products of hydrolysis are subsequently inhibited, hence hydrolysis rates could define circumstances under which destabilization may occur. Hydrolysis is affected by the pH, cell residence time (Verstraete *et al.* 1981) and the waste content of the reactor.

The major intermediate of acidogenesis is pyruvate yielding acetic, butyric and propionic acids, together with H_2, CO_2 and ATP (see Figure 2.1). Thauer *et al.* (1977) established that pyruvate was the starting point for acid fermentation reactions and that the availability of the energy for the fermentative and the hydrogen producing acetogens was dependant on the end products of acidogenesis. It is clear from Table 2.1 that more energy can be recovered by the acidogens if they oxidise pyruvic acid to acetic acid and carbon dioxide. However the preferred thermodynamic production of acetic acid is only possible if the partial pressure of H_2 is sufficiently low. The change in Gibbs free energy during the oxidation conversion of NADH to NAD^+ and H_2 becomes negative if the pH_2 is below 10^{-3} atmospheres. Hence the acidogenesis equilibrium is pulled towards the

production of H_2, CO_2 and acetic acid. However high hydrogen partial pressures will result in the increased production of products which are more reduced than acetate such as propionic and butyric acids. An increase of pH_2 to 10^{-4} atmospheres results in NADH ferredoxin oxido-reductase process (responsible for allowing the conversion of pyruvic acid to acetic acid) becoming energetically unfavourable. The net result is the reduced production of ATP molecules available to the bacteria. Table 2.1 shows the reduced energy yield per glucose molecule when the metabolic pathway reverts to the production of propionic and butyric acids that do not require such a low pH_2.

Table 2.1 Important acidogenic reactions.

Reaction Type.	$\Delta G^{0'}$ (KJ/ reaction)	ATP (Mol reaction^{-1})
Acetic acid fermentation.		
$C_6H_{12}O_6 + 4H_2O = 2CH_3COO^- + 4H^+ + 2HCO_3^-$	-206	4
Propionic acid fermentation.		
$C_6H_{12}O_6 = 4/3\ CH_3CH_2COO^- + CH_3COO^- + 8/3H^+ + 2HCO_3^-$	-220	3-4
Butyric acid fermentation.		
$C_6H_{12}O_6 + 2H_2O = CH_3CH_2CH_2COO^- + 3H^+ + 2H_2$	-255	3

(Gottschalk and Anderson, 1979).

$\Delta G^{0'}$ = standard free energy change of reaction at pH 7.0.

2.1.2 Acetogenesis.

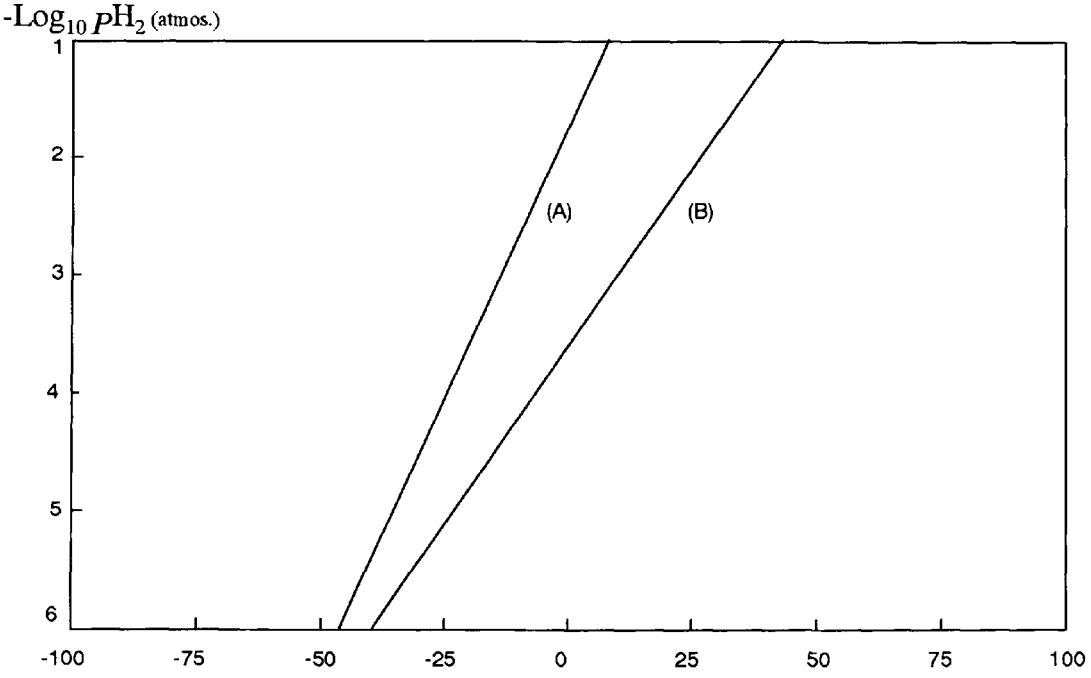
The acetogens (obligate hydrogen producing acetogenic bacteria) degrade the products of hydrolysis and acidogenesis that the methanogenic bacteria are unable to utilise

directly. Principally the methanogens are restricted to the following substrates; C_1 carbon compounds, acetate and hydrogen. The acetogens convert alcohols, fatty acids and aromatics to acetate, hydrogen and carbon dioxide.

CH_3CH_2COOH **(propionic)** + $2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2$ $\Delta G^{o'} = +74kJ\ mol^{-1}$ (1)

$CH_3CH_2CH_2COOH$ **(butyric)** + $2H_2O \rightarrow 2CH_3COOH + 2H_2$ $\Delta G^{o'} = +48.1kJ\ mol^{-1}$ (2)

The conversion of propionic and butyric acids to acetic acid which occurs during acetogenesis are endogonic (see equations 1 and 2) and therefore are energetically unfavourable. Figure 2.2 illustrates how the conversion of propionic and butyric acid is only energetically favourable when the partial pressure of hydrogen is low.



Acetogenesis from butyrate (A) and propionate (B).

Figure 2.2 Thermodynamic dependence of principal reactions in anaerobic digestion upon pH_2 (taken from Archer 1983).

If the equation for propionate oxidation is considered for example the $\Delta G^{o'}$ is equal to +74kJ mol^{-1} and unfavourable for bacterial growth (see equation 1). So for acetogenic reactions to occur their product concentrations must be reduced. This is normally achieved by the utilisation of acetate and hydrogen by the methanogens, provided the hydrogen partial pressure levels are maintained at low values (10^{-4}-10^{-5} atmos.) Thus oxidation of propionate (endogonic reaction) in the presence of methanogens and a low pH_2 (see Figure 2.2) will become exogonic and the acetogens can recover sufficient energy for growth (Thauer *et. al.* 1977 and Archer 1983).

Hence the production of 2 or 4 ATP molecules by substrate level phosphorylation from 1 glucose molecule is dependant on the environmental condition of the anaerobic process. This in turn is subject to the transfer efficiency of the intermediate molecules within the biological system. This is a good example of the important bacterial interdependency that exists between the different anaerobic species within a digester.

Thauer *et al.* (1977) reported a second type of acetogenic bacteria named the homoacetogens. The homoacetogens produce acetic acids and longer chain fatty acids by reducing CO_2 with H_2 via the intermediate acetyl coenzyme A. The role of these bacteria is not fully understood although Schoberth (1985) suggested that acetogenic reduction of CO_2 is probably more important at a lower pH range of 5.5 to 6.5, as homoacetogens dominate over the inactive lithotrophic methanogens at this lower pH range.

2.1.3 Hydrogen transfer.

The physiological partnership between non methanogenic chemoheterotrophs and methanogens was predicted by Hungate (1967) whilst investigating rumen fermentation. It is clear from Figure 2.1 and Figure 2.2 that the transfer of hydrogen plays a vital part in the anaerobic process. The term 'interspecies H_2 transfer' describes the systems in which the presence of one or more H_2-consuming species significantly alters the

metabolism of a fermentative organism towards production of more oxidised end products (McInerney *et al.*1980).

The interspecies hydrogen transfer system was thought to occur between the syntrophic bacterial associations and a hydrogen pool. Hence the H_2 produced by one set of bacteria should be able to equilibrate with the H_2 pool before it is utilised by the hydrogen consuming bacteria. However Conrad *et al.* (1985) reported that the hydrogen turnover rates and the hydrogen pool's size suggested that as much as 95% of the hydrogen produced never entered a common hydrogen pool. On the contrary they proposed that the transfer mechanism was dependant on the juxtaposition of the syntrophic bacterial association and that the hydrogen produced is utilised before it is able to equilibrate with the H_2-pool. This would explain the importance advantages of biofilm and floc formation in anaerobic filter reactors, or granules in a UASB reactor as the close orientation of the different bacterial groups increases the efficiency of the anaerobic process. Therefore the hydrogen transfer system results in greater availability of energy for non methanogens, increased substrate utilisation, increased growth of all participants and the displacement of unfavourable reaction equilibria (Ziekus 1977).

2.1.4 Methanogenesis.

The last link in the metabolic system of waste degradation in the anaerobic process is the methanogens. Consequently they are limited in the substrate that they are able to utilise. This together with the acute sensitivity to oxygen has not prevented the methanogens from becoming well established in many natural environments such as the mammalian rumen, and anaerobic sediments.

Common to all methanogenic bacteria is their ability to reduce carbon dioxide into methane, the end product of their energetic mechanism. The methanogens are dependant on the end products of other microbial groups such as the acetogens and the acid

forming bacteria. They strongly influence the chemical activity of the acetogenic, acidogenic and hydrolytic bacteria by removal of their end products, the reason the process fails shortly after the methanogens become inhibited. The main electron donors of methanogenesis are hydrogen and acetate, although only a few methanogens are able to utilise acetate. The acetoclastic methanogens obtain only small amounts of energy and therefore growth rates are slow with a doubling time of 48-72 hours (Mosey 1983). There are many more lithotrophic methanogen species, that play a vital part in the hydrogen transfer system, reducing the pH_2 and so increasing the energy available for non methanogens (see Table 2.1 and Figure 2.2). These bacteria grow quickly with a doubling time of just 6 hours (Mosey 1983). Approximately 70% of organic component of the waste (surplus to biomass growth) in an anaerobic digester is degraded to methane while the remaining 30% consists of carbon dioxide with associate trace concentrations of hydrogen, carbon monoxide and hydrogen sulphide gas (Gujer and Zehnder 1983 and Krzycki *et al.* 1984). Methanogenic bacteria contain co-factors such as coenzyme M, $factor_{420}$ and $factor_{430}$, which have been utilised to measure methanogen activities and the stability of the anaerobic process (see section 2.3).

2.2 ANAEROBIC PROCESS VARIABLES FOR MONITORING ANAEROBIC DIGESTER STABILITY.

Graef and Andrews (1974) suggested that process variables commonly used in anaerobic digestion can be defined as either stability indicators that should be used for early warning of unstable reactor conditions, or control variables that should be monitored for maintenance and restoration of stability. Rozzi *et al.* (1985) reported that the difference in the two different types of variable is often understated and that a good process variable should be intrinsically linked to the environment and behaviour of the anaerobic bacteria. Therefore the variable should ideally be a liquor phase parameter. Partial hydrogen pressure (pH_2), pH, volatile fatty acid (VFA) concentration, methane and carbon dioxide percentages in the biogas, chemical oxygen demand (COD) and bicarbonate alkalinity are process variables frequently used in anaerobic digestion.

The choice of process variables for on-line monitoring and control is the first stage in the construction of an on-line instrument. In this section the efficiency of different parameters as control and stability indicators are discussed with relevance to the biochemistry and microbiology of anaerobic digestion.

2.2.1 Volatile Fatty Acids (VFA) concentration.

It has been established that volatile fatty acids (VFA) concentration increases in anaerobic digesters under stress (Graef and Andrews 1974, Hill and Barth 1977). The increase in VFA concentration is accompanied by a drop in bicarbonate alkalinity and pH. The subsequent fall in pH as a result of depleted buffering inhibits methanogenesis, so the VFA concentration increases still further, as the methanogens are unable to utilise the acetic acid produced from acidogenesis and acetogenesis. Kroeker *et al.* (1979) attributed inhibition of anaerobic digestion during a decrease in pH to rise in the un-ionised form of the VFA. This hypothesis was re-enforced by Kell *et al.* (1981) who demonstrated that the bacterial cytoplasmic membrane is freely permeable to un-ionised

VFAs but not to ionised VFA. Unlike the fermentative anaerobes the methanogens generate ATP by a chemosmotic mechanism involving the pH gradient across the membrane. Hence the uVFAs are able to uncouple the synthesis of ATP by the disruption of the pH gradient (Zoetemeyer *et al.* 1982).

Asinari di San Marzano *et al.* (1981) suggested that individual VFA concentration increased disproportionately during process instability. A mathematical model developed by Mosey (1983) proposed that the increase in hydrogen partial pressure as a result of overloading the system would produce a larger increase in propionic acid than acetic acid. Peck *et al.* (1986) showed that individual VFA concentrations respond differently during temperature shocks and that the rise in the higher chain length VFA concentrations was unequalled by any other instability indicator.

In principle, measurement of individual VFA species concentration can be regarded as the best process control parameter as it indicates the specific methanogens and obligate hydrogen producing acetogenic bacteria activities, the most sensitive bacterial groups in the anaerobic system. Total VFA concentration is also a useful process control indicator even though the activities of the individual bacterial groups can not be discerned.

The build up in VFA concentration affects the biochemical pathways that are vital to the stability of the anaerobic bacteria. The acidogenic bacteria are initially unaffected, however the methanogens with lower growth rates are less equipped to cope with the increase in acetate and hydrogen produced, resulting from increased acidogenic activity. The over-production of acetic acid by the acetogenic bacteria compared to the utilisation of the methanogenic bacteria results in the rapid build up of acetate and hydrogen. The reactions of the acetogenic bacteria become increasingly unfavourable thermodynamically and the hydrogen transfer system begins to break down (see section 2.1.2) resulting in an increased production of propionic and butyric acids. The situation is exacerbated as the buffering capacity of the anaerobic system is depleted causing a fall in pH. The pH sensitive methanogens become more inhibited causing yet further increases

in VFA concentrations. The literature reviewed suggests that the VFA concentration is considered to be a very good parameter to monitor for early indications of instability and monitoring the individual VFA concentration would be a good basis for a process control strategy.

2.2.2 Bicarbonate alkalinity.

Some components within natural waters and wastewaters have a capacity for buffering pH changes referred to as alkalinity. Such components include hydroxide ions and anions of weak acids such as bicarbonates, carbonates, volatile fatty acids, ammonia, phosphates and silicates. The bicarbonate ion provides buffer capacity over a pH range from 5.3 to 7.3 (Stumm and Morgan 1981). Buffering capacity is typically determined by titration, and alkalinity is defined as the number of equivalents of acids (per litre of sample) required to titrate to pH 4.3, and expressed in terms of $mgCaCO_3l^{-1}$ (APHA Standard methods 1978). A review of different ways of measuring total alkalinity and bicarbonate alkalinity is given in section 2.3.2.

Mono-hydrogen carbonate concentration, or bicarbonate alkalinity is the main contributor to the buffering capacity and an important physico-chemical parameter for stabilising biological treatment process especially anaerobic digestion process (McCarty 1964, Rozzi and Labellarte, 1984. and Rozzi *et al.* 1985). If there is insufficient buffering capacity within an anaerobic reactor, the anaerobic process can be de-stabilised by organic overload or other disturbances such as temperature shocks. McCarty (1964), Graef and Andrews (1974) and Rozzi *et al.* (1988) recommended that the lower alkalinity limit for healthy anaerobic digestion should be at least 1000 $mgCaCO_3l^{-1}$. The naturally occurring buffering capacity in anaerobic digesters can vary considerably depending on the waste type (see Table 2.2).

Table 2.2 Bicarbonate concentration in different wastes.

Researchers	Waste description.	Bicarbonate alkalinity $mgCaCO_3l^{-1}$
Ripley *et al.* (1986)	Poultry manure	1200
Georgacakis *et al.* (1982)	Swine manure	10864
Asinari di san Marzano *et al.* (1981)	Bovine manure	3200
Ross and Low (1987)	Brewery waste	<1000
Ross and Low (1987)	Wine distillery waste	6000
Hawkes *et al.* (1992)	Ice cream waste	1000-1500
Kostenberg and Marchaim (1993)	Coffee waste	<1000

Under steady state conditions the rate of VFA production is balanced by the rate of consumption. However under stress conditions or overloading the rate of VFA production exceeds the rate of consumption. The transfer of active intermediates between the different members of the microbial consortium is interrupted and VFA and hydrogen concentration increase. If this condition is prolonged the bicarbonate alkalinity will be completely destroyed according to equation (3) causing the pH to drop and the methanogenic bacteria will be inhibited by a build up of uVFA's and a 'stuck' reactor will result.

Bicarbonate alkalinity is destroyed by volatile fatty acids and can be described as:

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \longleftrightarrow H_2O + CO_2 \qquad (3)$$

Deterioration of the process stability is rapid because the acetate consuming methanogens are inhibited by the increase in VFA concentration, whereas the VFA producing bacteria are initial unaffected by increased VFA levels. If however the disturbance is not severe and there is sufficient buffering capacity to neutralise the excess

VFAs, the pH and the stability of the process will be maintained (Powell and Archer 1989). Overloading occurs frequently in the treatment of industrial waste waters and therefore it is vital that the buffering capacity in the reactor is maintained to prevent digester failure.

Pohland and Bloodgood (1963), and Pohland (1967) emphasised the need for a balance between the VFA concentration and the buffering capacity for stability in anaerobic digestion. Extensive experimental studies of anaerobic digestion acid-base equilibria led to the development of a theoretical control model for the anaerobic process (Pohland 1968). The development of more sophisticated models of the anaerobic system by Andrews (1969) and later by Graef and Andrews (1974) to investigate the merits of various parameters in process control showed that bicarbonate alkalinity had a significant effect on the stability of the anaerobic bacteria.

During steady state conditions bicarbonate ions are produced during acidogenesis and acetogenesis (see Table 2.1) as the substrate is broken down. The cations released by the break down of VFA salts are free to combine with CO_2 to form bicarbonate. The remaining CO_2 exists as dissolved carbon dioxide or escapes into the gas phase. The proportion of CO_2 that remains in solution as inorganic carbon is dependant on the cations available in the liquor phase. (Rozzi 1981) described in a series of elementary equations as follows:

The inorganic carbon (IC) mass balance in the reactor liquor is;

$$[IC] = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \tag{4}$$

IC equilibrium constants are given by:

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} \tag{5}$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (6)$$

Henry's law relates $[CO_2]$ to the partial pressure of carbon dioxide, pCO_2 in the gas phase as follows:

$$[CO_2]=K_H \cdot pCO_2 \quad (7)$$

Where K_H is Henry's constant.

Therefore combining (5) and (7)

$$pCO_2 = \frac{[H^+][HCO_3^-]}{K_H \cdot K_{a1}} \quad (8)$$

Rozzi *et al.* (1985) suggested that equation (8), which correlates bicarbonate concentration, pH and CO_2 partial pressure, is useful for checking the consistency of experimental values of parameters. Equation 8 was used by McCarty (1964) to construct a plot illustrating the relationship between pH, bicarbonate alkalinity and pCO_2 at a temperature of 37°C (see Figure 2.3).

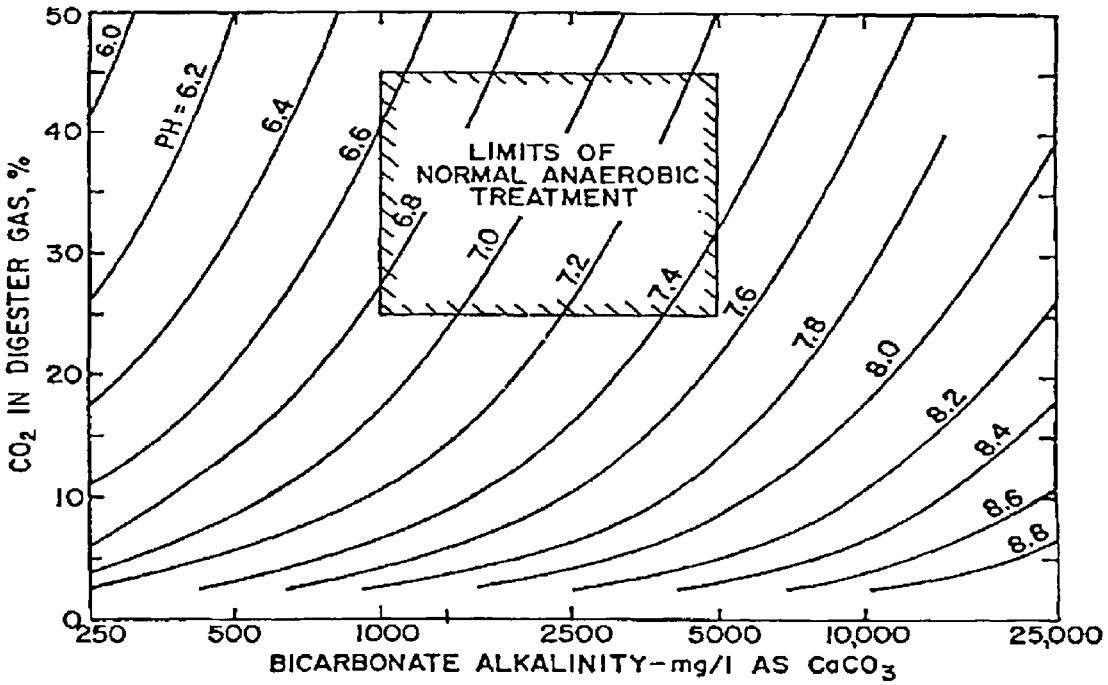


Figure 2.3 CO_2 partial pressure as a function of bicarbonate alkalinity and pH (taken from McCarty 1964).

The decrease in bicarbonate alkalinity concentration during overloading or inhibition is proportionate to the increase in total VFA concentration provided other weak anions are either negligible or constant, i.e. every $moll^{-1}$ of VFA that is allowed to build up will destroy (and replace) an equivalent concentration of bicarbonate. This property can be exploited to construct the following relationship;

$$[TA] = [BA] + (a_0+a_1)\,[TVFA] \qquad (9)$$

(a_0+a_1) = fractions of dissociated VFAs

Where [TA] is the total alkalinity, [BA] is the bicarbonate alkalinity, [TVFA] the volatile fatty acid contribution to alkalinity measurement as $mgCaCO_3l^{-1}$, and the fractions of dissociated volatile fatty acids ($TVFA^-$) over TVA concentrations. The pH of most anaerobic digesters is usually higher than 6.75 and hence a_0 and a_1 values are close to 1 for most VFAs. This relationship can be used to great effect for either the determination of bicarbonate alkalinity from the TA and TVFA alkalinity or to derive the TVFA variations from TA and BA analyses to detect incoming instability related to increases in volatile fatty acids. It follows that bicarbonate concentration is instantly effected by any disturbance in the transfer of intermediates and can be considered a sensitive stability process variable. Bicarbonate alkalinity can also be utilised as a control variable for industrial anaerobic treated waste waters particular those which are low in buffering (van Breusegem *et al.* 1990).

2.2.3 pH as a process variable.

The control of pH is essential to maintain the stability of anaerobic digestion because the methanogenic bacteria are inhibited outside the pH range of 6.5-7.5. A pH drop below this lower limit is intrinsically linked to the uVFA build up and depletion of bicarbonate alkalinity (buffering capacity) and typical of methanogenic inhibition as described earlier. Hence a lowering in pH is often associated with instability and possible failure of the anaerobic process (McCarty 1964). The pH controls the fraction of VFA which exists as

uVFA and can freely permeate across the cell membrane of the anaerobes. After the uVFAs permeate the membrane they dissociate, hence the cytoplasmic pH falls resulting in the inhibition of bacterial metabolism. (Zoetemayer *et al.* 1982). For organisms using a chemiosmotic mechanism (here methanogens) uVFA's uncouple the pH gradient across the cell membrane which drives ATP synthesis.

There is considerable difference of opinion as to the efficiency of pH as a reliable process control variable. Brovko *et al.* (1977) report that pH measurement does not constitute a good control variable or a stability indicator as it is a logarithmic rather than arithmetic function. They recommend that a bicarbonate alkalinity of 3200 mg $CaCO_3l^{-1}$ is the minimum concentration to safeguard against overloading. They showed that while bicarbonate alkalinity decreased from 3600 to 2250 mg $CaCO_3l^{-1}$, the pH dropped from 7.1 to 6.9, not significantly great considering the degree of error associated with pH measurement. Weiland and Rozzi (1990) also reported that for a given increase in VFA concentration the pH change is not constant. At high bicarbonate concentrations the pH change will be small as shown by Brovko *et al.* (1977). Anderson and Yang (1992) showed that pH is less responsive than bicarbonate alkalinity to increases in VFA concentration even at pH 6.0. Control of digester stability using pH as a control variable was shown to be effective by simulated studies carried out by Rozzi (1984) and later on laboratory scale digester (Denac *et al.* 1988, 1990). However the main problem with the use of pH as a control variable is the susceptibility to fouling and electronic drift in many anaerobic digester wastewaters (see section 2.3.3).

2.2.4 Biogas production.

Increases in the production rate of gas indicate increased organic loading to the anaerobic system (Seng *et al.* 1986). Results of temperature shocks to anaerobic digesters, carried out by Peck *et al.* (1986) show biogas production rate to be a good indicator of process stability. In their experiments the decrease in biogas production rate

was greater than the increase in the TVFA. Kidby and Nedwell (1991) also showed that the rate of biogas production responded rapidly to increased hydraulic loading in anaerobic digesters operating on raw settled primary sludge. However gas production rate is not a useful stand alone process control variable. Without the knowledge of organic input to the system or biogas composition for example, the cause of the process instability is difficult to determine. Initial increase in gas production during overloading is a function of the carbon dioxide produced by the destruction of bicarbonate. Therefore it is more appropriate to monitor variations in bicarbonate or carbon dioxide percentage rather than the gas production rate (Rozzi *et al.* 1985).

2.2.5 Gas composition.

The composition of the biogas is possibly a more useful indication of the anaerobic digester status than the biogas production rate as it reveals information about the methanogenic activity. The principal gases in the gas phase are methane and carbon dioxide as described in section 2.1. Increase in percentage carbon dioxide relative to the percentage methane has been known to indicate inhibition of the system, (McCarty 1964, Zickerfoose and Hayes, 1976). The methane production rate is directly related to the activity of the methanogens, but significant changes in the methane percentage are a consequence of inhibition and occur only after the imbalances to the anaerobic system are well developed (Hickey *et al.* 1990). The increase in carbon dioxide concentration during digester imbalance is mainly caused by the destruction of bicarbonate ions resulting from the rise in VFAs concentration due to the reduced activity of the methanogens. Therefore the suitability of percentage CO_2 as a control variable is questionable, as significant variations in pCO_2 are dependant on the carbon dioxide 'stored' in the liquid phase as bicarbonates. However increase in carbon dioxide percentage in the biogas as a result of overloading has been reported by Miller and Barron (1957) and more recently by Denac *et al.* (1988), Cayless *et al.* (1989) and Hawkes *et al.*(1992) .

However Rozzi *et al.* (1985) reported that although pCO_2 can be a good instability parameter, a control system using the addition of alkali, based on the partial pressure of carbon dioxide would be detrimental if it were to postpone and amplify the 'surge' of CO_2 due to bicarbonate decomposition. They showed that the addition of NaOH immediately after an overload caused the bicarbonate concentration to increase and the pCO_2 to decrease. Hence because the pCO_2 decreased the controller was switched off. However as the organic overload continued, the amount of acetic acid in the digester increased causing the pCO_2 to increase rapidly and the pH and bicarbonate concentration to decrease. In fact this effect would have been less pronounced if the control action was actuated with some delay and CO_2 was removed from the liquid phase more continuously.

2.2.6 Hydrogen concentration.

Hydrogen is involved in many of the vital stages of anaerobic digestion as shown in Figure 2.1 (the metabolic routes of anaerobic digestion.) Accurate measurement of very low partial pressures of hydrogen that occur in the biogas of a healthy anaerobic digester is difficult. However the recent development of more sensitive and reliable hydrogen monitors has resulted in work that investigates the effect of hydrogen concentration during unstable anaerobic digestion operation (Collins and Paskins 1987, Mosey and Fernandez 1989).

The equilibrium constants for all the reactions of anaerobic digestion involving hydrogen are affected by the increase in the partial pressure of hydrogen. During the anaerobic degradation of organic matter nicotinamide adenine dinucleotide (NAD^+) is reduced and must be re-oxidised in order that the process can continue. Therefore protons are reduced to hydrogen and utilised by the lithotrophic methanogens via the 'interspecies hydrogen transfer system'. However during overloading of the anaerobic system the slow growth rates of the methanogens compared to the acidogenic bacteria causes the

hydrogen to increase in the system and production of propionic acid instead of acetic acid (see section 2.1.2).

The principal reactions in anaerobic digestion are all associated with low free energy changes and are affected by changes in the pH_2 and therefore pH_2 should be a good indicator of digester performance. Whitmore and Lloyd (1986), Hickey *et al.* (1987), Collins and Paskins (1987) and Hickey *et al.* (1989) investigated the use of hydrogen partial pressure as a means of monitoring anaerobic digester performance. Hickey *et al.*, (1987 and 1989) investigated the effect of inorganic toxicants and organic overloads on the concentration of hydrogen in the biogas. The hydrogen concentration was shown to be dependant on the higher input concentrations and the presence of more easily fermented substrates resulted in different hydrogen response patterns. Collins and Paskins (1987) performed extensive studies investigating the pH_2 concentration in 20 mesophilic sludge digesters. They reported that the hydrogen partial pressure varied from 15-199ppm (see Table 2.3) for digesters with hydraulic retention times of 8-40 days.

Although hydrogen gas concentration responds quickly to changes in the substrate flow rate and composition, increases in hydrogen concentration do not necessarily mean that inhibition of the process has reached a critical point. Mosey and Fernandez (1989) showed that large changes in hydrogen concentration (10 to 120ppm) could occur without any significant changes in bacterial performance. At the end of a perturbation the hydrogen content in the biogas usually falls dramatically. Thus the concentration at which hydrogen becomes inhibitory to anaerobic digestion in practice is unclear. Therefore the pH_2 concentration is unlikely to provide an efficient process control variable. However as the residence time of hydrogen in the reactor is very low, detection of any variations in the H_2 concentrations in the gas is rapid. Hence it is more suitable as an instability indicator and be used to monitor changes in the organic input to the digester (Mosey and Fernandez 1989).

Table 2.3 Hydrogen concentration in 20 full-scale mesophilic anaerobic digesters in England and Wales.

Name of Works.	Hydrogen concentration in the biogas (ppm)
Avonmouth	15
Bedford	67
Brancote (3)	17-60
Checkley (4)	25-66
Chester	39
Claymills (5)	52-97
Cotton Valley	59
Flint	35
Greenfield	50
Hatfield	32
Hitchin	64
Letchworth	27
Mansfield (2)	65-199
Maple Lodge	17
Queensferry	78
Rugby	26
Ryemeads (2)	27-28
Strongford (4)	39-89
Southam	52
Westward Brook (2)	38-45

Taken from Collins and Paskins (1987)

( ) indicates the number of different occasions analysis was performed.

Dissolved hydrogen, arguably more useful than the biogas hydrogen concentration as it is in the liquor phase, can be estimated from the Bunsen coefficient (0.017 cm^3 hydrogen gas dissolves in 1cm^3 of water at 101325 Nm^2 and 37^{o}C). However, there is some controversy about correlation between the partial pressure of gaseous hydrogen and the dissolved hydrogen in anaerobic systems. Pauss *et al.* (1990) reported that dissolved hydrogen concentrations calculated from the partial pressure of hydrogen gas were up to 70 times less than the actual dissolved hydrogen concentrations. The transfer of

hydrogen from the liquid into the gas phase meets with large physico-chemical resistance (Robinson and Tiedje 1982).

2.2.7 Co-enzyme concentration.

As mentioned in section 2.1.4 the methanogens possess a unique set of structural and functional co-enzymes. The concentrations of these coenzymes are directly related to the effective methanogenic biomass present in a digester. The most researched co-enzyme for process monitoring has been the F_{420} (Delafontaine *et al.* 1982, Gorris *et al.* 1988, Samson *et al.* 1988, Peck and Chynoweth 1990 and 1991). However there does not seem to be a definite correlation between the concentration of F_{420} and the methanogenic activity. In addition, changes in the concentration of F_{420} co-factor during bacterial stress have not been proven to be rapid enough to be effective in preventing inhibition for control procedures although it has yet to implemented.

2.3 A REVIEW OF TECHNIQUES AND INSTRUMENTATION FOR MONITORING AND CONTROLLING ANAEROBIC DIGESTION.

2.3.1 Volatile Fatty Acid analysis using gas chromatography.

The determination of individual VFA concentration is possible using Gas Liquid Chromatography (GLC). To use a GLC system on-line the effluent injected must be free from suspended solids, which is seldom true of anaerobic wastewaters. Off-line determination is usually carried out on samples that have undergone extensive cleaning (see section 3.14). Automation of filtration or extraction is difficult, expensive and requires regular maintenance. Therefore GLC is currently an unsuitable technique for the control of anaerobic digestion.

Other techniques based on titrimetric methods have been proposed by Dillallo and Albertson (1961) and Powell and Archer (1989) for the determination of TVFA level. Although TVFA concentration is a very useful process control variable, on-line determination of TVFA in anaerobic digesters by these methods has not be attempted.

2.3.2 Techniques for monitoring bicarbonate alkalinity.

Methods for determining bicarbonate alkalinity in anaerobic digesters originate from the water purification industry and involve direct titration with acid to a fixed endpoint (APHA 1985.) However in wastewater treatment the solutions are more complex and contain other weak anions that severely affect the accuracy of measurement of bicarbonate alkalinity (Jenkins *et al.* 1983, Rozzi *et al.* 1985, Hill 1990 and Anderson and Yang 1992).

The effectiveness of the simple titration and back-titration methods in anaerobic digestion are based on the possibility of discriminating between bicarbonate alkalinity

from other acid-base couples, most importantly the volatile fatty acids. An approximation of the bicarbonate alkalinity can be obtained from a detailed knowledge of the titration curve and the pK values of the different buffering species. The standard method (APHA 1978) with an endpoint of 4.3 allowed the utilisation of colorimetric indicator, methyl orange. However determination of the useful buffering capacity (bicarbonate alkalinity) by this method is inaccurate due to the interferences of VFAs.

Acetic and propionic acids (the main organic acids formed in the anaerobic process) are only effective buffers in the pH range close to their pK values, 3.7 to 5.7 and 3.9 to 5.9 respectively. Therefore their buffering capacity is a useless part of the alkalinity in anaerobic digestion that operates in the pH range 6.5-7.5 (Jenkins *et al.* 1983). The true bicarbonate alkalinity is calculated by the equation (10) which is adapted from equation (9);

$$[TBA] = [TA] - (0.85 \times [VA]) \qquad (10)$$

Where [TBA] is the true bicarbonate alkalinity and the 0.85 is the multiplication factor which assumes that 85% of the VFAs have been titrated at the 4.3 endpoint. The [TA] is determined by titration to 4.3 and the volatile fatty acid concentration [VA] is determined by either steam distillation or gas chromatography.

Jenkins *et al.* (1983) identified the problems of inaccuracy and cumbersome procedures with the determination of bicarbonate alkalinity by the standard method (APHA 1978) and proposed an alternative method. The new method involved the titration with acid to a different endpoint, pH 5.75. At this pH a smaller percentage of compounds that offer no usable buffering capacity in the pH range 6.5-7.5, (the normal operating range for anaerobic digestion) are titrated. Using distribution diagrams and equilibria equations it was calculated that 80% of the bicarbonate species, and less than 20% of the VFA had been titrated at pH 5.75. Consequently even if the VFA concentration is 1000 mgl^{-1} as $CaCO_3l^{-1}$ and the BA is 2000 $mgCaCO_3l^{-1}$, less than 10% error is introduced in the

determination of TBA if the VFA contribution to bicarbonate determination is not ignored. Jenkins *et al.* (1983) proposed that the better estimation of true bicarbonate concentration can be calculated by the following equation;

$$[TBA] = 1.25 \times [ALK_{5.75}] \quad (11)$$

Where the TBA is the true bicarbonate alkalinity in $mgCaCO_3l^{-1}$; $[Alk_{5.75}]$ is the alkalinity as measured at the endpoint pH of 5.75 as $mgCaCO_3l^{-1}$. If the concentrations of other weak anions are negligible then the accuracy of the BA determination by this method is satisfactory in most anaerobic digesters, as the BA value is normally appreciably higher than that of the VFA concentrations.

This method was latter modified as shown in equation (12) by Hill and Jenkins (1989) to account for the 20% VFA that is titrated at the pH of 5.75.

$$[TBA] = 1.25 \times [ALK_{5.75}] - (0.2 \times [TVFA]) \quad (12)$$

The concentration of acetic, propionic, n-butyric, iso butyric, n-valeric and iso-valeric acids was determined by gas chromatography and the sum of the acids were converted from mgl^{-1} to $mgCaCO_3l^{-1}$. This can easily be achieved by multiplying the concentration of each acid by its molar mass and dividing by 100, the molar mass of $CaCO_3$. Hill (1990) later compared the performance of the standard method (APHA 1985) with Jenkins *et al.* (1983) method using real effluent and raw influent of an anaerobic digester. The errors encountered during the study ranged from 30% for the digester effluent to 560% for the influent waste when the bicarbonate alkalinity was determined by the standard method. However the method proposed by Jenkins *et al.* (1983) produced errors ranging from 1.6% to 56% for the same samples.

Ripley *et al.* (1986) proposed a method that was based on combining the Jenkins *et al.* (1983) method and the standard method (APHA 1978). The method required

determination of TBA (they called partial alkalinity, PA) that was obtained by titration with acid to the pH of 5.75, followed by the further titration down to 4.3 to give a second value, the intermediate alkalinity IA. IA represented the 20% portion of the bicarbonate alkalinity that is not titrated at pH 5.75 plus any other buffering species including the contribution from VFA. The $TA_{4.3}$, PA, IA and the IA/PA ratio were determined during a hydraulic loading of a poultry manure anaerobic digester. The IA/PA ratio responded quicker to the overloading than either of the other determinations making it a useful parameter for the early detection of instability. The IA/PA determination requires only two simple titrations rather than two separate measurements, namely [$ALK_{5.75}$] by titration and VFA concentration by GC.

Dilallo and Albertson (1961) developed a back titration technique that enabled the measurement of TA (total alkalinity), VA (the alkalinity contributed by VFA) and BA without the need for separate VFA analysis. The first step of the method requires the determination of the total alkalinity by titration with acid to pH 4. Further titration with acid to pH 3.3 ensures that all the bicarbonate has been converted to CO_2 which is subsequently removed from the sample by lightly boiling. The sample is then allowed to cool before titrating from pH 4 back to pH of 7 with standardised alkali. The amount of alkali titrated in this last step corresponds to the volatile fatty acids still left in solution, hence the bicarbonate alkalinity can be calculated by subtracting the volatile fatty acid alkalinity (the residual alkalinity) from the total alkalinity. Inaccuracies occur in this method because VFA is lost from the sample during the boiling stage to remove dissolved carbon dioxide.

A very similar method using the same principle as the method by Dilallo and Albertson was presented by Pauss *et al.* (1990). In this method however the CO_2 in the system after acidification to pH 4 was removed by vacuum boiling. A soda trap was used at the air intake so that the air entering the system during vacuum boiling was free from carbon dioxide. The most accurate measurements of bicarbonate concentration were obtained with a vacuum pressure of 4 kPa and a constant reaction vessel temperature of 30°C.

After removal of all the carbon dioxide from the system the pressure in the titration vessel was restored to atmospheric. A back titration to the initial sample pH was performed as in the other methods. The accuracy of the method was reported to be greater than 95% with negligible interference from volatile fatty acids. However high sulphide levels were shown to be detrimental to the accuracy of the method. Extraction of the sulphides from the sample using Spectroquant HS 14779 solution is therefore necessary before bicarbonate measurement. More recently Anderson and Yang (1992) have developed a simple three stage titration, which gives a direct measurement of both the bicarbonate alkalinity and the VFA concentration. The method relies on the titration of the effluent sample from the initial pH to 5.1 and 3.5 respectively. The initial pH of the sample is recorded and then titrated with standard sulphuric acid first to pH 5.1 and then to pH 3.5. The method was evaluated on standard solutions of; acetic, propionic, n-butyric and iso-butyric; bicarbonate; as well as mixtures of VFA and bicarbonate. The average recovery in all of the measurements undertaken was better than 96%. A good linear relationship between this method and gas chromotography was established for TVFA determination in anaerobic digesters treating five different wastes.

It is important to realise that titration methods all rely on the accuracy of the pH probe which are known to foul in some anaerobic effluents (see section 2.3.4). Secondly and more importantly these methods are difficult to adapt so that they can operate on-line. Techniques and methods that have been used for automatic and on-line determination of bicarbonate alkalinity are described below.

The principle of the Dilallo and Albertson (1961) method was used by Powell and Archer (1989) to develop an automatic device to determine the total volatile alkalinity (TVFA), total alkalinity (TA) and bicarbonate alkalinity (BA) concentrations of an anaerobic effluent. The method involves the measurements of weight changes as a result of titration between different pH values. Under computer control a sample of anaerobic effluent was pumped into a titration vessel and weighed. Alkali was then pumped into the vessel until pH 11.8 was reached and then acid was pumped into the vessel until pH 11. Acid

addition continues until pH 9.3 was reached and the vessel was again weighed. The increase in the weight due to the addition of acid between these two pH values corresponds to the acid required to neutralise the carbonate buffering. The acid titration continues, and the weight of acid required to titrate the pH interval 7 to 3.75 (in which both VFA and bicarbonate alkalinity occur) was recorded. The acid was added until all the bicarbonate and carbonate was converted to CO_2, at which point the CO_2 in the system was remove by sparging with CO_2 free air. The content of the vessel was then back-titrated with alkali and the weight of alkali required to titrate the pH interval of 3.75 to 7 (in which any VFA is actively buffering) was recorded. From the weights recorded, a titration curve was constructed which allowed the determination of the total alkalinity, the buffering capacity to any desired pH endpoint and VFA concentrations. This method takes approximately 25 minutes for a single analysis and was shown to be accurate and reliable for simulated wastes. However as this method is reliant on pH probes this method may not be as reliable and accurate when using real wastes as pH probes which are subject to fouling causing pH drift (see section 2.2.3).

The same problem is likely to be encountered when using the method proposed by Rozzi *et al.* (1985) who described an automatic off-line monitor also based on Dilallo and Albertson's back-titration method. A known volume of anaerobic effluent is delivered into a sealed reaction chamber and titrated with standardised acid to a pH of 4 to determine the total alkalinity (practically all the bicarbonate in the sample is converted to CO_2 at this pH). The carbon dioxide in the system is removed by a combination of stripping with nitrogen gas and vacuum boiling. The sample is then titrated back to the initial pH with standardised alkali to determine the residual alkalinity [RA] (due mainly to the VFA). So the bicarbonate alkalinity can be determined by subtraction of the [RA] from the total alkalinity.

Methods that do not utilise pH probes are more likely to offer reliable determination of bicarbonate alkalinity for longer periods. Such methods are described below;

Rozzi and Brunnetti (1980) showed that bicarbonate concentration can be determined from the inorganic carbon (IC) balance in solution if the carbon dioxide percentage is known:

$$[IC] = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \quad (13)$$

However CO_3^{2-} can be ignored as below a pH = 8

$$[CO_3^{2-}] < 6 \times 10^{-3} \cdot [IC] \quad (14)$$

Therefore equation (14) can be revised to:

$$[HCO_3^-] = [IC] - [CO_2] \quad (15)$$

Hence the bicarbonate concentration can be determined if the IC concentration and dissolved CO_2 is measured. Provided the gas/liquid interface is in equilibrium the $[CO_2]$ in the liquid phase can be determined as a function of the partial pressure of CO_2 gas, according to Henry's law (see equation 7). Alternatively the CO_2 can be stripped from the sample by bubbling the effluent sample with nitrogen gas.

The inorganic carbon [IC] concentration can be determined using a Total Organic Carbon analyser (TOC). On-line TOC (Beckman, Sussex UK) analysis is now available and could be used to control the bicarbonate concentration of the anaerobic digestion process using the method described by Rozzi and Brunnetti (1980). However there are three factors that are likely to limit the use of on-line measurement of bicarbonate concentrations by TOC. Firstly the instruments are expensive (£30,000 to £40,000) and require a lot of routine maintenance, secondly clarification is require for waste streams

high in suspended solids and thirdly the dissolved carbon dioxide concentration of the effluent must be determined or eliminated which requires further instrumentation.

Finally an off-line method for bicarbonate alkalinity determination that does not require the use of a pH electrode was described by Rozzi and Brunnetti (1981). This method makes use of the fact that 99.9% of the bicarbonate alkalinity in anaerobic effluents is converted to CO_2 below pH 4. So by measuring the volume of gaseous CO_2 evolved during an acid titration of a known sample volume the bicarbonate alkalinity can be calculated from the stoichiometric relationship i.e. 1 mol of bicarbonate reacts with acid to form 1 mol of CO_2.

The method is not affected by VFA interferences or weak anions as it is the bicarbonate ions alone which evolve gas with the addition of acid. However dissolved CO_2 already in the digester effluent fluctuates according to the performance of the digester, this will affect the carbon dioxide evolved as gas in the acidification step of the method. The problem was overcome by saturating the effluent sample with carbon dioxide before addition of acid. Complete saturation with CO_2 was achieved by a hypodermic needle that injected small bubbles of gaseous CO_2 above a magnetic stirrer.

Hence all the carbon dioxide produced by the destruction of bicarbonate ions by acid will be liberated as gas. The gaseous CO_2 evolved was measured by a gas meter based on the displacement of a liquid piston. The accuracy of this method is dependant on the accuracy of the gas measurement (see section 3.1.3). It is possible with an accurate gas measuring system to determine bicarbonate alkalinity below 10mM with an accuracy of 0.7mM for a 95% confidence interval. Therefore this method enables the detection of small changes in bicarbonate alkalinity and early warning of anaerobic digester instability. Typically anaerobic digestion requires a minimum bicarbonate concentration of 20mM or 1000 $mgCaCO_3l^{-1}$. This method is the basis for the research described in this thesis.

Rozzi and Labellarte (1984) later adapted the above method by recording the CO_2 evolved during acid addition by monitoring the pressure change in a sealed reaction vessel. The apparatus was more sophisticated than that used by Rozzi and Brunnetti (1981). The reaction vessel was constructed from perspex, was thermostatically controlled and the gaseous CO_2 was measured using a simple mercury manometer. The contents of the vessel were efficiently mixed by a centrifugal pump. The CO_2 for saturation was delivered to the suction side of a centrifugal pump, ensuring good gas dispersion and mixing. However the method was still off-line and problems were encountered when purging the system of its contents ready for the next measurement.

2.3.3 Monitoring pH on-line in anaerobic digesters.

The liquor phase of the digester effluent is in equilibrium with the carbon dioxide partial pressure of the biogas, a factor which affects the pH value. Removal of the effluent samples from the digester into the air changes this equilibrium and therefore off-line pH measurements are inaccurate. Carbon dioxide will escape from the effluent sample until a new equilibrium is reached with the atmosphere, hence the pH of the sample is increased. Therefore on-line pH monitoring of an anaerobic digester would be a more useful in the operation process.

One disadvantage of on-line pH measurement for monitoring is that it is measured on a logarithmic scale. However there is another more practical obstacle restricting the use of pH probes in anaerobic digesters, namely clogging or fouling of the probes occurs within hours (Monzambe *et al.* 1988). The most commonly used type of pH probe is a combination electrode that consists of a glass and a reference electrode. A gel layer forms on the outside of the glass membrane when in contact with the aqueous measuring solution. Such a gel layer is also present on the inside of the glass membrane which is in contact with a defined buffer solution. The H^+ ions either diffuse out or into the inside gel layer, depending on the pH value of the solution to be measured.

A thermodynamic equilibrium of the hydrogen ion arises at the phase boundary between the measuring solution and the outer gel layer. If the activity of the hydrogen ions is different in the two phases, hydrogen ion transport will occur. This causes a charge at the phase layer, and any further H^+ transport is prevented. This potential is the result of different hydrogen ion activities in the solution and the gel layer. The concentration of H^+ ions in the gel layer is constant and independent of the measured solution. The potential of the outer layer is transmitted to the inside of the glass membrane by the Li^+ ions found in the glass membrane itself. The difference of the two phases equals the total membrane potential and therefore the pH can be calculated (see equation 16.)

$$E = E_0 - 2.303 \cdot \frac{RT}{F} \cdot \Delta pH \qquad (16)$$

However to achieve a definite pH value the electrode potential has to relate to a reference electrode which has a defined stable potential independent of the measured solution. In order for a reference electrode to work the electrolyte must be in contact with the measured solution, this is achieved through a porous ceramic junction.

The potential of the reference electrode system is defined by its electrolyte and the reference element (e.g. silver/silver chloride). It is important that the reference electrolyte has a high ion concentration which results in a low electrical resistance. So the junction is crucial in the measurement of pH as the diffusion potential is a part of every measuring sequence. Strictly speaking the pH values can only be compared if the diffusion potential is identical in all solutions. In practice this is not generally the case but it is possible to keep the potential difference of the inner and outer layers constant and small by controlling the migration velocity of ions across the junction.

The nature of the junction limits the use of pH probes in anaerobic digester environments to wastes with low fat and protein concentrations which could otherwise contaminate the reference junction. The problem is exacerbated by the high solid content and dissolved

sulphide compounds present in an anaerobic digester. As a result unstable pH measurement occurs in a matter of hours of the pH probe insertion into the reactor.

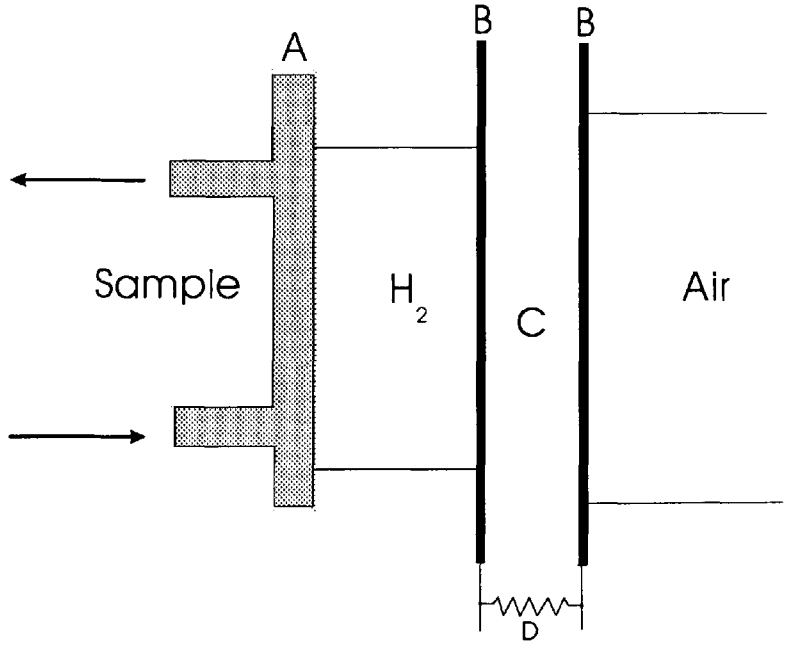
Xerolyte combined pH electrodes (Ingold, BHD Poole, UK) are less susceptable to fouling as they have a stiff polymer mass containing KCl but free from AgCl. They also have an aperture diaphragm (the sample medium comes in direct contact with the internal electrolyte) which allows accurate operation for 10 days without need for calibration. The most promising new development in pH probe technology is the EC1000 pH measuring system (Hach Floriffoux Belgium) which uses a probe that works by actively pumping the reference electrolyte through a tube and therefore the junction is less prone to fouling. However pH measurement of this type has not been tested on-line for anaerobic digester liquor.

2.3.4 Hydrogen analysers.

The hydrogen concentration in the biogas is usually determined by gas chromatography using specific detectors for example; the mercuric-mercuric oxide detector with a detection limit of 0.01% of H_2 gas and the thermal conductivity detector with a detection limit of 1 ppm. However on-line GC analysis is sophisticated and expensive which restricts the use of such techniques. Accurate inexpensive measurement of low hydrogen concentration (detection limit 0.1 ppm) has be made possible by the development of an instrument, the GMI Exhaled Hydrogen Monitor (Gas Measurements Ltd. Renfrew, Scotland), for investigation of inborn maladsorption of sugars in humans. The instrument has been widely used since its introduction in 1980 to investigate the hydrogen concentration of H_2 in the biogas of anaerobic digesters as originally suggested by Mosey (1983). The instrument's use in anaerobic digestion was reviewed by Collins and Paskins (1987). It is a polarographic instrument and is cross sensitive to hydrogen sulphide and mercaptans both of which are found in biogas from anaerobic digester. The instrument is easily calibrated using gravimetrically prepared standards but requires a minimum 20cm min^{-1} flow of gas for accurate and reliable measurement.

As mentioned earlier the determination of dissolved hydrogen concentration from the partial pressure of hydrogen using Bunsen's co-efficient can result in gross under-estimation of the actual dissolved hydrogen content. Scott *et al.* (1983) suggested that dissolved hydrogen could be determined continuously by a membrane inlet quadrapole mass spectrometer. However the high cost (in excess of £60,000) and high detection limit of 67 ppm for hydrogen together with interferences from other molecules present in anaerobic liquors severely restricts the use of this method. Conrad *et al.* (1985) described a method that consisted of the measurement of hydrogen in the gas phase after its quantitative extraction from the liquid phase. They could detect down to levels of 0.01 ppm, however this method involves many steps and is difficult to automate.

A much more robust and inexpensive method (see Figure 2.4) was used by Pauss *et al.* (1990) to monitor dissolved hydrogen in anaerobic digesters. The instrument was a simple miniature hydrogen/air fuel cell (Sypotec Pointe-Claire Quebec, Canada). An effluent sample is recycled so that it is in contact with a hydrophobic Teflon membrane, dissolved hydrogen diffuses across the membrane and reacts with a porous platinum electrode.



(A) selectively permeable membrane, (B) platinum porous electrode,
(C) acid electrolyte, and (D) load resistor

Figure 2.4 Schematic of the Syprotec hydrogen detector cell.

An acid electrolyte separates this electrode from a second electrode which reacts with atmospheric oxygen to complete the cell reaction. The reproducibility of the cell was found to be 1% and responded quickly to changes in dissolve hydrogen concentration (500 nM min^{-1} at a sample recirculation flowrate of 250 cm^3 min^{-1}) in the range 80 to 3500nM.

2.3.5 Carbon dioxide analysers.

Carbon dioxide gas can be measure on-line using infra-red analysers. This is less sophisticated and less expensive than gas chromatography techniques described by (Denac *et al.* 1988) and TOC methods of carbon dioxide determinations (Rozzi and Brunnetti 1980).

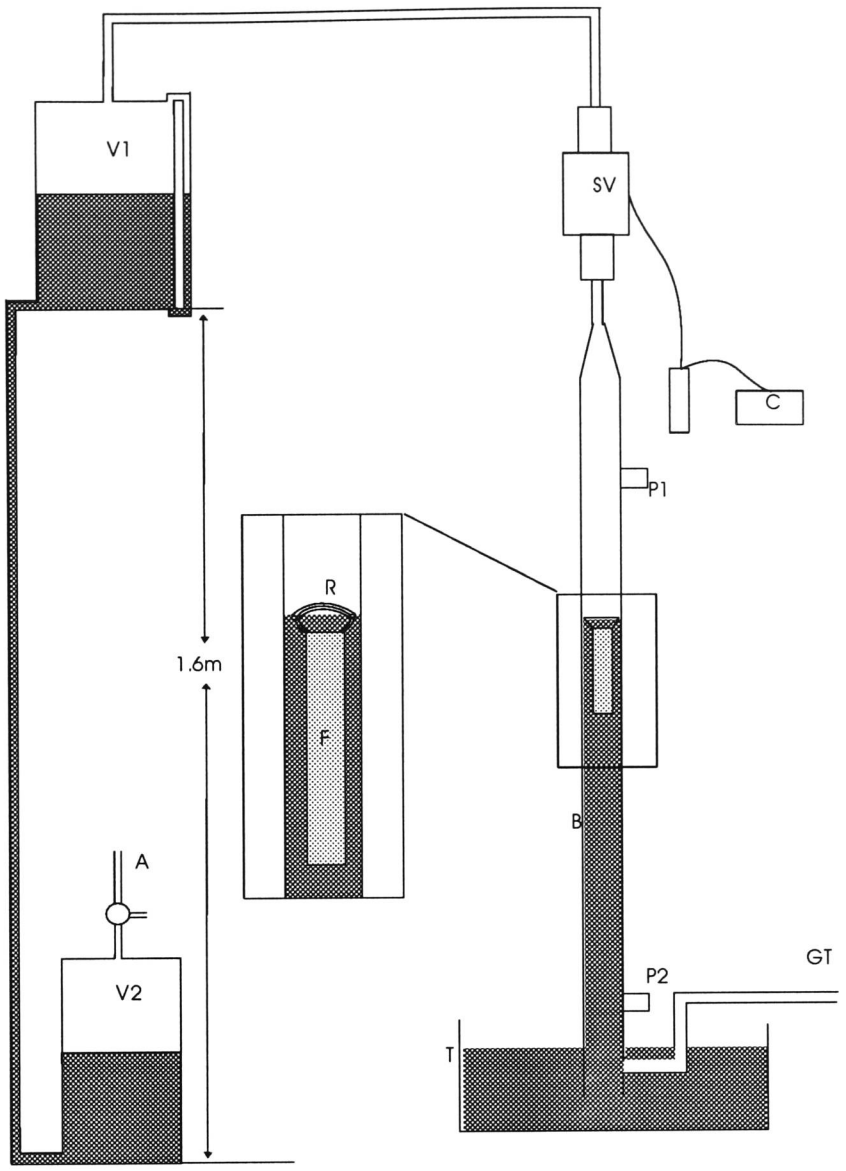
An infra-red analyser consists of a light source, optical section and sensor. The light source emits light at the required wavelength for absorption by the gas. The biogas is pumped through a cell in the path between the radiation source and the detector. The carbon dioxide will absorb the specific radiation, thus reducing the energy level reaching the detector. This difference in energy is amplified to give a signal proportional to the partial pressure CO_2 that is translated into a percentage value. The sensitivity of the analyser is less at high carbon dioxide concentration as the relationship between the partial pressure and the IR absorption is logarithmic.

2.3.6 Gas flow meters.

Gas production is a commonly used process variable in anaerobic digestion at laboratory scale. However problems of inaccuracy, corrosion and unreliability are common with conventional gas meters.

The measurement of irregular low gas flowrates (0-45 cm^3 min^{-1}) has been a problem addressed in several ways. The majority of meters for the measurement of such flowrates utilise liquid displacement. There are several criteria which a gas metering system needs to meet to be effective in measuring low gas flow from dynamic processes such as anaerobic digestion. The precision and reproducibility should not be effected by turbulence and irregular gas production. The device must be resistant to corrosion and should not cause sudden large changes in pressure inside the gas headspace.

Wet gas meters, (example Alexander Wright and Company Ltd. London UK.) work simply by moving a vane which is partially immersed in oil and connected to a tachometer. The gas measured is collected in the cups of the vane gradually rotating the vane, the gas in each cup is vented into the head space and the atmosphere as it reaches the liquid interface. Meters of this type have the disadvantages of being costly (approximately £2000) and of poor sensitivity at flowrates lower than 100 cm^3 min^{-1}. Many low flow gas meters utilise the displacement of a column of liquid. Glauser *et al.* (1984) developed such a meter (see Figure 2.5) that consisted of a hollow float (F) with a magnetic ring (R) which sits on the displacement liquid surface in a burette (B).



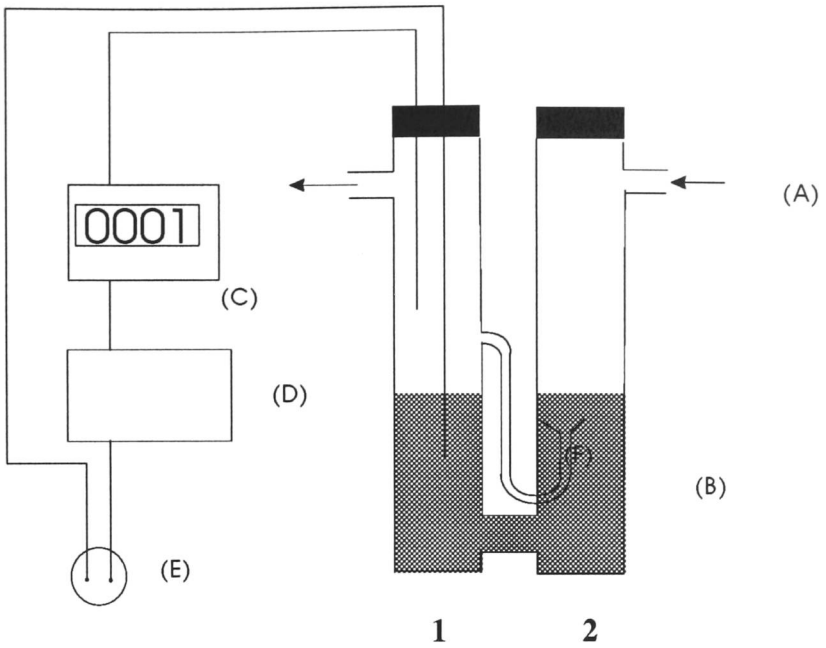
(V1) Vessel 1, (V2) vessel 2, (A) inlet of compressed air, (SV) solenoid valve, (P1) upper proximity detector. (P2) lower proximity detector, (B) burette, (T) water tank, (GT) gas inlet tube, (F) glass float, (R) magnetic ring and (C) digital counter.

Figure 2.5 Schematic diagram of automatic glass float gas meter. (taken from Glauser *et al.* 1984).

At the top of the burette is a 2 way valve (SV) controlled by the two inductive proximity detectors (P1 and P2). Water is pushed into the upper vessel (V2) from the lower vessel (V1) by compressed air entering (A) when the solenoid valve (SV) is open. When V2 is filled the compressed air is switched off and V1 is opened to the atmosphere. A partial pressure is produced by the water in V2 re-entering V2, which draws water from the water tank (T) up the burette until the magnetic ring reaches the upper proximity

detector (D1) at which point the solenoid valve is closed. Gas from the reactor enters the meter through a gas inlet (GT) at the base of the tube which is immersed in a liquid tank (T). The gas displaces the liquid until the magnetic ring (R), which sits on top of the glass float, reaches the lower detector at the base of the tube. The solenoid valve is opened and a negative pressure in a ballast containers (V2) causes the refilling of the glass tube to the level determined by the upper detector. The time taken for a set number of cycles is recorded and the flowrate calculated. Glauser *et al.* reported that the gas meter was capable of monitoring flowrates of approximately $1cm^3\ min^{-1}$ with errors of ±1% when the volume of each cycle was set at 100 cm^3. However the sensitivity and accuracy calculations were based on the duration of 1 cycle. In a real situation where gas is being produced at irregular rates there is likely to be greater errors during the refilling step of this gas metering method. Gwatkin *et al.* (1986) produced a very similar device which vented the gas to atmosphere at the end of each cycle.

A device operating on the same general principles but using different sensors was described by Moletta and Albanac (1982), that works by the liquid displacement round a closed circuit between two communicating vessels. Gas enters one of the vessels through a 3-way solenoid valve and electrodes control the state of the solenoid valve so that a set gas volume is vented through the exit ports of the valve with each cycle. The system refills with liquid and the cycle is repeated. Viega *et al.* (1990) developed this method further producing a gas meter consisting of two 20 cm high glass columns (3 cm in diameter), which were connected at the base and at the centre by a hydraulic valve J shape tube of internal diameter 0.5cm (F) as shown in Figure 2.6. The columns contained liquid whose initial level is slightly below half-way between the mouths of the J-tube. In the first column there are two electrodes of different depths; the shorter of the two is positioned at the same height as the exit port of the hydraulic valve.



(A) Gas inlet, (B) glass columns, (C) counter, (D) electric circuit, (E) a.c. power supply and (F) Hydraulic valve.

Figure 2.6 A gas meter using a hydraulic valve (Veiga *et al.* 1990).

The electrodes are connected to a counter that records the number of contacts the liquid had with both electrodes. The gas enters into column 2 displacing the liquid into column 1 until the gas is allowed to escape via the hydraulic valve. The pressure is released and the liquid in the first column drops breaking the contact between the two electrodes and a count is recorded. Veiga *et al.* stated that the gas meter operated so that 50.4 cm^3 of gas was expelled per count with an error of approximately 0.8%. However as stated previously they give no indication of the accuracy and reproducibility of the flowrate measurement over a suitable duration.

In recent years the low cost of sensitive pressure transducers has resulted in many new developments for gas measurement. Beaubien *et al.* (1988) developed a simple gas meter using a 3-way solenoid and a pressure transducer. In this device, gas passed through the valve to a 0-1.33kPa pressure transducer until a set pressure is reached. At this pressure the solenoid valve is activated closing the gas inlet port and opening the gas outlet port so the pressure in the system is released to atmosphere. The valve is held in its activated state for 2 seconds to allow all the gas to escape before the valve is de-activated and the

cycle repeated. Here again there is insufficient information given to establish how accurate or reproducible the meter is at measuring the actual gas flowrate as opposed to the volume of gas measured by 1 complete cycle of the gas meter. However this method of gas measurement is reported to be able to measure flowrates as low as $0.02cm^3\ min^{-1}$ with long term reproducibility of better than 2%.

2.3.7 On-line BOD and COD analysers.

The BOD_5 (HMSO 1988) method was totally unsuitable for control taking 5 days per measurement and therefore BOD measurements were not considered for anaerobic process control until the development of an on-line BOD instrument. Genner (1991) reviewed the recently developed on-line Biological Oxygen Demand (BOD) instrument (BIOX 1000 Envitech Ltd. UK) and the instrument was found to have a response time of 3 minutes compared with the 5 day measurement of the BOD_5 (HMSO 1988) method. The reproducibility of the on-line instrument was 3% compared with 25% for the BOD_5 off-line measurement. The development of this new monitor opens up new possibilities of control in waste water treatment processes.

A continuous flow of the effluent stream enters the instrument through a coarse screen (0.5 mm mesh). The effluent is mixed with a precise flow of warmed aerated dilution water; the combined flow then passes through a dissolved oxygen flow cell. The mixed stream enters a bioreactor containing respiring microbes that consequently remove oxygen. The outflow from this reactor then passes through a second oxygen electrode cell. The computer adjusts the relative flowrates of the effluent and the dilution pumps to maintain a constant difference of 3 $mg(O)l^{-1}$. Using the pump ratios the computer can calculate the BOD. However the instrument costs approximately $40,000 and requires extensive routine maintenance, therefore the instrument is limited to large scale industrial use.

The short-time Phoenix on-line Chemical Oxygen Demand (COD) instrument (Envitech Ltd. Cardiff UK) is similar in principle to the operation of the BIOX 1000. A feedback control circuit ensures a very low COD/ozone ratio on a continuous basis. The waste water stream is pumped into the instrument through a coarse filtration unit and diluted with ozone enriched water in such a ratio that only 25% of the ozone concentration is oxidised in the reaction chamber. The computer is able to calculate the COD from the pump settings of the effluent stream and the dilution stream pumps. The standard version of this instrument has a measuring range of 2-5000 $mgCODl^{-1}$ while a modified version can extend the range up to 50,000 $mgCODl^{-1}$. As in the case of the on-line BOD measuring instruments the cost (more than £20,000) limits its use to industrial scale digesters.

These sophisticated instruments require routine maintenance especially in high strength wastewaters such as those for anaerobic digestion, and the removal of coarse solids can cause under-estimations in COD and BOD levels.

2.3.8 On-line monitoring of co-enzymes in anaerobic digesters.

The quantification of F_{420} in anaerobes has received a lot of attention in recent years. High pressure liquid chromatography (HPLC) was used by Gorris *et al.* (1988) for measuring F_{420} concentrations. However expensive instrumentation and sophisticated laboratory protocols are necessary; furthermore on-line analysis necessary for control systems is extremely difficult. Samson *et al.* (1988) used a small fluorescence detector to monitor F_{420} on-line without the need for extraction procedures. However, although the detector was effective on pure bacterial cultures, it was effected severely by the darkness of the real digester waste.

More recently Peck and Chynoweth (1990 and 1991) used a NAD(P)H probe (BioChem Technology, Malvern, PA., USA.) to monitor NAD(P)H and a modified NAD(P)H

probe to monitor F_{420} during substrate overload of an CSTR reactor operating on a glucose waste. The response of the probes was compared with off-line measurements of VFA concentration, pH, gas production and gas composition. The assumption that NAD(P)H concentration is approximately the same in all micro-organisms including methanogens allows a determination of the entire population activity. The NAD(P)H probe output increased with the increase in glucose, as did the F_{420}, while the VFA concentration, pH and gas composition remained constant. The NAD(P)H measurement was seen to decrease before any change in the VFA concentration, pH or gas composition. The same may also be said of the F_{420} measurements although the change is far from dramatic. However these probes like most probes are subject to fouling and therefore evaluation of this technique for the measurement of F_{420} and NAD(P)H in an anaerobic digester operating on real waste is necessary.

2.4 CONTROLLING ANAEROBIC DIGESTER STABILITY.

The most commonly used form of feed-back controller is the Proportional-Integral-Derivative (PID) device. The three actions (proportional, integral and differential) combine to provide a correcting signal that is proportional to the error between the controlled variable and a desired set-point and to the integral of this error and to its time derivative. In this way even a small error that is present for a long time can produce quite a considerable corrective action. PID controllers were popular long before mathematical modelling became fashionable and do not necessarily require a model of the process which is to be controlled. In this case empirical rules exist to tune a PID directly upon system response. However, there is no guarantee that the first choice of controller parameters will be the right or at least an acceptable one. In principle the closed-loop system may behave even worse than the original system, so tuning of the PID while the process is operating is hazardous. If a model is available, simulations can be performed

to "tune in" the PID and the resulting parameters can be transferred to the real-time application when a satisfactory performance is achieved and only finer tuning is required. The first dynamic models of the anaerobic treatment process were developed by Andrews (1969) and Andrews and Graef (1971). The models were based on a single group of bacteria converting a single substrate to methane. They assumed that the biodegradability of the VFA was the rate limiting step of the process. The model identified several process control parameters, namely VFA concentration, bicarbonate alkalinity, pH and gas composition.

A two population model was later developed which considered the anaerobic process as an acid forming and a methanogenic phase (Hill and Barth 1977). Rozzi (1984) also developed such a model which considered the acetogenic and the acetoclastic bacteria. The model was used in a series of simulated experiments to investigate the process control properties of pH, pCO_2 and bicarbonate alkalinity. This type of model was superseded by models that incorporated the complex metabolic pathways of all four microbial groups (Mosey, 1983, Dalla Torre and Stephanopoulos 1986 and Rozzi *et al.* 1985). However the microbial groups' response is non-linear especially after perturbations.

The non-linear adaptive control strategy is a recent development which overcomes the problems related to the non-linear behaviour of the biological component of the process by external linearisation. Therefore the dynamic behaviour of the feed-back system, consisting of the biological process and the controller which are both non-linear, becomes linear. Using this approach the biological system is simply described by the mass balance of the anaerobic process and growth rate equations are not required. A detailed description of the theoretical approach is given by Bastin and Dochain (1988). Such non-linear adaptive control algorithms have been developed by Bastin and Dochain (1988), Renard *et al.* (1988) and van Breusegem *et al.* (1990).

Renard *et al.* (1988) performed validation experiments on a pilot scale CSTR reactor during 'shock' overloading. The algorithm was successfully used in maintaining reactor stability using the influent hydraulic rate as the control input. Further work using this controller illustrated that the controller could be used during start up to minimise the effects of overloading (Renard *et al.* 1991).

The models developed by Bastin and Dochain (1988) and Renard *et al.* (1988) are dependant on the measurement of volatile fatty acid concentration, which is difficult to achieve on-line (as described in section 2.3.1) therefore the application of this model in a control system is inappropriate.

van Breusegem *et al.* (1990) identified the lack of reliable on-line instrumentation capable of measuring the vital process control variables for the empirical approach adopted in the anaerobic digestion industry. Using an automatic bicarbonate alkalinity instrument developed by Rozzi *et al.* (1990) they developed a non-linear adaptive model and a L/A model (a modified non-linear approach which can also handle negative values of the variables). Simulation experiments for both model types investigated the effectiveness of the hydraulic retention time and influent bicarbonate concentration as control inputs in separate cases. They concluded that the regulation of bicarbonate concentration with the hydraulic retention time was a suitable process control action. The bicarbonate regulation with bicarbonate as the control input did not lead to the control of volatile fatty acid concentration. However maintenance of the VFA concentration within admissible bounds was accomplished.

2.4.1 Input variables.

There are three input variables to consider in anaerobic digestion namely, the influent flow rate or the addition of chemical compounds (such as alkali or bicarbonate) or removal of inhibitory factors. The most common form of chemical input variable is the

addition of alkali that restored the bicarbonate alkalinity which has been destroyed by the increased VFA concentration. Calcium hydroxide has traditionally been used to restore the buffering capacity in anaerobic digesters. However calcium hydroxide addition can cause undesirable side effects namely precipitation of $CaCO_3$ and vacuum pressures in the headspace (see Table 2.4). Calcium hydroxide cannot directly increase the bicarbonate concentration in the reactor without first reacting with dissolved carbon dioxide according to equation (17).

$$[Ca^{2+}+2OH^-] + 2CO_2 \rightarrow [Ca^{2+}+2HCO_3^-] \qquad (17)$$

Table 2.4 Vacuum pressures created in a typical digester by calcium hydroxide addition.

$Ca(OH)_2$ Added mgl^{-1}	Vacuum created ($pCO2$ in Nm^{-2})
20	1.72
60	5.17
100	8.71
200	17.33
300	26.04
400	34.65

The removal of the dissolved carbon dioxide from the system has to be replenished by the carbon dioxide in the gaseous phase to re-establish the equilibrium resulting in an vacuum, causing mechanical stress on the reactor structure. In addition Barber (1977) reports that the application of lime as an input control variable increases the probability of $CaCO_3$ saturation. If the $CaCO_3$ concentrations exceeds 500 $mgCaCO_3l^{-1}$, or if more than 370 $mgCaCO_3l^{-1}$ as $CaOH_2$ is added, precipitation will occur which can cause blocking.

Therefore it is better to add sodium bicarbonate which will restore the buffering capacity of the anaerobic digester directly without creating a vacuum or precipitation. The higher cost of sodium bicarbonate increases the need for a control system so that the addition of $NaHCO_3^-$ can be applied to maximum effect.

3. MATERIALS AND METHODS.

3.1 LABORATORY REACTOR DESIGN AND OPERATION.

Two identical 10 litre anaerobic up-flow filter reactors were constructed in perspex for laboratory experiments. Each reactor consisted of a perspex cylinder of internal diameter 177 mm moulded from a perspex sheet. Sampling ports 70 mm long and 6.3 mm internal diameter were positioned 90 mm apart down the front of the cylinder. The cylinder was capped at both ends by identical perspex square plates with a 20 mm port in the centre that acted as the feed inlet (bottom plate) and the gas outlet (top plate). The end plates were attached to the cylinder by 76 mm bolts and sealed by a 6 mm 'O' ring. The inner surface of each end plate was machined to give a recess of 14 mm at its centre. Each reactor had an internal volume of 12.5 litres, a liquid volume of 10 litres and a head space of 2.5 litres (see Figure 3.1).

The effluent port consisted of a manometer overflow constructed out of PVC plumbing pipe. The manometer overflow was fitted to the sample port positioned 157 mm from the top of the reactor (see Figure 3.1). A pH probe was housed in a 'T' joint built into the overflow unit, and the bulb of the probe was positioned in effluent stream, so constantly immersed. The ports for recycle of effluent (X), the sample port to the on-line BA monitor (Y), and the sample port to an effluent auto sampler (Z) were positioned directly below the pH probe. It was important for all the sample ports to be close to each other so that objective comparison of the different parametric measurements could be made even when the reactor was not 100% mixed.

The liquid phase of each reactor was filled with packing material that consisted of 26 ETAPAK 120 polypropylene rings (ETA Process Effluent Plant Ltd. The Levels Brereton, Staffordshire, England).

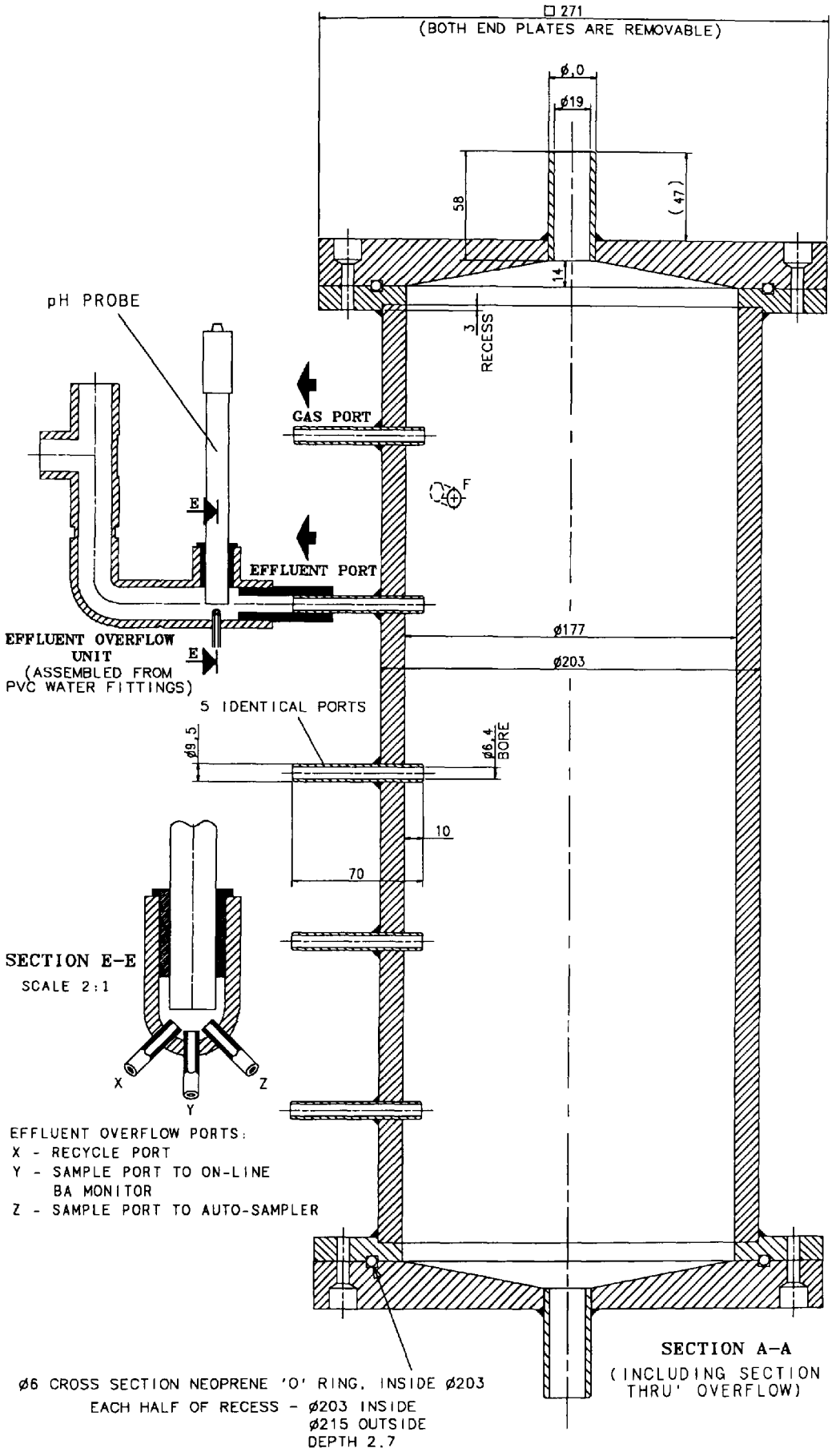


Figure 3.1 Construction diagram of 10 litre anaerobic filter reactor.

The ETAPAK support media was supplied pre-colonised by the Birds Eye Wall's pilot facility at Gloucester in the United Kingdom. The dimensions of the support media constituted a surface area to volume ratio of 160 m^2m^{-3} and voidage of 95%. This packing material provided an ideal environment for the growth of biofilm and flocculate biomass.

3.2 ANAEROBIC PILOT FACILITY.

The UK Science and Engineering Research Council's (SERC) Anaerobic Facility was sited at Bird's Eye Wall's ice cream factory from 1986 to 1989. The facility consisted of the four most common types of anaerobic digester for agro-industrial waste treatment namely: a completely mixed contact process (CP) reactor (5 m^3), an up flow anaerobic filter (5 m^3), an up flow anaerobic sludge blanket (UASB) reactor (5 m^3) and a 0.5 m^3 fluidized bed reactor (Hawkes *et al.* 1995) All the reactors were constructed from steel and coated internally with epoxy paint. The exterior of the reactors was insulated and water proofed by aluminium cladding. The influent for each of the reactors was heated independently of the others by electrically heated water loop exchangers, thermostatically controlled to ensure that the temperature of the liquor phase was constant at 37°C. The anaerobic filter contained an independent electrical booster element in the recycle line in addition to the heat exchanger. The gas pressure in each reactor was maintained by a simple gas bubbler unit. A safety pressure device was installed to sound an alarm if the gas pressure exceeded 12" WG. The full details of the SERC Anaerobic Facility has been described previously by Forster (1988) and Anderson *et al.* (1988).

Work presented in this thesis was carried out on the anaerobic filter pilot scale reactor. The pilot scale anaerobic filter had a 1 m^2 cross-sectional area and contained 5 cm pall ring polypropylene packing (ETAPAK) which had a surface area of 160 m^2m^{-3} and voidage of 95%. This media was positioned in two compartments each 1.64 m^3 in

volume as described by Caine *et al.* (1990). In the last year of operation the lower half of the packing material was removed from the reactor, in an attempt to develop a hybrid digester that consisted of a sludge blanket in the lower portion of the reactor (Hawkes *et al.* 1995).

3.3 INFLUENT (SIMULATED ICE-CREAM WASTE).

The waste water produced at the Birds Eye Wall's, Gloucester UK contained a cleaning agent. This was thought to have a detrimental effect on the microflora and resulted in poor reactor performance, therefore it was necessary to produce a synthetic waste water for use in both the pilot and laboratory scale reactors. The synthetic waste consisted of a mixture of chocolate ice-cream and water ice from the factory, approximately 7 kg of this mixture in $1m^3$ of water produced at a target COD of 4500 mgl^{-1}. The nitrogen and phosphate nutrients necessary for optimum bacterial growth were added to the synthetic waste in the form of 0.178 gl^{-1} of urea and 0.183 gl^{-1} ammonium orthophosphate respectively producing a COD:N:P ratio of 200:2:1.

The synthetic waste produced a low pH during storage, the rate of the acidification was especially rapid during summer months when the ambient temperature increased to above $20^{o}C$. To prevent this the laboratory scale reactors' influent pH was maintained between 6.5 and 7.5, by the addition of 2.5 g of sodium bicarbonate per litre of waste. In addition the influent used in the laboratory set-up was cooled (see section 3.4). The pH of the influent used at the pilot scale facility was automatically controlled to a pH of 6.6-6.8 by the addition of approximately 0.54 kg sodium hydroxide per m^3. Cooling of the waste in a full scale operation is not required as hydraulic retention time of the buffering tank should be less than 1 day during normal operation. The waste for both applications had a very high fat content and contained about 610 mgl^{-1} of oil and grease.

3.4 REACTOR SUPPORT SYSTEM AT LABORATORY SCALE.

The temperature of the reactors was maintained at 37°C by recycling water around a tubular heating jacket (see Figure 3.5) consisting of 50 metres of silicon tubing (Watson and Marlow, Poole, UK). A F1-15 thermostatically controlled water heating pump (Grant Instruments, Cambridge) was set to give 37°C in the reactor.

The synthetic ice-cream substrate was stored in a 200 litre cooled plastic tank (influent tank). The influent tank was placed in a larger tank (cooling tank) which was filled with tap water. The influent temperature was maintained at 5 ± 1°C by recycling the water in the cooling tank through a FC20 flow cooler (Grant Instruments, Cambridge UK). The influent waste was continually mixed by two Heidolph RZR 50 stirrers (Heidolph, Yorkshire, UK) to prevent the settlement of the suspended solids.

Influent was pumped into the reactors using a 10 rpm, 503S/R variable speed peristaltic pump (Watson-Marlow Poole UK). The pumps were fitted with three roller pump head units (303D/A Watson-Marlow, Poole, UK) and 4.8 mm silicone peristaltic tubing. It was necessary to replace the peristaltic tubing every 14 days to prevent flowrate losses caused by fat build up on the internal walls of the tubing. The influent pumps were calibrated on a weekly basis by recording the volume of influent delivered during 30 minute periods. Three measurements were performed and the mean flowrate calculated. The influent was pumped into the reactors through an inlet tube (A) at the bottom of the reactor and effluent was discharged through overflow unit (B) as shown in Figure 3.1.

An effluent recycle system was employed during the course of the reactor operation using a 503S/R peristaltic pump with an eight roller micro cassette manifold. This allowed the use of peristaltic tubing with an internal diameter of 1.85 mm which minimised the pulsing effect on the reactor. The effluent was pumped from the outlet pipe at point (X) shown in Figure 3.1 and returned to the influent pipe at point (R)

shown in Figure 3.5. The upflow velocity produced as a result of the recycle and the influent flowrate was $0.083mh^{-1}$.

3.5 ON-LINE DATA ACQUISITION.

A viglen III 386SX PC was fitted with an analogue to digital conversion board (RTI 800/815 A/D board Analog Devices) and interfaced to on-line analytical hardware via an interface unit. A program was specifically (R.Kingdom IT centre University of Glamorgan) written to monitor the output from the on-line hardware, attached to the anaerobic digester. The program was written in Turbo C++ (version 2) and ran under the Microsoft Windows environment. It was driven by a set of parameters that allow great flexibility in both what was displayed and recorded. The program graphically displayed the various analogues and binary values read from the RTI board on screen (see figure 3.2). These values were written to a text file at a specified time interval for later input to another application. Microsoft Excel was used in this case to represent the on-line data graphically. The program had the ability to control electronic and mechanical devices (such as analogue peristaltic pumps) through simple timed sequences, or through more complex input value set points.

The RTI board provided facilities for 16 analogue single ended inputs and 2 analogue outputs, plus 8 binary inputs and 8 binary outputs. The analogue inputs had four gain settings and (1,10,10 and 500) calibration and offset settings, all of which were input channel dependant. The program was designed so that analogue values could be stored as 'snapshot' values or averaged values. The analogue value could be averaged by any given time interval and the number of samples taken in that interval can also be specified. It follows that by averaging a large number of samples over a large time interval the profile will be smoother than a small sample number over a short time interval.

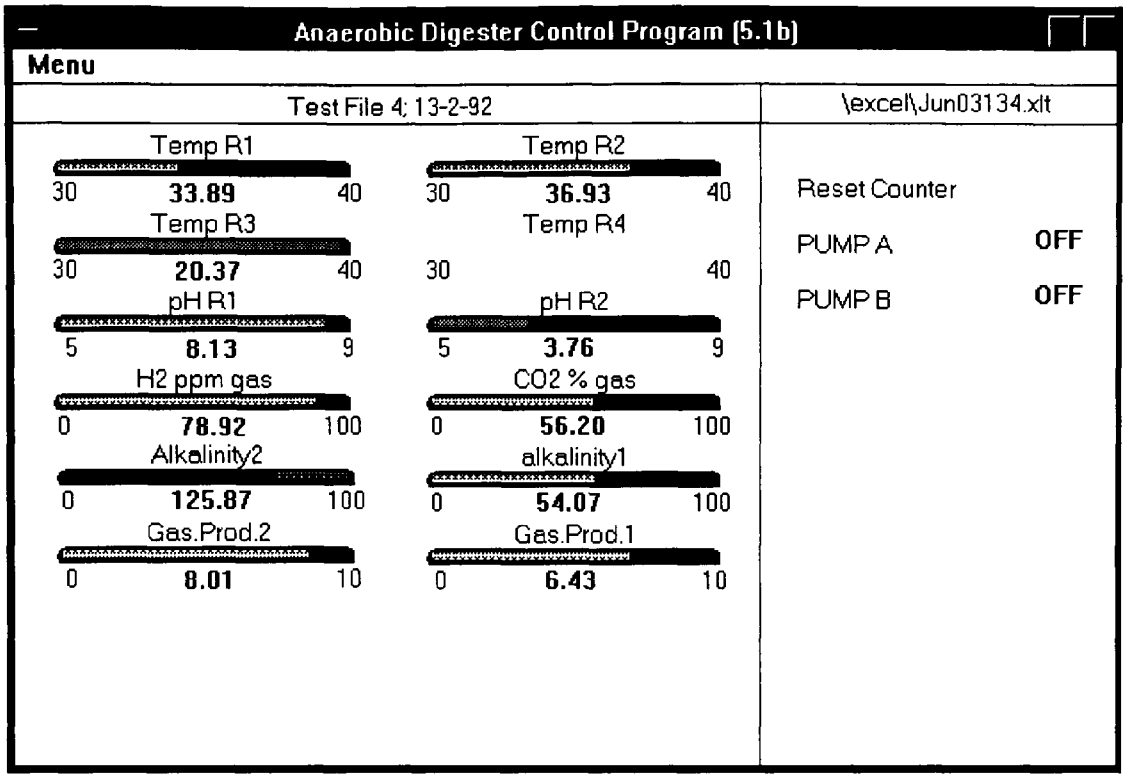


Figure 3.2 Screen display of the data acquisition program.

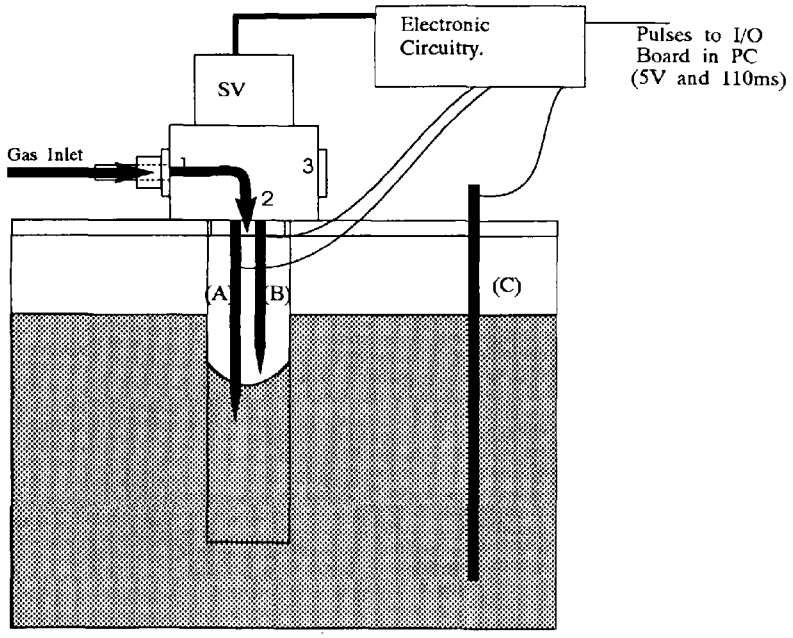
The binary input channels could be used to sense whether a particular line was high or low which is displayed as 'ON' or 'OFF' respectively on the screen. The binary function of any of the 8 input channels could be used in a more sophisticated manner (count mode) to count pulses or pulse width. A moving average of the binary pulse rate could be generated as for the analogue input channels. In addition to the application of moving averaged data, a weighted value can also be employed to increase sensitivity. When the weighted command was activated, the older values in the time interval are given less weight than the newer values in a simple linear proportion.

The input lines were monitored every 55 millisecond. Therefore, providing that the pulse widths are not less than 110 milliseconds, reproducible and accurate measurements of the frequency could be attained. The count mode was used for the measurement of flowrates from gas meters that generated pulses corresponding to a volume of gas being vented.

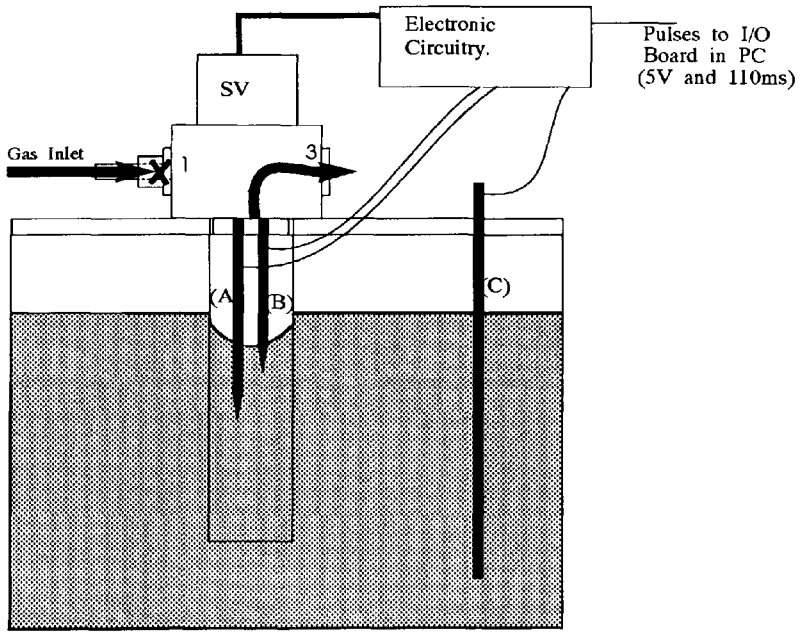
3.6 ON-LINE BIOGAS PRODUCTION DETERMINATION.

An electrode gas meter (EGM) similar to the device developed by Moletta and Albagnac (1982), was used for measuring gas production at laboratory scale. The gas meter is based on the liquid displacement by gas to break an electrical circuit between two electrodes (A) and (B) as shown in Figure 3.3. The breaking of the circuit that controls the opening of a solenoid three-way valve is used to release a gas volume equal to the liquid volume displaced. Normally ports 1 and 2 of the solenoid valve are open while port 3 is closed, so gas produced by the anaerobic digester enters port 1 and exits port 2 (see Figure 3.3). Port 2 opens into a perspex tube that is immersed in a vessel containing 2% perchloric acid. Two stainless steel electrodes of different lengths (A and B) project into the solution inside the perspex tube, a third electrode (C) positioned outside the perspex tube is also immersed in the solution. All three electrodes are connected by an electronic control circuit. The gas displaces the acid solution in the sealed tube past the longer of the two electrodes (A), breaking the electrochemical circuit between electrode (A) and electrode (C). This triggers the energising of the solenoid valve that causes port 1 to close whilst opening the path between ports 2 and 3. The gas (under pressure) is released to the atmosphere causing the liquid level to rise until it contacts electrode (B), at which point the solenoid valve is de-energised and the cycle is repeated.

Normal Solenoid State.



Energised Solenoid State



SV Solenoid valve

(A)
(B)
(C) } Electrodes.

(Path 1 to 2) normally open

(Path 2 to 3) open when the SV is energised.

Figure 3.3 Diagram of electrode gas meter operation.

Each cycle corresponds to the release of a constant volume of gas, which is determined by the distance between the ends of electrodes (A) and (B). The gas volume measured by each cycle was 1.5 cm^3. Therefore by monitoring the number of cycles in a specified time interval the flowrate could be calculated. The energising of the solenoid valve simultaneously produced a voltage output that was smoothed by an RC circuit and passed through a buffer amplifier. The resultant pulse was fed into a monostable that conditioned the pulse such that it was suitable for input into I/O board. The pulse output of the electrode gas meter was monitored by the data acquisition program in a count mode. Each pulse was entered into a moving average that was taken over a 15 minute interval. The value of the moving average was written to a text file every 2 minutes as a flowrate (cm^3min^{-1}).

The gas meter was calibrated using a variable speed peristaltic pump (model N°·502s, Watson-Marlow Ltd. Falmouth UK) fitted with 5 channel micro-cassette 8 roller pump heads. Marprene tubing with an internal diameter of 0.25 mm at 55 rpm resulted in a flowrate of 0.23 cm^3min^{-1}. Therefore 440 roller contacts are made with the tubing per minute, ensuring a precise and constant gas delivery over a long time.

The flowrate generated by the peristaltic pump was measured by a digital bubble flow meter (SAGA 4000 Ion Science Ltd. Cambridge, UK) which was connected to the suction side of the pump, thus bubble movement was the result of negative pressure. This meant that measurement of the gas flow by the digital bubble meter could be recorded simultaneously with the electrode gas meter. By variation of the rpm, the tubing bore, and the number of channels connected in parallel to the gas meter inlet port a range of flowrates were tested. Bubble meter readings for each flowrate were taken at intervals of 2 minutes for one hour. A linear regression was performed on the averaged flowrates measured by the digital bubble meter and the averaged pulse min^{-1} generated by the electrode gas meter. The data was found to fit a straight line with a confidence limit of 95% (see Figure 3.4).

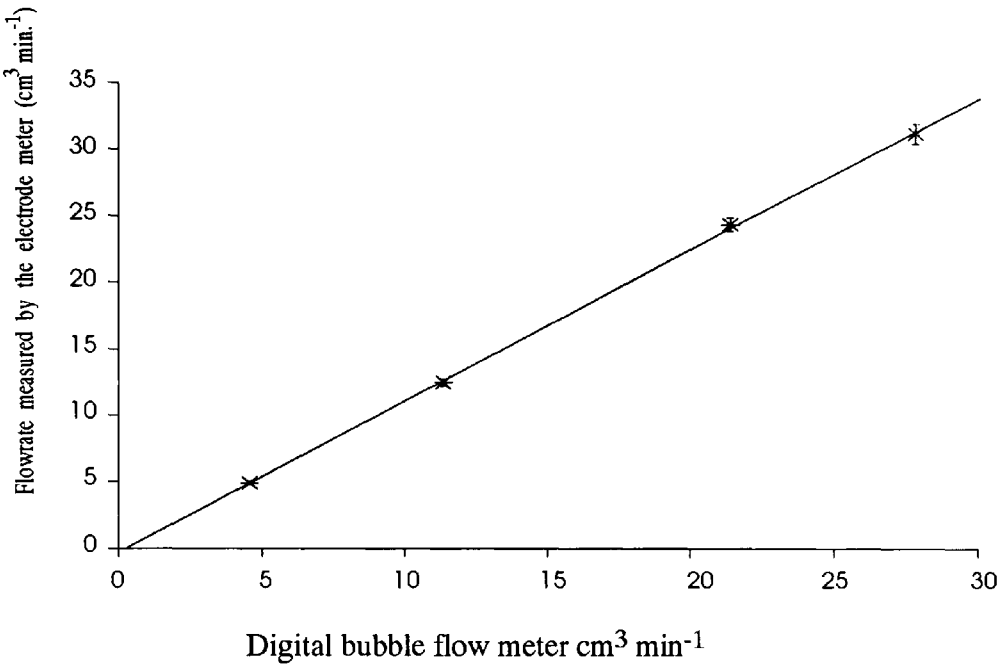


Figure 3.4 Calibration of electrode gas meter.

The gradient of the line was installed in the command file of the data acquisition program as a calibration factor to converts the pulse width to a flow rate $cm^3\ min^{-1}$.

3.7 ON-LINE DETERMINATION OF HYDROGEN AND CARBON DIOXIDE CONCENTRATIONS IN THE BIOGAS.

A GMI exhaled hydrogen monitor (Gas Measurement Instrument Ltd., Renfrew, Scotland) with a 0-100 mA output range was connected to the data acquisitioning computer via an interface unit.

The hydrogen monitor is a polarographic instrument and cross sensitivity to hydrogen sulphide therefore it is essential to strip the biogas with lead acetate before analysis. Collins and Paskins (1987) showed that the instrument gave no response to methane and carbon dioxide (60:40 standard mixture) and therefore was suitable for use in anaerobic digestion.

The instrument's electrochemical sensor can be affected by moisture, therefore the biogas was passed through a condensation trap that consisted of a double condenser (see Figure 3.5). The double condenser was cooled by water that was recycled through a FC20 flow cooler by a F1-15 water pump (Grant Instruments, Cambridge UK). The flow cooler maintained the condenser at a temperature of 5 $\pm 1^{o}$C therefore removing most of the water vapour. The dried air was passed over lead acetate crystals (BDH Ltd. Poole UK) to remove hydrogen sulphide before entering the hydrogen analyser. The device was calibrated with 99 ppm hydrogen gas (Gas Measurement Instrument Ltd., Renfrew, Scotland) as instructed in the exhaled hydrogen monitor's operation manual.

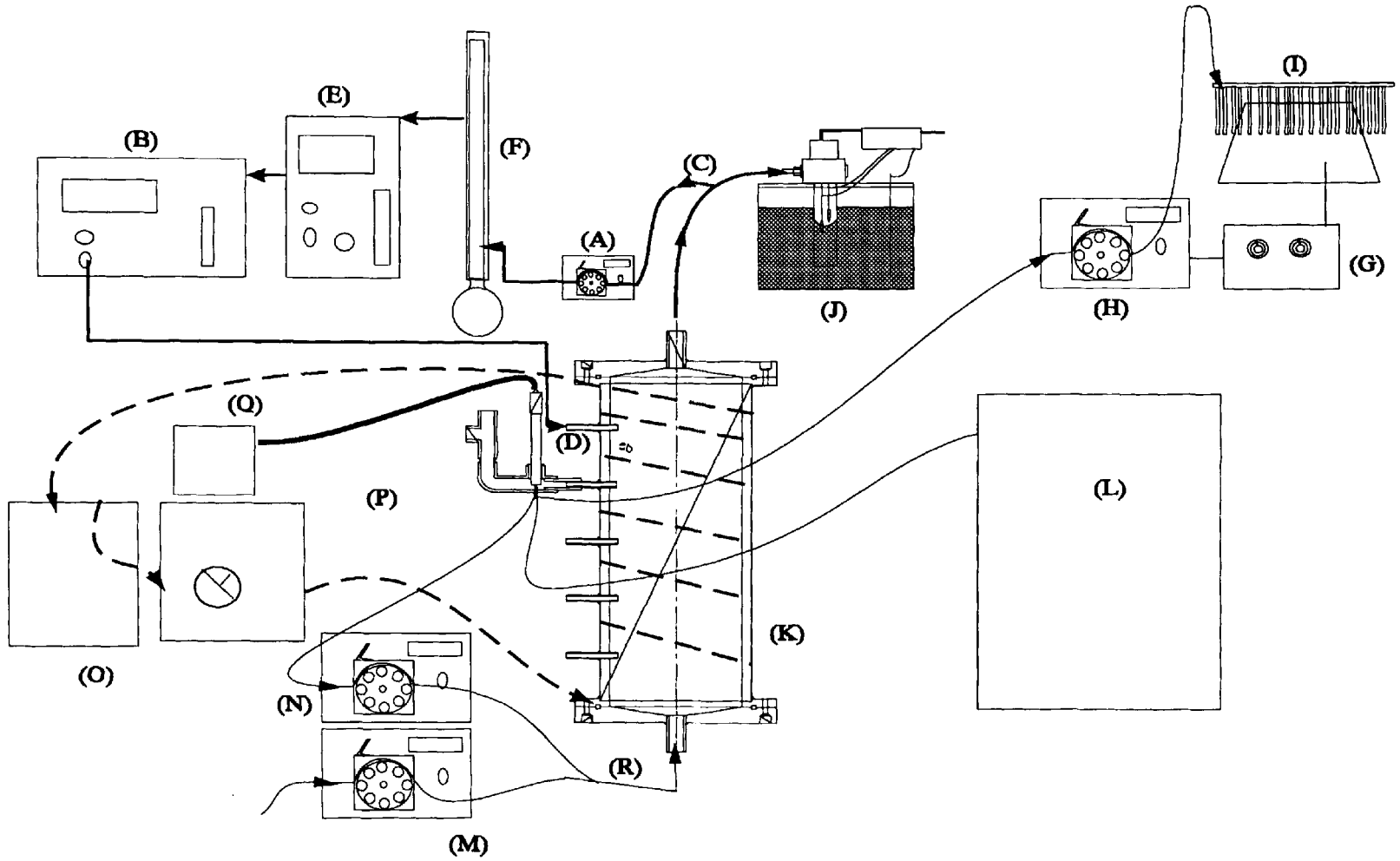
A sb-100 carbon dioxide analyser (ADC Ltd., Hodderson, England) was used to monitor the percentage carbon dioxide in the biogas (see Figure 3.5). The instrument's response time is dependant on the gas flow through the infra red unit it was therefore important to maintain a constant gas flow.

The carbon dioxide analyser output (0-100 mA) was connected to the RTI I/O board of the PC via an interface unit that converted the current output to a voltage output. The instrument was calibrated using methane and carbon dioxide 60:40 standard mixture. The accuracy of the instrument was checked daily by GC gas analysis (see section 4.6).

Biogas was supplied to the gas analysers using two different sampling techniques. Initially the hydrogen and carbon dioxide analysers were connected in series and the biogas was pumped from the head space periodically by a computer controlled 101 peristaltic pump (Watson and Marlow Ltd. Falmouth UK). The pump was set to deliver the biogas at a rate of 20 cm^3 min^{-1}. At such a delivery rate the response time of the hydrogen analyser was approximately 25 minutes. Therefore the data acquisition program activated the pump every 2 hours for 30 minutes at which point the output of the analysers was written to the data file. Later the method of gas delivery was modified so that biogas was continually recycled in a closed loop through the analysers (still connected in series) which allowed in-situ measurements to be made. The output was received by the data acquisition program as analogue signals and written to a data file at 2 minute intervals. The biogas was recycled at a rate of 20 cm^3 min^{-1} by an 303D/A peristaltic pump (Watson and Marlow Ltd. Falmouth UK) from point (C) and returned to point (D) shown in Figure 3.5.

3.8 ON-LINE pH MEASUREMENT.

On-line pH measurement was achieved using a 1180-1170 combination electrode and an EIL1942 metering unit (Kent Industries Ltd.) The pH probe was housed in a 'T' joint attached to the effluent overflow. The glass bulb of the probe and was in constant contact with effluent in the overflow unit as shown in Figure 3.1. Before the pH probe was installed it was calibrated using standard buffer solutions of 7 and 4 (BDH Ltd. Poole UK).



(A) Biogas dosing pump. (B) Hydrogen monitor. (C) Gas sampling point. (D) Return port for gas recycle loop. (E) Carbon dioxide monitor. (F) Condenser (G) Electronic relay unit controlling autosampler (H) Autosampler pump. (I) Autosampler rotary disc. (J) Electrode gas meter. (K) Anaerobic filter digester. (L) On-line BA monitor. (M) Influent pump. (N) Effluent recycle pump. (O) Water bath (P) Water recycle heating pump. (Q) EIL1942 pH metering unit(R) Return point for effluent recycle loop. ——► Effluent path. ——► Biogas path. - - - ► Heating water path

Figure 3.5 Laboratory anaerobic filter reactor support system and on-line monitoring hardware.

The current output (4-20 mA) from the EIL1942 pH metering unit (Q in Figure 3.5) was converted to a voltage signal by circuitry in the interface unit and fed into an analogue input of the I/O board. The calibration and offset values were calculated and entered into the command file of the data acquisition program.

3.9 ON-LINE TEMPERATURE MEASUREMENT.

Temperature sensors were constructed using inexpensive temperature transducers (RS Components Ltd. Corby UK), which act as a constant current regulator passing 1 μA per ^{o}K (hence the associated software could be kept simple). The current output of the transducers was converted and amplified by a circuit board by the interface unit and the resulting voltage signal was sent to an analogue input channel of the I/O board in the PC. Each temperature probe was calibrated in the range 25-45^{o}C using an accurate thermometer. One of these temperature probes was inserted into the reactor liquid through a side port at point (F) see Figure 3.4.

3.10 AUTO SAMPLING TECHNIQUES.

So that samples for off-line determinations of VFA and COD concentrations can be obtained at set time intervals for periods greater than 24 hours, an automatic sample collection system (ASCS) was developed. The ASCS consisted of a rotary file cassette, a 10 rpm 503S/R and a reversible flow variable speed peristaltic pump (Watson-Marlow Poole UK) and an electronic relay unit (see Figure 3.5). The relays controlled the direction of a peristaltic pump and the ratchet mechanism is responsible for rotation of the file cassette. Each relay was activated by a timer circuit, one controlling the duration of the clockwise motion and the other the duration of the anti-clockwise motion. The clockwise duration was set so that 25 cm^3 of effluent was delivered to one of the 60

auto-sample test tubes in the rotary cassette. The duration of the anti-clockwise pump operation was set to clear the effluent from sample tubing to prevent contamination of the next sample. After this the cassette rotated so a new tube was positioned beneath the sample tubing outlet ready for the collection of the next sample. The cycle was repeated at intervals of either 7.5, 15, 30, 60, 120, 180 and 240 minutes. Therefore samples could be collected at precise time intervals throughout the day and night, using this autosampler.

To prevent bacterial activity a few drops of concentrated sulphuric acid was pipetted into each tube. The contents of the tubes were transferred to sample bottles and refrigerated at the earliest opportunity.

3.11 LITHIUM ANALYSIS.

Lithium concentration was determined using a single beam Corning 400 Flame Photometer. The intensity of the filtered light from the flame is measured with a photoelectric detector. The filter interposed between the flame and the detector, transmits only the strong line of the element's emission.

A stock solution of lithium chloride (1000μg cm^{-3}) solution was prepared from which suitable dilutions were prepared to calibrate the flame photometer. The stock solutions and their associated standard dilutions were prepared on the day of analysis as sample deterioration occurred within 24 hours at low concentrations. The standards were aspirated into the flame by a small pump and a capillary tube and the absorption recorded. In the same way the lithium concentrations of the effluent samples from the digester were analysed. Each sample injection was separated by a blank injection of double distilled water. The lithium concentration of each sample was determined using a calibration plot of standard lithium solutions against absorption.

3.12 OFF-LINE BICARBONATE ALKALINITY.

Several off-line bicarbonate alkalinity methods were used in the course of this research. They can be subdivided into simple titration and more elaborate back titration methods. A review and discussion of the bicarbonate alkalinity methods are given in section 2.2.3.

3.12.1 Titration to pH of 5.75.

This method uses a EIL1940 pH meter and a 1180-1170 combination probe (Kent Industries Ltd.). An effluent sample (25 cm^3) was pipetted into a 100 cm^3 beaker that contained a magnetic flea. The jet of the pipette was placed at the bottom of the beaker and kept submerged to minimise the loss of dissolved CO_2 from the sample. For the same reason the analysis was performed without delay. The beaker and its contents were placed on a magnetic stirrer set at 75 rpm. The pH probe was immersed in the solution and standardised (0.05 M) HCl acid solution was delivered from a 25 cm^3 auto-filling burette into the mixed effluent sample until pH 5.75 was reached. At pH 5.75, 80% of the bicarbonate will be titrated and less than 20% of the volatile fatty acids will have contributed to the alkalinity measurement. Therefore an estimate of the bicarbonate alkalinity can be calculated by the following equation

$$BA = Alk_{5.75} \cdot 1.25 \qquad (18)$$

Where $Alk_{5.75}$ = alkalinity as measured at pH 5.75.

The theoretical true bicarbonate alkalinity (TBA) can be calculated by determination of the total volatile fatty acid concentration (TVFA) as $mgCaCO_3l^{-1}$ and the substitution into the following equation;

$$TBA_{5.75} = 1.25 \cdot Alk_{5.75} - 0.2\ (TVFA) \qquad (19)$$

3.12.2 Determination of BA by inorganic analysis.

The determination of bicarbonate concentration using inorganic carbon analysis was reported by Rozzi and Brunnetti (1980) and the theory of the measurement is described in section 2.2.3. Total inorganic carbon analysis will determine all the inorganic carbon present in a sample, including dissolved carbon dioxide. Therefore to obtain an accurate measurement of true bicarbonate alkalinity in anaerobic effluents requires the separate determination of the dissolved CO_2 concentration. Dissolved carbon dioxide concentration fluctuates significantly in an anaerobic digester and cannot be regarded as constant. Carbonate concentration can be assumed to be negligible for anaerobic wastewaters, therefore the bicarbonate concentration can be calculated using the following equation.

$$HCO_3^- = IC - CO_2 \qquad (20)$$

The dissolved carbon dioxide concentration was calculated from the partial pressure of CO_2 of the biogas using Henry's law. The pCO_2 of the biogas was determined using an on-line IR carbon dioxide analyser (see section 2.3.5).

The IC concentration was determined using a Mod. 915a Total Organic Carbon Analyser (Beckman, Fullerton, USA). The operating conditions were as follows: pure oxygen grade was used as the carrier gas (Distillers MG Ltd. Surrey, UK), inorganic column temperature was set at 150°C, the coarse pressure gauge was set at of 20.68 to 34.47 KPa. Fine flow control of the carrier gas (100 to 150 cm^3min^{-1}) was achieved by adjustment of the needle valve.

A 0.2 µl sample of effluent was taken from the reactor using a constant rate syringe with an accuracy of ± 1% (Hamilton Bonaduz, Switzerland). The syringe plunger was pumped several times to expel any trapped bubbles from the sample and the excess solution was wiped from the needle before injection. The sample is injected into the carrier gas stream

that passes through the column packed with silica granules soaked in phosphoric acid. The syringe was left in the injection port until the peak height had reached a maximum value. Each sample injection was repeated three times to obtain a mean value. The inorganic carbon component of the sample is converted to carbon dioxide and exhausted from the column to an infra red detector of the TOC (model 865 Beckman, Sussex UK). The infra red beams pass through two cells; one a reference cell containing a non-absorbing background gas, the other a sample cell containing the sample. The difference in energy between the sample and the reference cell measured by the detector is converted to a capacitance that is proportional to the carbon dioxide concentration. This capacitance change is registered as a peak on a chart recorder.

Calibration of the inorganic carbon analyser was performed by injection of several standard IC concentrations to construct a calibration plot. Inorganic carbon stock solution was prepared by the addition of 17.6g of anhydrous sodium carbonate to 500 cm^3 of CO_2-free water in a 1 litre volumetric flask. Anhydrous sodium bicarbonate (14g) was then added to the flask and diluted to 1 litre with CO_2-free water. The resulting stock solution contained 4000 ppm inorganic carbon. Different IC standards were prepared by taking aliquots of the stock solution and diluting with CO_2-free water. Triplicate (0.2 μl) injections of each standard were made to construct a calibration curve (see Figure 3.6).

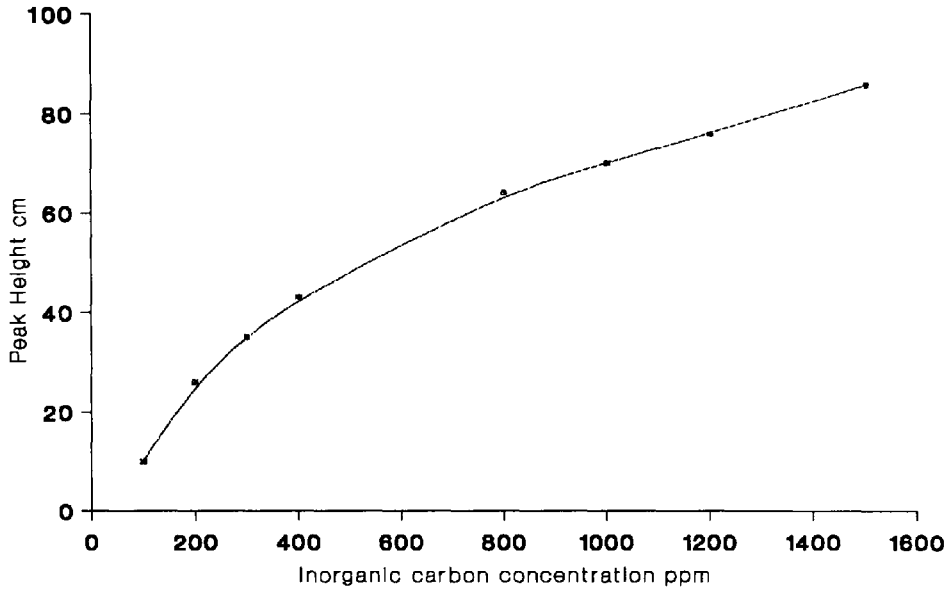


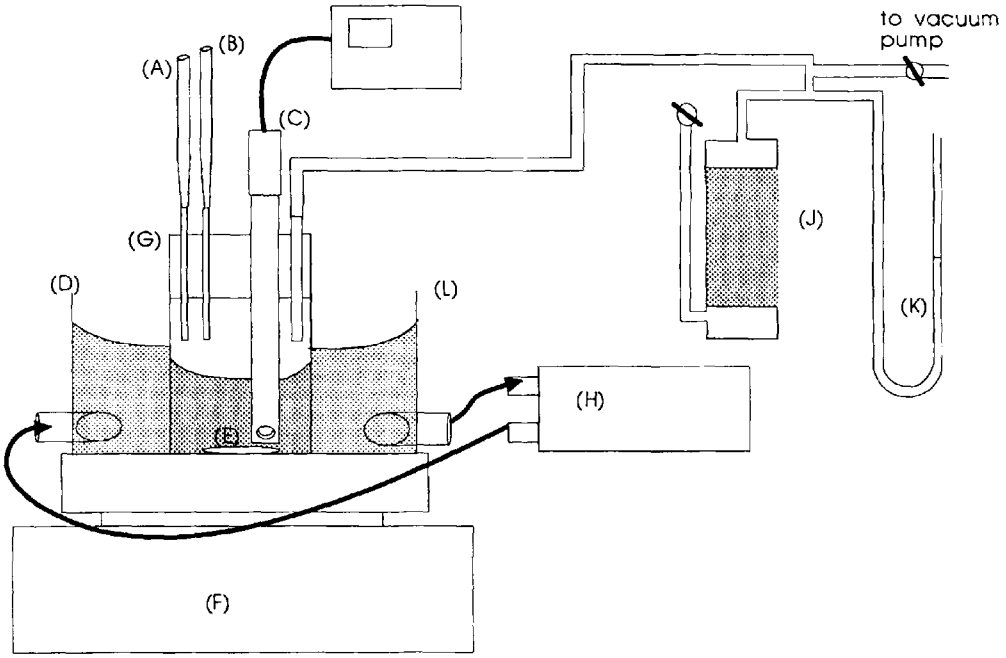
Figure 3.6 Calibration plot of the inorganic carbon analyser.

The errors associated with bicarbonate alkalinity determination by inorganic carbon analysis were found to be in the order of 15% for the range 0 to 1500 ppm inorganic carbon. Elimination of air bubbles is essential to the accuracy of this method.

3.12.3 Back titration method.

The apparatus used in this determination is illustrated in Figure 3.7. An effluent sample (25 cm^3) was transferred to the reaction chamber (G) and continually stirred at approximately 150 rpm by a magnetic stirrer (F) and flea. The temperature of the effluent sample was controlled (30 $\pm 0.5^{o}C$) by recycling water around the reaction vessel and through a thermostatically controlled heating pump. The initial pH and the volume of 0.05 M HCl solution required to reduce the pH to 4.0 (V_1) were recorded. The carbon dioxide produced by the destruction of bicarbonate was removed from the effluent and the reaction vessel head space by vacuum boiling (with a back pressure of 30 mm Hg). After 15 minutes of vacuum boiling the gas line to the water vacuum pump was closed and the pressure in the vessel was slowly returned to atmospheric pressure. Air that entered the system passed through the soda trap which removed any carbon dioxide.

NaOH (0.1M) solution was then added until the initial pH was reached and the volume recorded (V_2).



(A) a 25 cm^3 burette containing HCl (0.05 M), (B) a 25cm^3 burette containing NaOH (0.1 M), (C) a pH probe, (D) a water bath with recycle ports, (E) a magnetic flea (F) a magnetic stirrer (G) a 100 cm^3 sealed reaction vessel (H) a heated water recycle pump , (J) a CO_2 soda-lime trap, (K) a mercury differential manometer.

Figure 3.7 Back titration apparatus for the determination of bicarbonate alkalinity.

The bicarbonate concentration in the sample was then calculated according to the following equation:

$$[HCO_3^-] = \left\{ \frac{V_1 \cdot N_1 - V_2 \cdot N_2}{V_0} \right\} \qquad (21)$$

Where: V1= volume of HCl titrated. V_2 = volume of NaOH titrated.
N2 = concentration of NaOH. V_0 = volume of sample introduced.
N_1= HCl concentration.

The accuracy of this method was reported to be at least 95% (Pauss *et al.* 1990).

3.13 INDIVIDUAL VOLATILE FATTY ACID ANALYSIS.

Techniques for the determination of free fatty acids have been reviewed by Cochrane (1975). Individual volatile fatty acid (C2-C6) analysis was performed using a modified gas chromatographical method described by Peck *et al.* (1986). This method involves the extraction of the volatile fatty acids into diethyl ether before injection onto the column. The separation of acids achieved by this method was found to be better than with determination using aqueous injection and avoided the associated problems of column fouling.

The extraction of the VFAs was performed by transferring a sample (5 $cm^{3)}$ to a 12.5 cm^3 screw capped reflux tube (BDH Ltd. Poole UK) which contained 0.5 cm^3 formic acid (AnaLaR grade, Low in acetic acid BDH Ltd. Poole UK). The addition of formic acid ensures that all the VFAs are in their associated forms which is necessary for detection by gas chromatography. Then 5 cm^3 of chromatography grade diethyl ether (BDH Ltd. Poole UK) was added to the reflux tube contents. The diethyl ether contained 0.1cm^3 l^{-1} iso-caproic acid as the internal standard.

To extract the volatile organic acids from the acidified effluent samples the tubes were sealed and inverted 10 times and left to equilibrate for 3 minutes, after which 95% of the volatile fatty acids are extracted into the diethyl ether layer. The ether layer (supernatant) was pipetted into vials ready for automated injection onto the GC column. The vials were sealed with a PTFE septum necessary for pressurised filling of the automatic injection system (Varian 6500 operation manual).

The use of an internal standard increases the accuracy and reproducibility of the method, especially when small injection volumes and auto sampler are employed. Iso-caproic acid was chosen as the internal standard as its concentration in anaerobic digesters is undetectable even under the severest of overload conditions. The elution time of

iso-caproic acid off the column was the shortest of all the alternative VFAs that are undetectable in anaerobic processes, reducing the analysis running time.

The volatile fatty acid concentrations in the ether layer were determined using a Varian 6000 series GC fitted with a Flame Ionisation detector (FID). A 6ft by 4mm i.d glass column packed with 15% SP1220/1% H_3PO_4 on 100/120 Chromosorb W/AW (Supelco Inc., USA) was used to separated the individual VFAs. The GC was also fitted with an automatic injection unit that allowed multiple injections (Varian Assoc. Ltd. Walton on Thames UK). The operating conditions of the GC are shown in Table 3.1.

Good resolution of the C2-C6 volatile fatty acids from the diethyl ether peak (solvent peak) and a short running time was achieved as shown in a typical chromatogram in Figure 3.8).

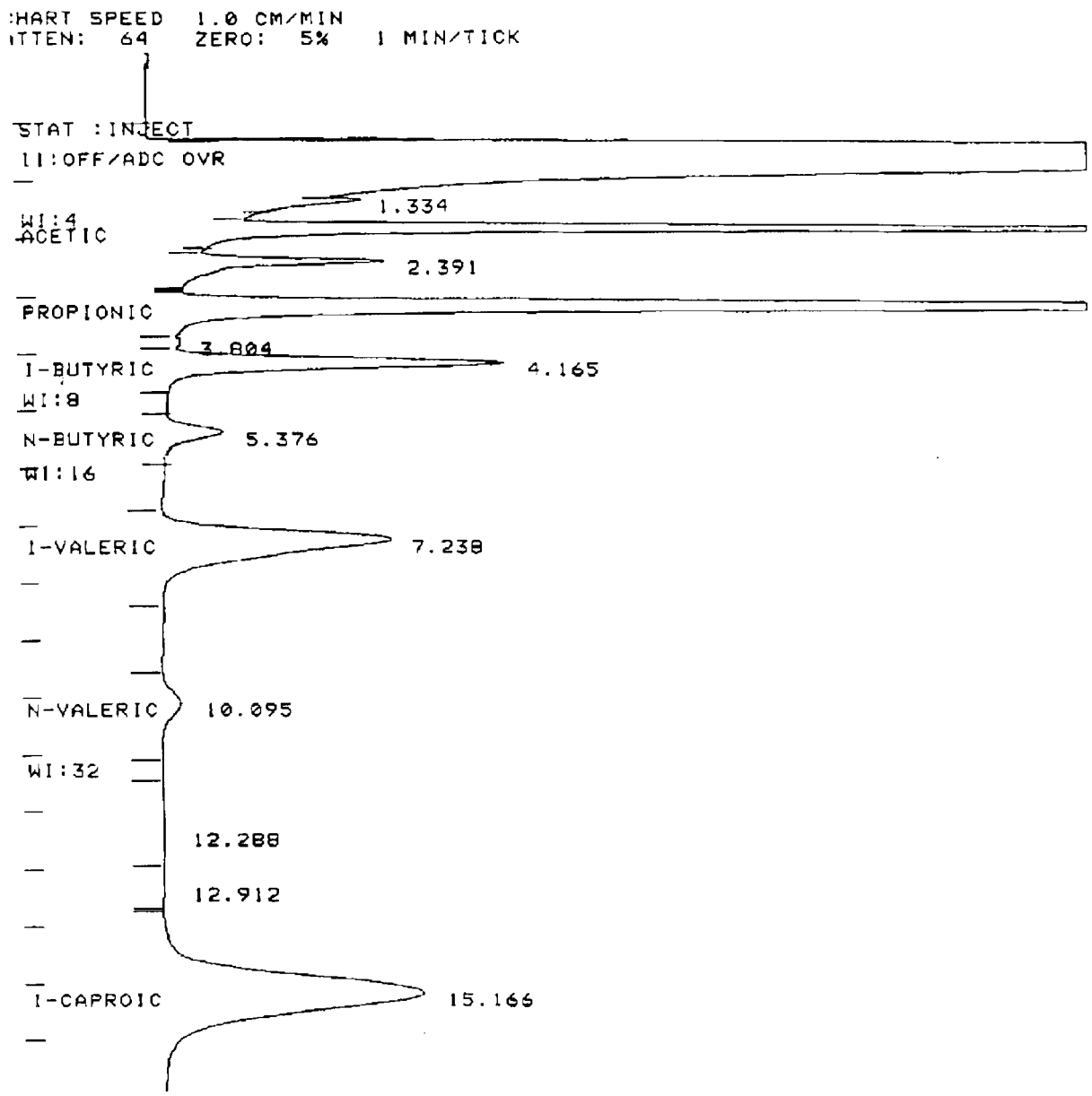


Figure 3.8 Typical gas chromatogram of volatile fatty acids.

The temperatures of the detector, column and injector were controlled by the GC software. The column temperature was held at 115°C for 5 minutes after injection before being increased at a rate of 10°C min^{-1} to 130°C, this temperature was maintained until the end of the run (17 minutes). The temperature program was necessary to ensure resolution of the acetic and propionic acid from the ether solvent peak and reduce the running time.

Table 3.1 Operating conditions for GC analysis of volatile fatty acids.

Injection temperature	130°C
FID temperature	155°C
Injection volume	1.5μl
Carrier gas (Nitrogen)	30 cm^3 min^{-1}
Air	25 cm^3 min^{-1}
Hydrogen	300 cm^3 min^{-1}

The C2-C6 volatile fatty acids are extremely polar and absorption to the column packing can occur. This effect is known as 'ghosting' and is greatest after injection of high VFA concentration onto the column. Therefore it was necessary to injected an ether formate (10% formic acid in diethyl ether) wash onto the column after each sample injection to prevent peak tailing and 'ghosting'. Each time a set of samples was analysed the GC was re-calibrated using a standard VFA mix. The standard volatile fatty acid mix was prepared by the addition of AnaLaR grade VFAs to a 5 litre volumetric flask half filled with distilled water (volumes of each acid are given in Table 3.2). The content of the flask is then made up to the 5 litres. The concentrations of the VFAs are given in Table 3.2. The VFAs in the standard solution were extracted by the same technique used for the extraction of VFAs for the effluent sample. The ether layer was transferred to a vial and injected on to the column as described previously. The retention times of the individual peaks for the standard and their area counts (relative to that of the internal standard) were automatically updated by the 401 database software and saved as a calibration file.

Table 3.2 Concentrations of VFAs in the standard VFA cocktail.

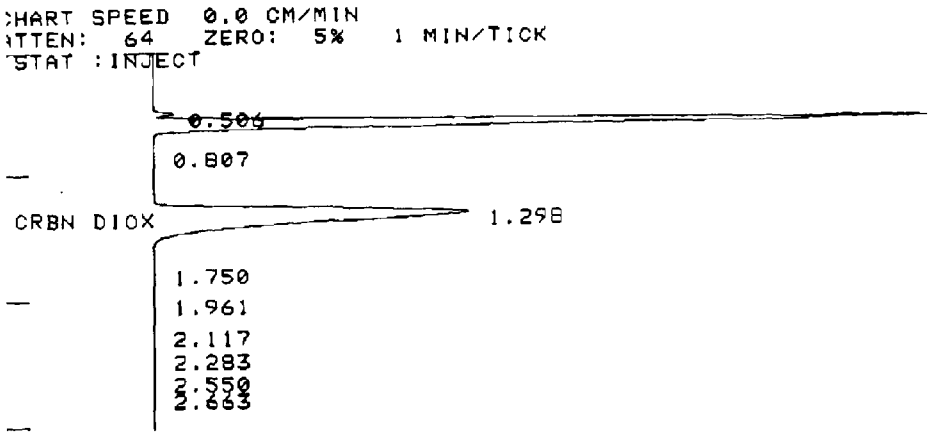
Volatile Fatty Acid	Grade.	Volume added to 5 litres (cm^3)	Concentration (ppm.)
Acetic acid.	AnaLaR.	0.5	100
Propionic acid.	"	0.2	40
Iso-Butyric acid.	"	0.1	20
n-Butyric acid.	"	0.1	20
Iso-Valeric acid.	"	0.05	10
n-Valeric acid	"	0.05	10

Using this method the individual VFA concentration of an anaerobic effluent sample could be determined with an accuracy of ±2% in the range 10-1000 ppm where (ppm=mgl^{-1}).

3.14 ANALYSIS OF GAS COMPOSITION.

The methane and carbon dioxide percentage of the biogas was analysed off-line by gas chromatography. A Varian 6500 GC was fitted with a Thermal Conductivity Detector (TCD) and a Porapak Q 80-100 mesh packed column (Supelco Inc., USA). The temperature programme was iso-thermal (60°C) and the TCD temperature was set at 200°C. High grade helium (Distillers MG Ltd. Surrey UK) was used as the carrier gas at a flow rate of 30 cm^3 min^{-1}. A 25 cm^3 gas-tight syringe fitted with a 3 way valve was used to obtain a sample of biogas. The syringe was connected to the gas sample port (C) of the reactor shown in Figure 3.5. The 'T' clamp sealing the gas sample port was opened and approximately 15 cm^3 of biogas slowly drawn from the head space into the syringe. The syringe was flushed with biogas twice to ensure that a representative gas sample was collected. The biogas was then injected into a $1cm^3$ pre-loop tube connected to the front end of the GC column. An accurate volume of gas was introduced from the pre-loop on

to the column by a manually operated valve. The methane and carbon dioxide components were separated by the column with approximate retention times of 0.45 and 0.94 minutes respectively (see Figure 3.9). The percentages of each gas were obtained by the integration of the peaks by a specific program stored in the RAM of a Varian 401 database. The GC was calibrated daily by injection of an accurately prepared 60:40 % mix of methane and carbon dioxide gas (Distillers MG Ltd. Surrey UK) which produced an error of less than 0.5%.



TITLE: GAS SAMPLES 11:23 30 JUN 94

CHANNEL NO: 2 SAMPLE: CAL METHOD: G

PEAK NO	PEAK NAME	RESULT %	TIME (MIN)	TIME OFFSET	AREA COUNTS	SEP CODE	W1/2 (SEC)
1	METHANE	61.56	0.572	0.002	156881	VV	3.15
2	CRBN DIOX	39.34	1.298	0.008	146921	BV	7.10
TOTALS:		100.90		0.010	303802		

Figure 3.9 A typical gas chromatogram of biogas.

3.15 CHEMICAL OXYGEN DEMAND DETERMINATION.

The Chemical Oxygen Demand (COD) is a measure of the oxygen equivalent of the organic matter in a sample that can be oxidised by a strong oxidant. The methods generally approved for COD determination in waste waters involve cumbersome and expensive dichromate reflux methods, (EPA 1975; EPA 1979 and HMSO 1977). The sample is oxidised by refluxing with sulphuric acid and standard potassium dichromate solution in the presence of silver sulphate and mercuric sulphate. The amount of oxidisable organic compounds in the sample, measured as COD, is proportional to the potassium dichromate consumed during refluxing. Therefore the residual dichromate is then determined either by titration, with standard ferrous ammonium sulphate (FAS) using 1:10 phenanthroline ferrous complex as an indicator, or UV spectrophometry.

The COD method used in this work was based on the closed tube method described in standard methods (HMSO 1986) which requires smaller quantities of reagents and can be performed more quickly and more easily than the methods mentioned previously. Firstly 5 cm^3 of standard COD reagent (May & Baker Ltd., Dagenham, England. UK) was pipetted into a PTFE lined screw top Pyrex incubation tube (BDH Ltd. Poole UK). To suppress chloride interferences 0.5 cm^3 of ($250gl^{-1}$) chromium (III) potassium sulphate solution was added to the contents of the reflux tube. Chromium potassium sulphate was used instead of mercuric sulphate because it has environmental disposal and safety benefits. The sample (2.5 cm^3) was then added to the COD reagent chromium (III) potassium sulphate mix. The incubation tubes were sealed and heated to 150 ± 3 ^{o}C in a DriBlock DB4 heating block (Techne Ltd. Cambridge UK) for 2 hours.

The maximum COD value that can be measured accurately using this method is equal to 50% of the usage of the potassium dichromate which is 250 $mgCODl^{-1}$. Therefore dilution of the sample was normally necessary for both feed and effluent samples. A de-ionised blank was also prepared for each set of analysis to account for oxidisable matter in the water used in dilution.

After refluxing for 2 hours, the incubation tubes were removed from the heating block and allowed to cool. The content of each tube was transferred to a clean conical flask and 2 to 3 drops of 1,10-phenanthroline-ferrous sulphate complex solution (ferroin) was used as an indicator. The residual dichromate concentration was determined by titration with (0.025 M) ferrous ammonium sulphate (FAS) to an endpoint (orange in colour). The COD of the sample can be calculated from the volume of the FAS titrated using the calculation in Appendix 1.

The limit of COD detection using this method is quoted to be 9 $mgCODl^{-1}$ (HMSO 1986). However the accuracy of the analysis is dependant on the nature of the wastewater used. The precision of this method of COD analysis for effluent from an anaerobic digesters operating on ice-cream waste was found to as be much as ±100 $mgCODl^{-1}$ for duplicate samples.

4. MONITORING THE STABILITY OF A PILOT SCALE ANAEROBIC FILTER DURING ORGANIC OVERLOADING.

Initial investigation to determine the effectiveness of bicarbonate alkalinity as a control variable was carried out on the pilot scale anaerobic filter reactor at the SERC Anaerobic Facility by overloading the digester (Hawkes *et al.* 1992). Operation of the Bird's Eye Wall's ice cream factory involved the flushing of ingredient tanks and piping every 8 hours which coincided with the shift rotation. Hence every 8 hours the COD strength fluctuated strongly, the severity of the COD fluctuations was dependant on a variety of factors such as the quantity and type foodstuff being produced. It was estimated that an anaerobic digester treating this type of factory wastewater should be able to cope with a 400% increases in COD strength for 8 hours.

4.1. EXPERIMENTAL APPARATUS AND PROCEDURES.

The actual liquid volume of the upflow anaerobic filter at the time of investigation was 5.28 m^3 and contained 1.64 m^3 of Pall ring packing which was positioned in the upper third of the reactor. The digester had been operating relatively successfully for 3 years and studies carried out by Smith (1991) had established that the reactor was completely mixed. Hence the response of the gas phase parameters can easily be related to the liquid phase parameters.

To investigate the suitability of bicarbonate alkalinity as a process control parameter compared to other gas and liquid gas parameters an organic overload was administered to the anaerobic filter for 8 hours. The influent COD was increased from 4.7 $kgCODm^{-3}$ to 13.6 $kgCODm^{-3}$ by addition of three times the normal volume of concentrated ice-cream to the balance tank. The average loading rate (B_v) taken from a five week period of steady state operation before the overload was 6.8 $kgCODm^{-3}d^{-1}$. The mean hydraulic

retention time during this period was 16.6 hours, and the averaged conditions over this period are shown in Table 4.1.

The acetic acid and propionic acid concentrations varied considerably during this time whereas as the methane percentage was relatively constant as was the pH. Such large fluctuations in VFA concentrations are difficult to explain and could be attributed to poor technique performed at the pilot plant. The technique used for the analysis of these VFA concentrations was an aqueous method which require filtration before injection onto the GC column whereas the method used during the overload was based on the extraction of the VFA into diethyl ether which contained an internal standard as described in section 3.15.

Table 4.1 Analysis of a pilot scale filter reactor during steady state operation.

Off-line analysis	mean
Effluent bicarbonate alkalinity ($mgCaCO_3l^{-1}$)	(380) 1660 [12]
Effluent pH	(0.17) 7.04 [36]
Methane percentage in the biogas	(4) 73 [12]
Acetic acid concentration of effluent (ppm)	(127) 96 [12]
Propionic acid concentration of effluent (ppm)	(110) 118 [12]

( ) Standard deviation [ ] Number of samples
Results in the Table above were supplied by the pilot plant operators

4.2. RESULTS AND DISCUSSION OF THE ORGANIC OVERLOAD.

The results of the 8 hour organic overload (4.7 to 13.6 $kgCODm^{-3}d^{-1}$) are presented by Hawkes *et al.* (1992) and shown here in Figures 4.1 and 4.2. All the analysis was

performed off-line on every hour and the method of analysis used are as described in section 3. The bicarbonate alkalinity was determined using the titration method to pH 5.75 as described in section 3.1 and determined at the pilot facility along with pH, gas composition and biogas production. Samples of effluent and influent were also collected and stored with a few drops of concentrated sulphuric acid for analysis at the University of Glamorgan.

It can be seen from Figure 4.1 that the bicarbonate concentration responds immediately to the organic overload, dropping by 10 % from 1575 to 1410 mg $CaCO_3l^{-1}$ in 1 hour. This corresponded to a 12 % increase in propionic acid which rose from 170 to 190 ppm during the same period. This underlines the value of bicarbonate alkalinity as a process control parameter, as acetogenesis from propionic acid becomes thermodynamically unfavourable during high hydrogen concentration which occurs during instability (see section 2.11).

It is clear from Figure 4.1 that the TVFA concentration increases with the increasing duration of the overload. The rate of propionic acid increase was not as rapid as the acetic acid or TVFA concentrations and after the overload was stopped the removal of propionic acid was slower than the acetic acid. This illustrates that the obligate hydrogen producing acidogens are inhibited as a result of the overload probably by an increase in hydrogen concentration in the liquor. However the less sensitive acetoclastic methanogens are able to remove the acetic acid available quickly. These results show how propionic could be used as a good indicator of reactor stability whereas TVFA and acetic acid are more effective early warning parameters.

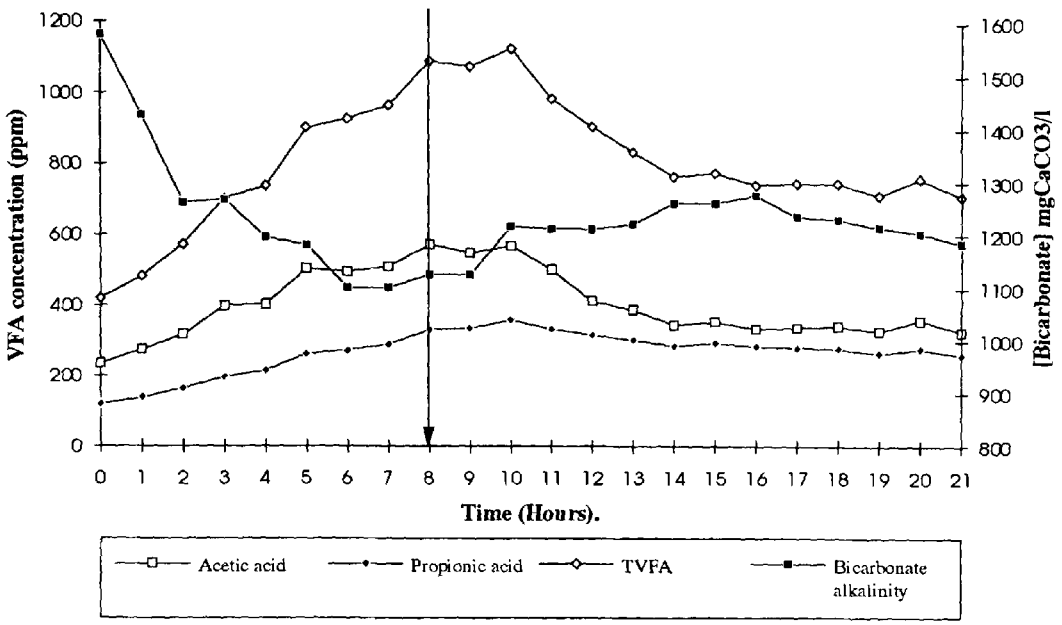


Figure 4.1 The VFA concentration and bicarbonate alkalinity during an organic overload (4.7 to 13.6 kgCODm^{-3}d^{-1}) between 0 to 8 hours to pilot scale AF digester.

The percentage methane shows an immediate response to the overload contrary to the model developed by Rozzi (1984) which suggested that changes in gas composition are a result of inhibition and insufficiently rapid to be used as a control variable. In this overload the methane composition in the biogas dropped from 80% to 71% in the first hour (see Figure 4.2). The percentage methane reaches its lowest level 7 hours into the overload and starts to rise after the end of the overload. Hence the results in this experiment would suggest that methane composition is adequate as a control variable.

In contrast the pH measurements fluctuated considerably and it is difficult to determine whether the overload has resulted in a depression of the pH level. The main problem with off-line pH measurement is the dissolved CO_2 that is always present in anaerobic digester liquors is able to escape to the atmosphere as gaseous carbon dioxide, so reducing the pH. The problems are exacerbated during anaerobic process instability as the dissolved carbon dioxide levels are much higher due to increased partial pressure of carbon dioxide in the head space.

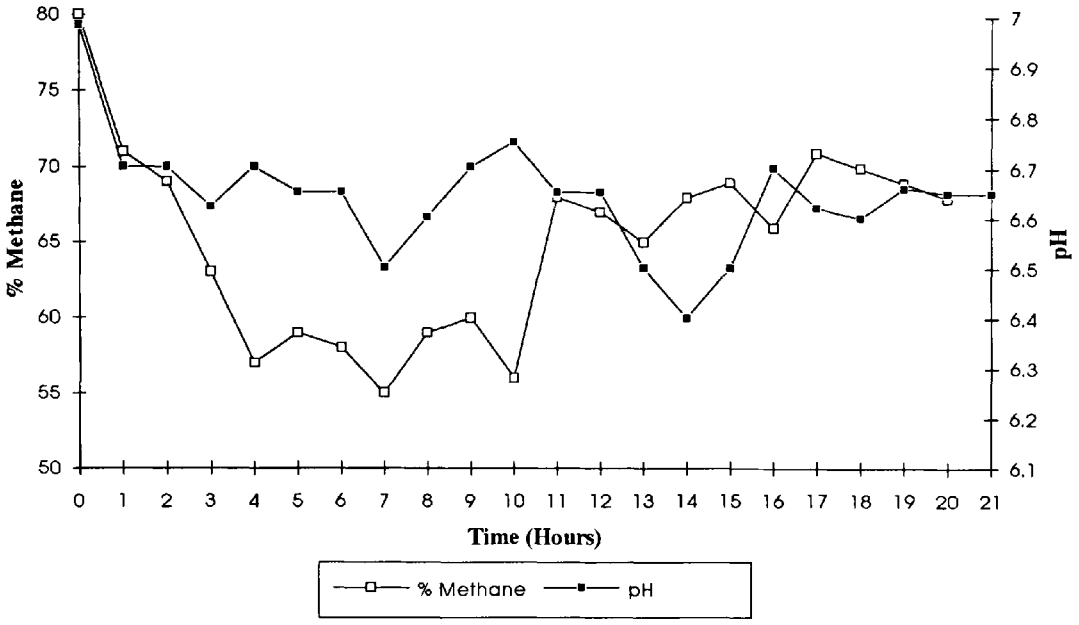


Figure 4.2 Percentage methane and off-line pH during an organic overloading (4.7 to 13.6 kgCODm^{-3}d^{-1})between 0 to 8 hours to a pilot scale AF digester.

The percentage methane increased from 55% to 68% at the 21 hour point, 10% lower than at the start of the overload. However it is important to note that the initial level of methane in the gas was unusually high. Under normal loading the average methane percentage was 73±4% (see Table 4.1). The bicarbonate concentration was slow to recover to the concentration before the overload. At 16 hours the bicarbonate concentration was 1250 mg$CaCO_3l^{-1}$ compared to 1580 before the overload. Similarly the acetic and propionic acid concentrations are approximately 300 ppm higher at time 21 hours than at the initiation of the overload.

The experiment highlights the problems associated with monitoring the performance of anaerobic digestion. Often analysis is not performed regularly enough for easy assessment of underlying performance trends. Plant operators favour parameters which are quick to measure rather than parameters that are more useful in the determination of anaerobic stability such as bicarbonate alkalinity and VFA.

The results of the overload show that bicarbonate alkalinity is an effective control variable as the response to anaerobic instability was quicker than off-line pH. This was in agreement with previous work carried out by Rozzi *et al.* (1985) and van Breusegen *et al.* (1990) who stressed the importance of bicarbonate alkalinity in the control of anaerobic digestion.

4.3. CONCLUSIONS.

The overloading experiment performed on the pilot scale anaerobic filter showed that the bicarbonate alkalinity responded only marginally slower than propionic acid (often regarded as one of the best parameter to indicate digester stability) to the organic overload. The experiment also showed that off-line bicarbonate measurements were subject to less fluctuations than either off-line pH or % carbon dioxide measurements. Hence the availability of a monitor that could determine the bicarbonate concentration of anaerobic liquors on-line could be useful for control of anaerobic digestion.

5. DESIGN AND DEVELOPMENT OF A BICARBONATE ALKALINITY MONITOR.

It is clear from sections 2.2 and 2.3 that a reliable on-line bicarbonate alkalinity monitor would be useful for control of anaerobic digestion and other biological treatment process. The proposed bicarbonate alkalinity instrument described in this chapter is operational on-line, does not require the use of a pH probe and is not affected by the presence of volatile fatty acids. The method of analysis is based on a continuous measurement of the volume of carbon dioxide evolved after subsequent acidification with excess strong acid (Hawkes *et al.* 1993).

5.1 THEORY OF BICARBONATE ALKALINITY MEASUREMENT.

The operation of the instrument is based on the simple physico-chemical equilibria related to the inorganic carbon (IC) system in biological treatment waste waters. The following IC are considered, gaseous CO_2, dissolved CO_2 and bicarbonate ions, (HCO_3^-). Undissociated H_2CO_3 and CO_3^{2-} species are neglected because the molar ratio $[H_2CO_3]/[CO_2]$ is of the order 0.02 at 25°C, (Stumm and Morgan, 1981), and because at pH<8.2 the molar ratio, (as carbon) $[CO_3^{2-}]/[IC]$, is lower than 0.01.

Hence there is a direct relationship between bicarbonate concentration and the amount of carbon dioxide liberated when strong acid is added (to < pH 3.75) to a known volume of anaerobic effluent. This relationship can be represented by the following equation;

$$2NaHCO_{3(aq)} + H_2SO_{4(aq)} \rightarrow 2CO_{2(g)} + Na_2SO_{4(aq)} + 2H_2O_{(aq)} \qquad (22)$$

However the liquor content of an anaerobic digester is partially saturated with dissolved carbon dioxide, and the dissolved CO_2 concentration fluctuates considerably during overloading of the process. Therefore to ensure that all the carbon dioxide evolved from the destruction of bicarbonate by strong acid is liberated as a gas and does not dissolve in

the liquid phase, the sample is pre-saturated with CO_2 gas. Hence the dissolved carbon dioxide content of the sample before acidification is constantly 100%, so all the CO_2 produced in the acidification of bicarbonate is evolved as gas.

Small changes in bicarbonate concentration occur during saturation that can be attributed to the reaction between carbon dioxide and OH^- ions according to equation (23). However the increase in bicarbonate concentration will be less than 10^{-6} M if the sample pH <8 before saturation, so the increase is negligible. The related variation of pH during saturation can be express as in equation (24.)

$$CO_2 + OH^- \leftrightarrow HCO_3^- \tag{23}$$

$$pH = -Log\left\{\frac{K_{a1} \cdot K_H \cdot pCO_2}{[HCO_3^-]}\right\} \tag{24}$$

Assuming that the change in solubility of evolved CO_2 during acidification is negligible then the CO_2 volume produced corresponds to equation 25 below;

$$BA = \frac{Q_g.P}{dQ_s.RT} = \frac{knP}{dQ_sRT} \tag{25}$$

Where

BA = Bicarbonate concentration mol l^{-1}

R = Gas constant 8.3143 J. K^{-1} mol^{-1}

T = Temperature °K (Kelvin)

d = Dilution factor due to acid addition.

n = frequency of the counts (counts min^{-1})

P = Atmospheric pressure 101325 Pa

Q_g = Flow rate of evolved gas m^3min^{-1}

Q_s = Flow rate of effluent sample m^3min^{-1}

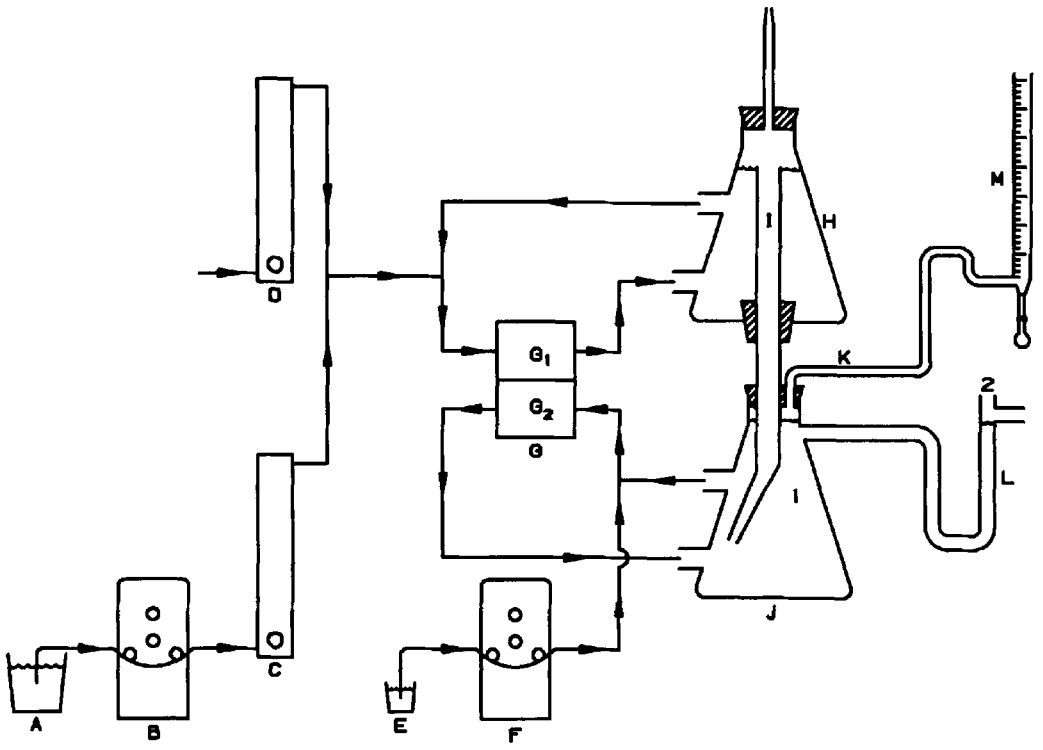
k = gas meter constant (cm^3count^{-1})

From the equation (25) clearly the flowrate CO_2 (Q_g) produced is dependant on the volume and concentration of bicarbonate. Therefore it is essential that the Q_s is accurate and reproducible and (Q_g) is measured accurately.

5.2 CONSTRUCTION AND OPERATION (DESIGN 1).

The first BA monitor design suggested that the proposed method of on-line bicarbonate alkalinity measurement was possible (Hawkes *et al.* 1993). The bicarbonate monitor at this stage of design consisted of two modified conical flasks connected by a vertical overflow tube and is illustrated in Figure 5.1. In order to calibrate the BA monitor sodium bicarbonate solution was delivered into the saturation chamber, (A) at a steady flow rate of $10cm^3\ min^{-1}$ by a peristaltic pump, (B). Solutions were prepared by adding weighed amounts of AnalaR sodium bicarbonate (BDH, Poole UK) to measured volumes of CO_2 free distilled water (water temperature T=25 $\pm$ 2°C). The distilled water had been acidified with concentrated H_2SO_4 in order to remove any trace bicarbonates and nitrogen was then bubbled through the acidified water to drive off the dissolved CO_2. The acidified CO_2 free water was then neutralised using concentrated NaOH to pH 7.

The flow rate of both the $NaHCO_3$ and the CO_2 were monitored by rotameters, (C and D respectively). Carbon dioxide gas was introduced into the chamber (H) at a constant rate, (14 cm min^{-1}) from a gas cylinder (BOC Ltd. Guildford UK). Effective saturation was vital for accurate measurement of bicarbonate alkalinity using this method for the reasons outlined previously. Consequently the saturating CO_2 and $NaHCO_3$ solutions were efficiently mixed by a EHEIM 1020 (Monside Ltd. Herts. UK) centrifugal pump, (G1) which recycled the liquid at a rate of approximately 1 litre min^{-1}. This provided better gas dispersion than other methods of saturation, (i.e. airstone and needle delivery, with mixing by a magnetic stirrer) examined by inorganic carbon analysis with a Beckman 915A Total Carbon analyser.



(A) Sample container. (B) Peristaltic pump for sample solution. (C) Sample rotameter. (D)CO_2 gas rotameter. (E) Sulphuric acid container. (F) Peristaltic pump for H_2SO_4. (G1/G2) Twin centrifugal pump. (H) Saturation chamber. (I) Vertical overflow tube. (J) Acidification chamber. (K) Gas tube to bubble meter. (L) Overflow tube. (M) Bubble meter. (1&2).Points at which the temperature was measured.

Figure 5.1 Experimental apparatus of bicarbonate alkalinity monitoring device.

Apparatus dimensions.

Liquid volume of saturation chamber.	0.5 l
Liquid volume of acidification chamber.	0.5 l
Diameter of vertical tube I.	0.8 cm
Diameter of gas tube.	0.5 cm
Diameter of bubble tube.	1.0 cm

The CO_2 saturated $NaHCO_3$ solution passes from vessel (H) by gravity, through the vertical tube (I), into vessel (J). Sulphuric acid (5M) was pumped into vessel (J) by a second peristaltic pump (F), and the resulting solution was recycled and mixed by the second centrifugal pump (G2). The flow rate of the acid was kept constant at

0.25 cm^3 min^{-1} and well in excess of the concentration required to neutralise the bicarbonate concentration typically found in an anaerobic digester. Waste solution which contained products of the reaction between bicarbonate and the acid, overflowed through tube (L). The temperature of the solution was measured using thermocouples in vessel (J), and at the overflow tube (L). Gaseous CO_2 released during acidification was measured by a simple soap bubble flow meter (M) which provided more accurate measurement of gas flowrate than available automatic gas meters because it was less sensitive to pulsing (see section 3.6). The CO_2 yield was determined by measuring the time taken for $10cm^3$ of gas to pass through the gas meter. This measurement was repeated at equilibrium conditions for each concentration a minimum of ten times, from which the CO_2 yield was calculated (see Table 5.1) using equation (25).

Table 5.1 Relationship of experimental and theoretical gas yield to bicarbonate alkalinity at temperature range 18°C-30°C.

$NaHCO_3$ Concentration mol l^{-1}	Equivalent Alkalinity $mgCaCO_3l^{-1}$	Experimental CO_2 Yield cm^3CO_2/cm^3sol^n	Theoretical CO_2 Yield cm^3CO_2/cm^3sol^n
0.01	500	(17) 0.264 [0.018]	0.253
0.02	1000	(20) 0.514 [0.010]	0.505
0.025	1250	(15) 0.573 [0.040]	0.614
0.03	1500	(19) 0.723 [0.041]	0.763
0.04	2000	(16) 0.987 [0.045]	1.034
0.05	2500	(10) 1.217 [0.037]	1.226
0.065	3250	(10) 1.527 [0.043]	1.591

[ ]-standard deviation. ( )-Number of readings.

Experimental and theoretical evolved CO_2 yields were plotted against bicarbonate concentration in the temperature range 18°C -30°C (see Figure 5.2). The best fit straight line was drawn through the mean CO_2 yield for theoretical and experimental results.

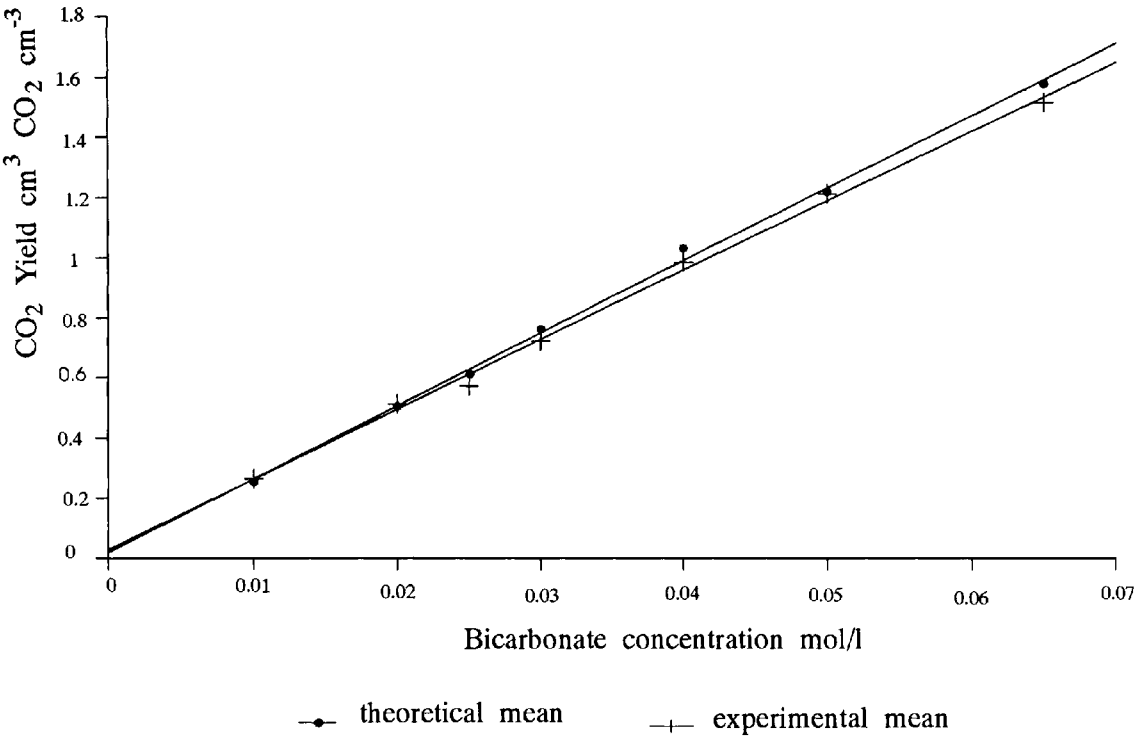


Figure 5.2 Relationship of evolved CO_2 to bicarbonate concentration in the temperature range 18°C-30°C.

The system was also tested on anaerobic effluent from an upflow anaerobic sludge blanket (UASB) laboratory reactor, that had been operating on simulated ice-cream waste, at a loading rate of 15 kg $CODm^{-3}d^{-1}$ and a hydraulic retention time (HRT) of 8 hours. Concentrated acid was added to the waste to remove all the bicarbonate and nitrogen gas was then bubbled through the waste in order to remove any dissolved carbon dioxide. Different weights of AnaLaR sodium bicarbonate (BDH Poole UK) were added to 2 litre volumes of the waste to produce a range of bicarbonate concentrations (see Table 5.2). The bicarbonate alkalinity for each effluent sample was determined titrimetrically to pH 5.75 (Jenkins *et al.* 1983) for comparison (see Table 5.2).

Table 5.2 Bicarbonate alkalinity in anaerobic digester effluent determined using the BA monitor (design 1) and Jenkins *et al.*(1983) titrimetric method.

Theoretical bicarbonate Alkalinity. ($mgCaCO_3l^{-1}$)	Experimental CO_2 Yield (cm^3CO_2/cm^3sol^n)	Experimental $NaHCO_3$ concentration ($mgCaCO_3l^{-1}$)	Mean titrimetric bicarbonate Alkalinity ($mgCaCO_3l^{-1}$)
950	(11) 0.412 [0.01]	845	(5) 906 [40.50]
1290	(11) 0.612 [0.01]	1287	(5) 1294 [10.18]
1350	(13) 0.621 [0.02]	1307	(4) 1379 [7.17]
1450	(19) 0.666 [0.02]	1406	(7) 1459 [38.00]
2000	(15) 0.930 [0.08]	1988	(5) 2225 [22.36]

[ ]-Standard deviation ( ) Number of readings.

The CO_2 yields measured by the BA monitor were converted to the equivalent bicarbonate concentration using the calibration plot shown in Figure 5.2. This showed that the initial design was feasible as an on-line bicarbonate alkalinity instrument (Hawkes *et al.* 1993). However the BA monitor (design 1) had several operational disadvantages that limited its potential as an instrument for control.

The limitations were;

(1) Measurement of the CO_2 gas evolved was not on-line. There were no suitably accurate and inexpensive methods of measuring the low flowrate available off the shelf. Therefore it was necessary to build such a gas meter so the BA monitor could be used on-line.

(2) The hydraulic retention time of the device was too long, so the instrument response time was sluggish. The reduction in volume of the device would enable more rapidly detection any changes in bicarbonate concentration in the digester. The reduced size would also reduce the production cost of the BA monitor.

5.3 OPERATION, CONSTRUCTION AND CALIBRATION OF A LOW FLOW ON-LINE GAS METERING SYSTEM (GMS).

The gas measurement in the initial design was achieved by a manual operated digital bubble meter. Although automation was possible using this technique it would involve extensive development of existing automatic calculation bubble meters (SAGA 4000, Ion Science Ltd., Cambridge, UK). Therefore the method of gas measurement for the BA monitor was re-evaluated. An extensive survey of the literature was carried out to ascertain the best method of low flow gas measurement. Moletta and Albagnac (1982) Glauser *et al.* (1984), Gwatkin *et al.* (1986), Erdman and Delwiche (1986) and Beaubien (1988) and Veiga *et al.* (1989) had described gas meters which could measure low gas flows.

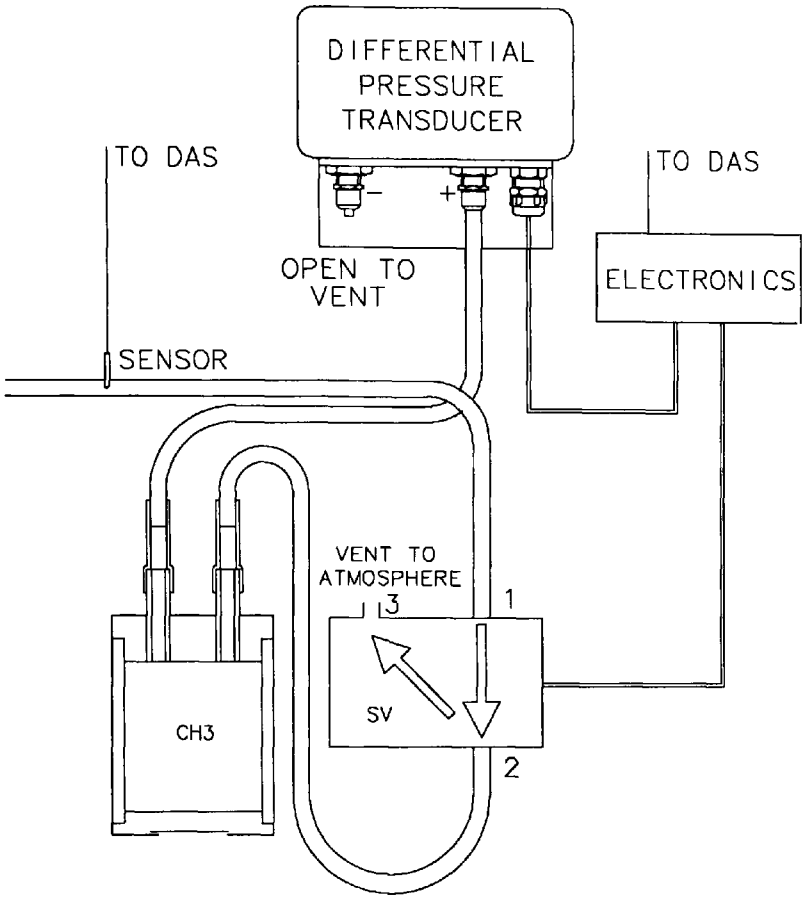
However the meter described by Beaubien *et al.* (1988) was considered the best instrument for monitoring irregular low gas flow (see section 2.3.6). This method was of higher sensitivity and needed less frequent re-calibration compared to other methods surveyed in the literature. The device of Beaubien *et al.* (1988) was reported to have long-term (several weeks) reproducibility better than 2%. Fluctuations in output were attributed mainly to normal daily variations in atmospheric pressure. They also reported that the device was capable of measuring a minimum flowrate of $0.02cm^3\ min^{-1}$ at a differential pressure trigger of 1.33 kPa. However for a given gas flow, it is not clear from Beaubien's paper what number of open-closed cycles was recorded and the time interval over which they were obtained. Calculation from equations used by Beaubien *et al.* to determine the flowrate suggest that at $0.02cm^3\ min^{-1}$ only 1.5 cycles per minute would be registered. Therefore unless an average of the pulses was taken over large time duration (e.g. 15 minutes) the accuracy of this meter would be poor. Furthermore the method of generating the low gas flows is unspecified, and a limited number of data points are given to support the accuracy stated.

To develop the BA monitor further an on-line gas meter was required which gave reproducible and accurate measurements of low and irregular gas flows with a low back

pressure. As the solenoid valve used by Beaubien was not characterised, and the exact pressure transducer described could not be obtained, an improved meter was developed using the more precise pressure transducers now available and a valve of known characteristics.

5.3.1 Configuration and operation of GMS.

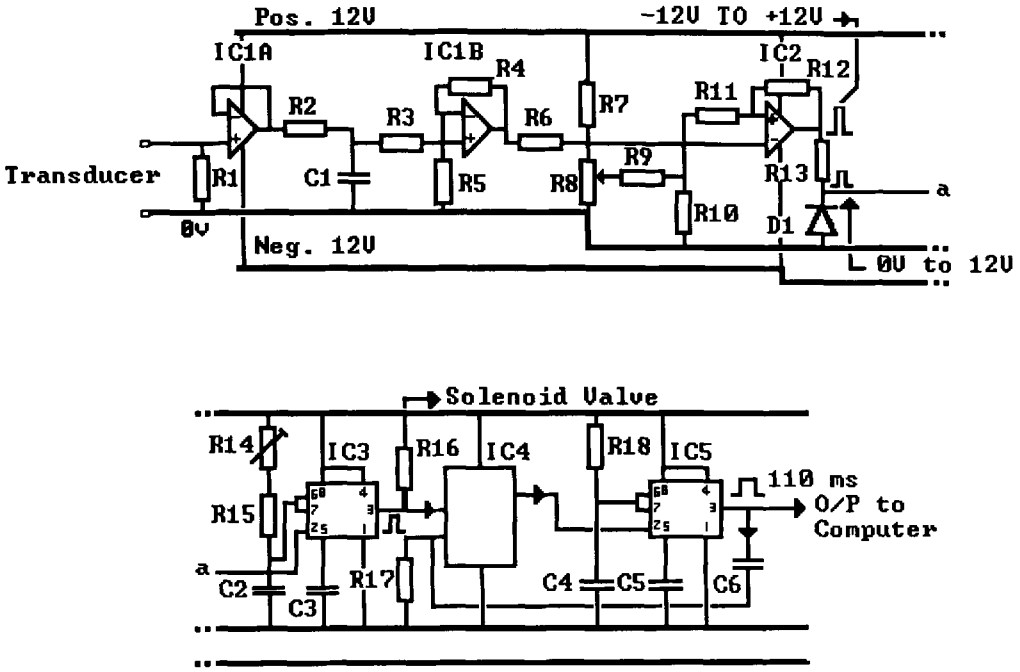
The improved Gas Metering System (see Figure 5.3) consisted of a three way spool sleeved solenoid valve (Beech, Hunter Ltd. Cardiff, UK) a 0-98Pa differential pressure transducer (model FCO 44 Furnace Control Ltd. East Sussex UK) and a ballast chamber (volume of 212cm^3) which smoothed gas pulses (Guwy *et al.* In Press). The gas produced enters the ballast chamber through the normally open path of the solenoid valve entering at port 1 and exiting from port 2 (Figures 5.3 and 5.6). When the solenoid valve is energised port 1 is closed and path 2 to 3 is open so the gas in the ballast chamber and connecting tubes is released to the atmosphere. The ballast chamber is also connected to the positive side of the sensitive differential pressure transducer. As the gas fills the gas meter, the differential pressure output voltage increases, this output is received by the GMS control circuitry (see Figure 5.4).



(DAS)	Data acquisition system
(SV)	Solenoid valve
PATH 1& 2	Normally open.
PATH 2 & 3	Open when solenoid is energised.
CH3	Ballast chamber.
SENSOR	Temperature transducer

Figure 5.3 On-line Gas Metering System configuration.

The output from the differential pressure transducer was smoothed by an RC circuit and passed through a buffer amplifier before the signal was fed into a comparator circuit, set at a voltage level which corresponded to 31.4Pa for the transducer used. The resultant pulse triggers a monostable resistor which gives a signal of width 110 ms (necessary for the pulses to be detected reliably) to energise and open the solenoid valve. The solenoid valve is kept open long enough for the pressure to equilibrate to atmospheric pressure, so the solenoid is de-energised and the cycle repeated.



IC1a non inverting amplifier. **IC1b** non inverting amplifier. **IC2** amplifier configured as a Schmitt Trigger. **IC3** monostable timer. **IC4** 12 bit counter configured as a divide by 4 circuit **IC5** monostable timer.

Figure 5.4 The electronic circuit for the GMS.

These pulses are fed into a 12 bit counter configured as a divide by 4 circuit. A second monostable resistor conditions the pulses such that they are suitable for input into the computer I/O RTI-815 board (Analogue Devices Ltd. UK). The output of the pressure transducer and pulses signal inputting the I/O board during operation of the GMS is shown in Figure 5.5.

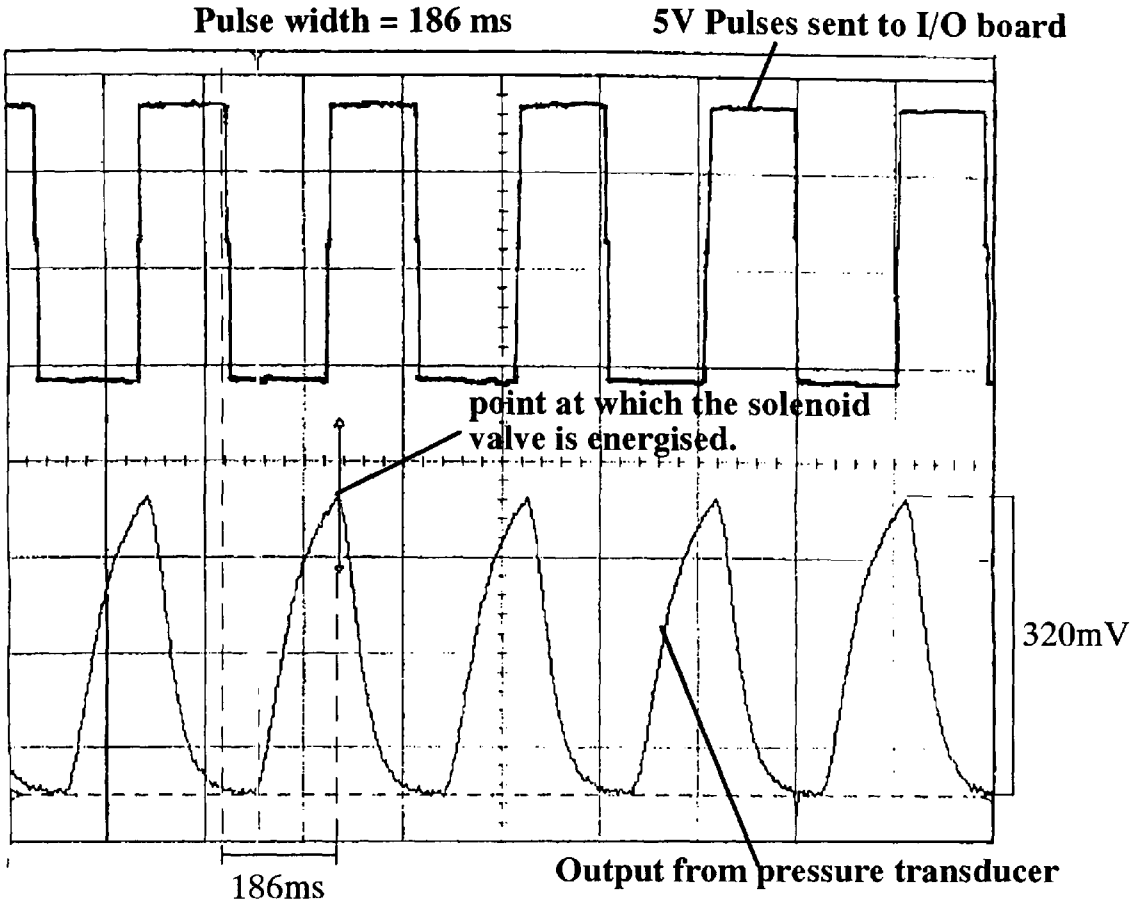


Figure 5.5 Pressure transducer output to counter and the pulse sent to the I/O board after conditioning and amplification.

A temperature probe constructed using an inexpensive temperature transducer (model 590 sensor RS Components Ltd.), was placed in the gas line. The probe was also connected to the computer RTI I/O board enabling temperature compensation of the gas flow measurements to be made.

5.3.2. Theory of gas measurement using the GMS.

Assuming that the ideal gas laws can be applied to the gas being measured, it follows that when the volume of the ballast chamber and connecting tubing (V_b) are vented to the atmosphere the amount of gas leaving the system can be expressed as follows:

$$\Delta n = \frac{V_b \cdot \Delta P}{RT} \tag{26}$$

where; V_b is the volume of the ballast, ΔP is the change in pressure (0-0.031KPa), Δn is the change in the number of moles and T is the temperature of the gas ^{o}K.

$$P \cdot \Delta V_c = \Delta n \cdot RT \tag{27}$$

Where,ΔV_c = The volume of gas that is expelled from the ballast chamber at each cycle.

Re-arrangement of the ideal gas law and combination with equation (26) gives an expression (28) for the amount of gas that leaves the system after each cycle.

$$\Delta V_c = \frac{\Delta_n RT}{P} = \frac{V_b \Delta P}{RT} \bullet \frac{RT}{P} \tag{28}$$

Therefore;

$$\Delta V_c = \frac{V_b \cdot \Delta P}{P} \tag{29}$$

Therefore the flowrate can be calibrated from the sum of the pulses and the time.

$$\text{Flowrate} = \frac{\sum \Delta_c}{\Delta t} \tag{30}$$

5.3.3 Data acquisition of GMS.

The output from the GMS control circuitry is received by a digital input counter channel. In the count mode each pulse is fed into a moving average with a time base of 5 minutes. The value of the moving average is written to a data file every 2 minutes which is the length of the program command loop. The number of pulses per minute is the raw value which can be re-calibrated to give a flowrate value. The data acquisition program monitored the input line every 55 milliseconds. Therefore providing that the pulses were

greater than 110 milliseconds long measurement of the pulse rate was reproducible and accurate.

5.3.4. Solenoid valve and pressure transducer design.

The solenoid valve configuration used in the GMS is shown in Figure 5.6. The valve used was a standard unit with six ports but only ports 1, 2 and 3 were used and the remaining ports sealed.

Central to the success of this type of gas metering system was accuracy and reliability of the solenoid valve and the pressure transducer. The improved Gas Metering System (see Figure 5.3) consisted of a three way spool sleeved solenoid valve (Beech, Hunter Ltd. Cardiff. UK). Both the spool and the sleeve are made from martensitic stainless steel and fully hardened to 60° Rockwell 'C' (cutting tool hardness) which gave corrosion resistance plus a common expansion/contraction rate for both spool and sleeve eliminating expansion problems over a wide range of temperatures (-40 to 150°C). The spools and sleeves were manufactured round and parallel to within 1 micron with diametrical clearances of 4 microns ensuring a good seal without the need of any elastic dynamic seals. The machine finish was between 0.075 and 0.125 μm ensuring extremely low friction and a fast response. The friction between the spool and sleeve is constant for its operation life span. These design specifications give an accurate and reproducible operational response for long periods of time.

In the normal de-energised state gas can enter through port 1 passing around the spool to exit at port 3 as shown in Figure 5.6. The shoulder of the spool forms a gas tight seal between it and the sleeve wall, preventing the passage of gas through port 3. In the energised state the spool is pushed rapidly into the sleeve so that the spool shoulder blocks the passage of gas from port 1 to either port 2 or port 3. This motion also opens the path between port 2 and 3, venting the gas in the ballast chamber to atmosphere.

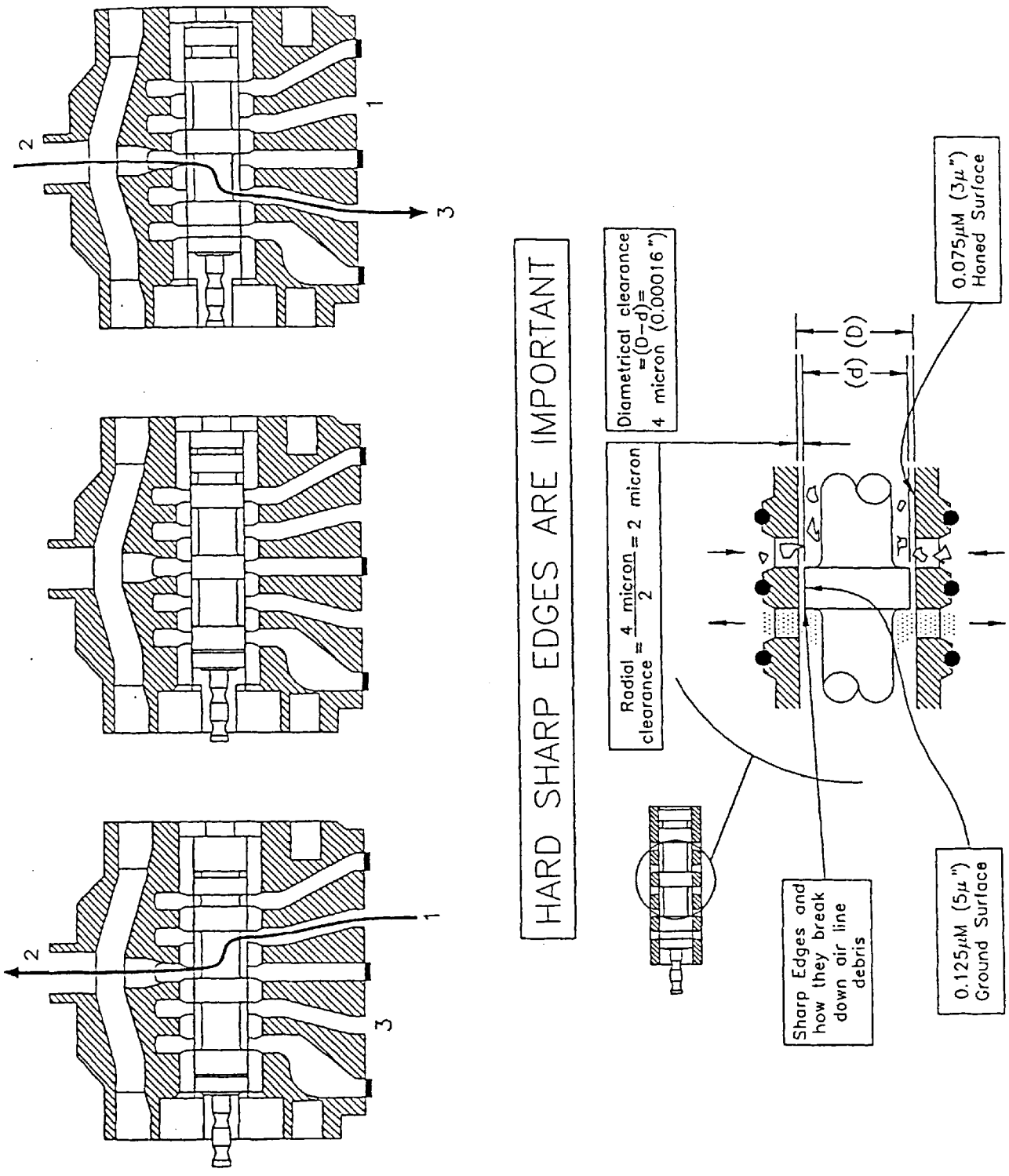


Figure 5.6 Diagram of solenoid valve construction.

The FCO44 differential pressure transducer used in GMS had an accuracy of 1% across the full measurement range (0-0.098KPa). This transducer type is more reliable and accurate than earlier transducer types. The FCO44 transducer is also less sensitive to the humidity of the gas which was an important consideration in the choice of transducer for the GMS. The transducer unit itself consists of a stretched metal diaphragm, the tension of which is adjusted until a certain value of mechanical movement equates to the required pressure range (0-0.098 KPa). This movement is converted to a change in capacitance which is set with fine tolerances by the manufacturers. The electronic measurement of the capacitance is based on the Wheatstone Bridge principle using positive and negative rails to provide true differential output signals from the transducer.

5.3.5. Calibration of Gas Measurement System.

The on-line low flow GMS was calibrated using a variable speed peristaltic pump (model №· 502s, Watson-Marlow Ltd. Falmouth UK) fitted with 5 channel micro-cassette 8 roller pumphead to produce a precise and constant gas delivery over a long time. Marprene tubing with an internal diameter of 0.25mm used at 55 rpm gave a flowrate of 0.23cm^3 min^{-1}. At this flowrate 440 roller contacts were made with the tubing per minute reducing the size of the pulses to a minimum. A range of flowrates was achieved by variation of the rpm, the tubing bore, and the number of channels connected in parallel to the GMS inlet port. Gas generation by this method was found to be controllable and reproducible. Gas from a cylinder for example produced fluctuating flowrates and control at low gas flow was difficult.

The flowrate generated by the peristaltic pump was measured by a digital bubble flow meter (SAGA 4000 Ion Science Ltd. Cambridge, UK) connected to the suction side of the pump, thus bubble movement was the result of negative pressure. This meant that measurement of the gas flow by the digital bubble meter could be recorded during the measurement by the GMS. The bubble meter accuracy was calibrated at the factory to

±0.5% of the reading and was a suitable method for calibrating the GMS. Bubble meter readings were taken at 2 minutes intervals for 1 hour for each flowrate. A regression analysis was performed on the on the averaged flowrates measured by the digital bubble meter and the averaged pulse rate determined by the GMS system. The data showed a linear correlation coefficient equal to 0.9997 as shown in Figure 5.7.

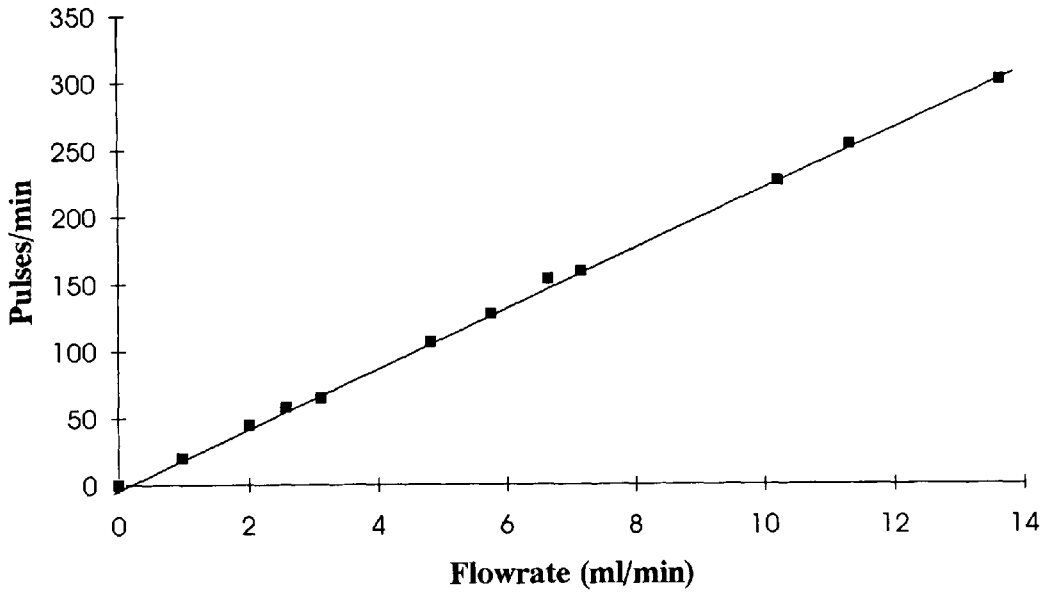


Figure 5.7 Calibration plot of GMS using a digital bubble meter.

Hence the flowrate was calculated by the following expression;

$$\text{Flow rate (ml/min)} = (\text{counts/min} + 0.1876)/ 5.614 \qquad (31)$$

This calibration expression was entered into the command file of the data acquisition program.

On-line measurements of low (0.1-14cm^3min^{-1}) gas flows has been achieved with small changes (31Pa) in back pressure and a response time in the order of 1 minute (Guwy *et al.* In Press). The flow of 0.1cm^3min^{-1} was the lowest accurately measurable by the bubble meter, so does not necessarily represent the lowest flow measurable by the on-line

GMS. If measurements of high flowrates are require either the ballast volume can be increased or the differential pressure set point as shown in equation (29). The gas meter operated reliably without any problems during the experimental work described in the following chapters of this thesis.

5.4. CONCLUSIONS

The direct on-line determination of bicarbonate alkalinity by measuring the carbon dioxide yield from a sample stream, after addition of excess acid was shown to an effective method for standard solutions and anaerobic effluents. Therefore a method was established which could be used as the basis for an instrument to monitor on-line bicarbonate in biological treatment processes.

A new low flow gas meter was developed that was able to measure on-line gas flows of 0.1 to 14cm^3min^{-1} with an accuracy of ±5% and a response time of 1 minute. The gas meter produced only very small changes in back pressure which made it suitable for use in the method proposed for the on-line BA monitor.

6. DESIGN, DEVELOPMENT AND OPERATION OF AN IMPROVED BA MONITOR.

6.1 DESIGN AND DEVELOPMENT.

The reduction of the hydraulic retention time (HRT) and therefore the response time of the BA monitor design 1 and the production of a more robust BA monitor was the objective of the work described in this chapter. Reduction of the HRT and response time of the BA monitor could be achieved by reduction of the liquid volume of the monitor, and secondly by an increase in the flowrate of effluent supplied to the monitor. Increased flow rate to the BA monitor was unfavourable as this would limit use of the instrument to large scale reactors. Therefore the shortening of the HRT of the BA monitor (design 1) was achieved by reducing the liquid volume of the system approximately to 200 cm^3. It was calculated that this would reduce the response time to approximately 60 minutes at an effluent delivery rate of 10 cm^3 min^{-1}.

Essentially the newly designed bicarbonate alkalinity (BA) monitor (shown in Figure 6.1) configuration and operation were the same as in design 1. The saturation CO_2 flowrate was unchanged at 14cm^3 min^{-1}, and the contents of the saturation and the acidification chambers were mixed by recycle pumps (Monside Ltd. Herts. UK). The saturation and acidification chambers were constructed from a single length of extruded perspex tubing of internal diameter 40 mm. The ports (perspex tube of internal diameter 8 mm) for the attachment of the recycle pumps were set at an angle of 45^o to improve the mixing in the chamber. The saturation and acidification chamber were separated from each other by a partition (A). The contents of the saturation chamber passed into the acidification chamber through a vertical tube (B) of internal diameter 10 mm. Along with the structural modifications of the BA monitor, the on-line gas metering system was connected to the gas outlet at the top of the acidification chamber.

The BA monitor was tested using standard sodium bicarbonate solutions (AnaLaR grade BDH Poole UK). The resulting measurement of carbon dioxide flow fluctuated significantly. Surface tension of the solution at the mouth of the vertical overflow tube in the saturation chamber exaggerated pulses from the peristaltic dosing pumps severely effecting the gas flow measurement.

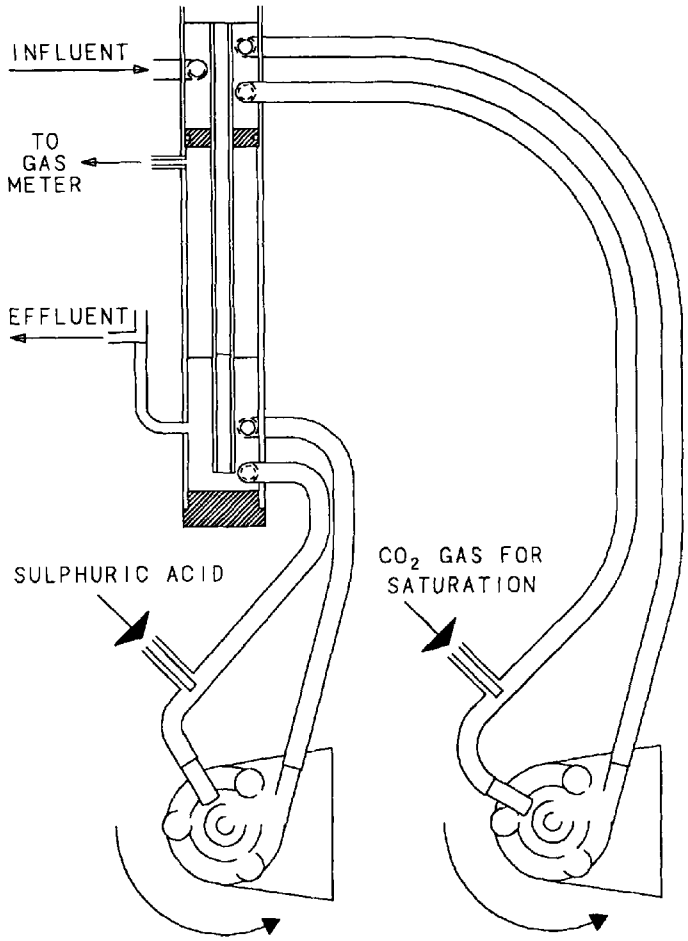


Figure 6.1 Bicarbonate monitor (design 2).

The pulsing was reduced by replacement of the dosing pumps with more accurate 302F 55 rpm peristaltic pump, fitted with a twin cassette 8 roller pump head which increased the roller contacts to 400 per minute (Watson and Marlow, Falmouth, UK). The tubing used to pump the effluent had a diameter of 1.85 mm and delivered 9.5 cm^3 min^{-1}. The

2.5 M H_2SO_4 was delivered by the other channel of the pump head using 0.25 mm bore marprene tubing delivering 0.14 cm^3 min^{-1}.

It was thought that if the entrance of the vertical overflow tube could be submerged, the pulsing effects caused by the liquid surface tension would be eliminated. To maximise the internal diameter of the overflow tube the height between the liquid levels of the saturation chamber and the acidification chamber was kept to a minimum. It was important that the internal diameter of the vertical tube was not reduced too much as this would increase the chance of blocking when operating on real waste. The maximum internal diameter that still allowed submersion of the vertical tube was found by experiment to be 1.3mm.

6.2 OPERATION OF DESIGN 2 WITH MODIFICATIONS.

The modified design was tested using 0.03 M standard sodium bicarbonate solution prepared using sodium bicarbonate (AnaLaR grade BDH Ltd. Poole UK). After 5 hours of on-line operation no significant pulses were recorded. The effectiveness of this design using real anaerobic effluent was investigated before any further calibration of the monitor.

The BA monitor was connected to the manometer overflow unit of an anaerobic filter reactor operating on simulated ice cream waste (see Figure 3.1). The loading rate of the reactor was 6.2 $kgCODm^{-3}d^{-1}$ with a 80% reduction in the organic content of the waste and an off-line bicarbonate concentration of 1200 $mgCaCO_3l^{-1}$ (using the method of Jenkins *et al.* 1983). Within 5 minutes of operation foam began to form in the acidification chamber, after a further 10 minutes the gas line to the GMS became blocked. The foaming was attributed to the volatile fatty acids and proteins present in the

effluent. The apparatus was washed with de-ionised water several times and reconnected to the anaerobic digester, foaming again blocked the gas line.

In order to prevent foaming a silicon based antifoam (BDH Ltd. Poole UK) was pumped into the influent line of the BA monitor using a second 302F 55 rpm peristaltic pump, fitted with a twin cassette 8 roller pump head. (Watson and Marlow, Falmouth, UK). A 10% dilution of antifoam (Dow Corning 1510 BDH LTD. Poole) was pumped at a flowrate of 0.14 cm^3min^{-1} using 0.25 mm bore marprene tubing. Initially the foaming was suppressed, however in the acid conditions of the acidification chamber the anti-foam formed a residue which built up at the exit point of the vertical overflow tube and blocked the entrance of effluent into the acidification chamber. An alternative approach to the addition of anti-foaming agent was required for foam prevention. The foaming seemed to originated at the liquid/gas interface where the mixing was less vigorous. It was postulated that increased mixing might prevent the foam from occurring. So, the mixing was increased by reducing the length of the recycle tubing to the pump mixing the acidification chamber. The monitor was again connected to the anaerobic reactor and operated on-line reliably for 15 days with no signs of foaming or blocking. However this investigation was carried out during steady state operation of the anaerobic filter when the effluent COD and TVFA levels were in the order of 1000 mgCOD/l and 100 ppm respectively. It was important to show that the monitor could operate effectively during conditions of anaerobic instability, such as organic overloading when the COD and TVFA levels are much greater. Under such conditions there is a higher chance of blockage since protein and fat levels in the effluent will increase. Therefore the organic loading rate of the 10 litre anaerobic filter was increased from 6.2 to 23.3 $kgCODm^{-3}d^{-1}$ for 8 hours to induce process instability. Twelve hours after the overload had been initiated the effluent COD concentration had increased from 360 to 6167 $mgCODl^{-1}$.

Figure 6.2 shows that bicarbonate concentration measured by the on-line BA monitor was relatively constant during the steady state operation before administering the overload (the vertical arrows in the Figures signify the start and end of the overload).

The bicarbonate concentration began to fall approximately 2 to 3 hours after the start of the overload. This lag phase was attributed to plug flow affect of the anaerobic digester, which was confirmed by later by lithium tracer studies (see section 7.3).

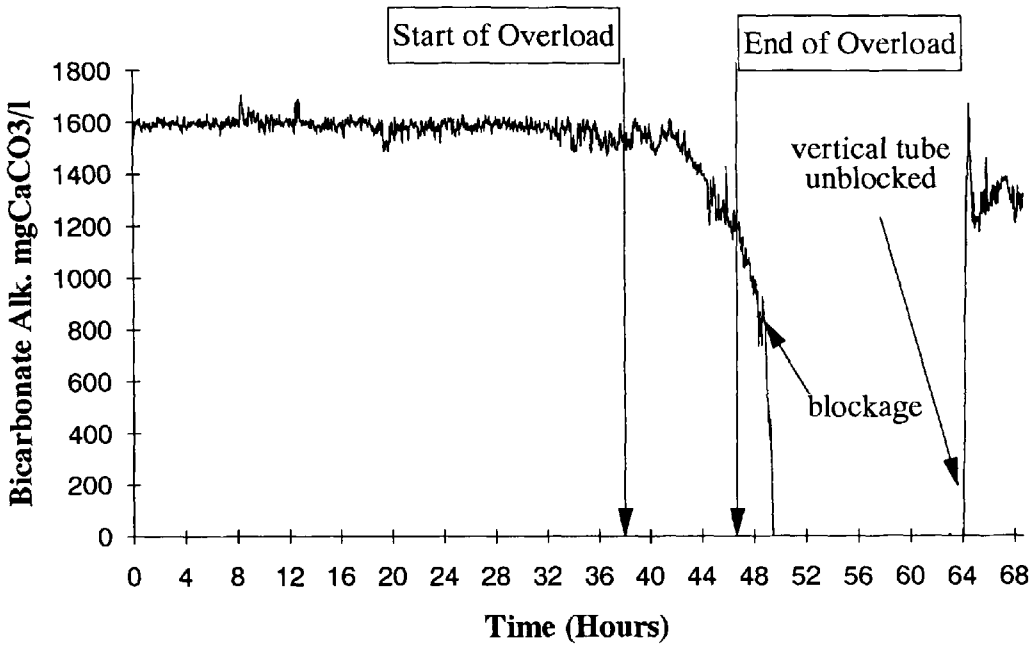


Figure 6.2 Blockage of the BA monitor on-line to an anaerobic filter during an organic overloading of 23.3 kgCODm^{-3}d^{-1}.

Contrary to Monzambe *et al.* (1988) and Kennedy and Muzar (1984) the on-line pH probe appeared to operated throughout the overloading. However the BA measurement dropped dramatically at 48 hours to zero, before the full affect of the overloaded on the anaerobic process had occurred suggesting that the BA monitor had malfunctioned. The minimum pH value was recorded at time 54 hours (see Figure 6.3) but the BA measurement at this point was zero. It was clear after inspection of the BA monitor that the narrow vertical overflow tube had become blocked with fats and suspended matter. As the blockage occurred during the night the blockage was not cleared so the effluent was not able to flow from the saturation chamber to the acidification chamber. So the production of carbon dioxide from the reaction of bicarbonate ions with acid rapidly ceased in the acidification chamber.

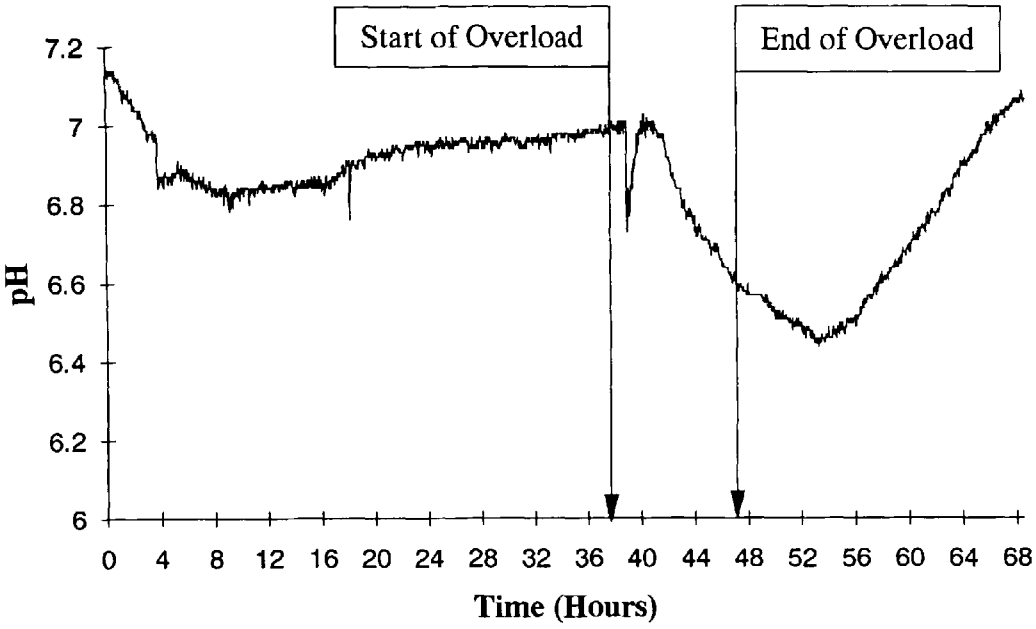


Figure 6.3 On-line pH measurement of an anaerobic filter during an organic overloading of 23.3 kgCODm^{-3}d^{-1}.

The blockage was removed from the vertical overflow to restore the flow of effluent to the acidification chamber. Immediately the GMS began to monitor a production of gas and on-line bicarbonate concentration measurement was resumed. The bicarbonate alkalinity returned to a level approximately 200 mg$CaCO_3$l^{-1} below the steady state concentration before the start of the overload. A loading rate of 6.2 kgCODm^{-3}d^{-1} was maintained for 24 hours to allow the return to steady state process conditions. During the recovery period the BA monitor performed reliably and bicarbonate concentration returned to 1600 mg$CaCO_3$l^{-1}. The overloading experiment was repeated with the same outcome, blockage due to fats and suspended solids (see Figure 6.4 and 6.5). The results of the overload suggested that the BA monitor could be used reliably during periods when the TVFA concentration and COD in the anaerobic effluent were relatively low. The experiments also showed that on-line bicarbonate alkalinity is a good parameter to monitor the onset of digester instability. However during overloading when the effluent TVFA and COD concentration increased the vertical overflow tube was easily blocked.

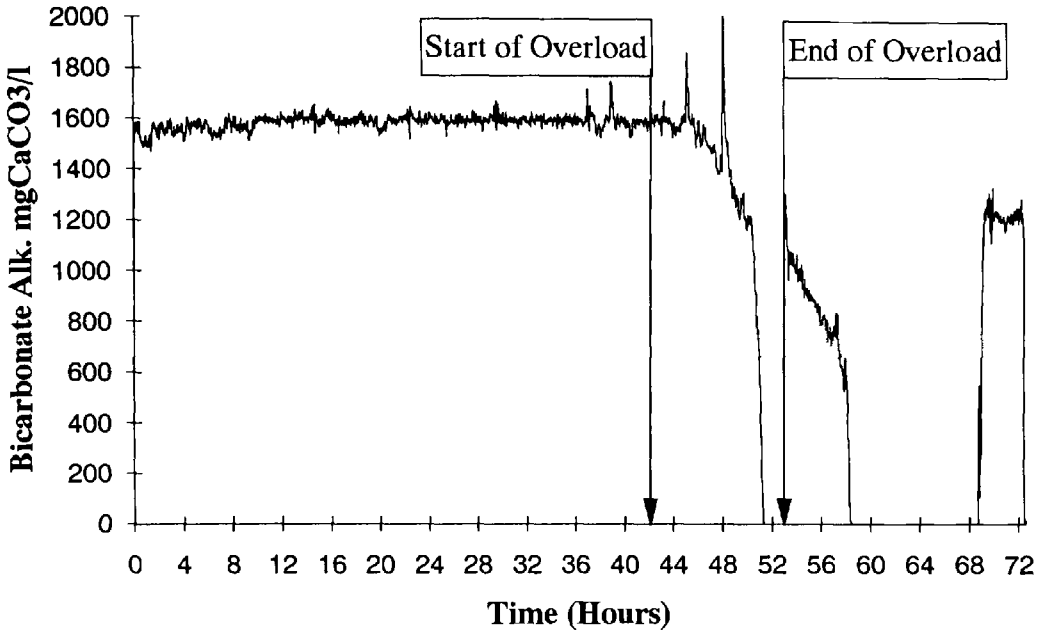


Figure 6.4 Blockage of the BA monitor on-line to an anaerobic filter during an organic overloading of 24.7 kgCODm^{-3}d^{-1}.

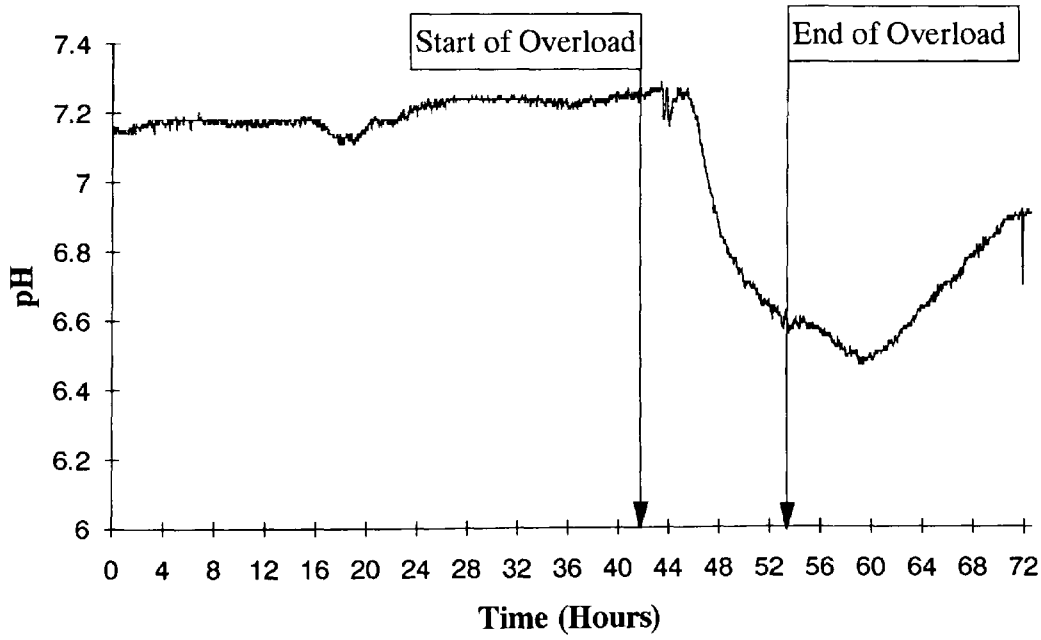
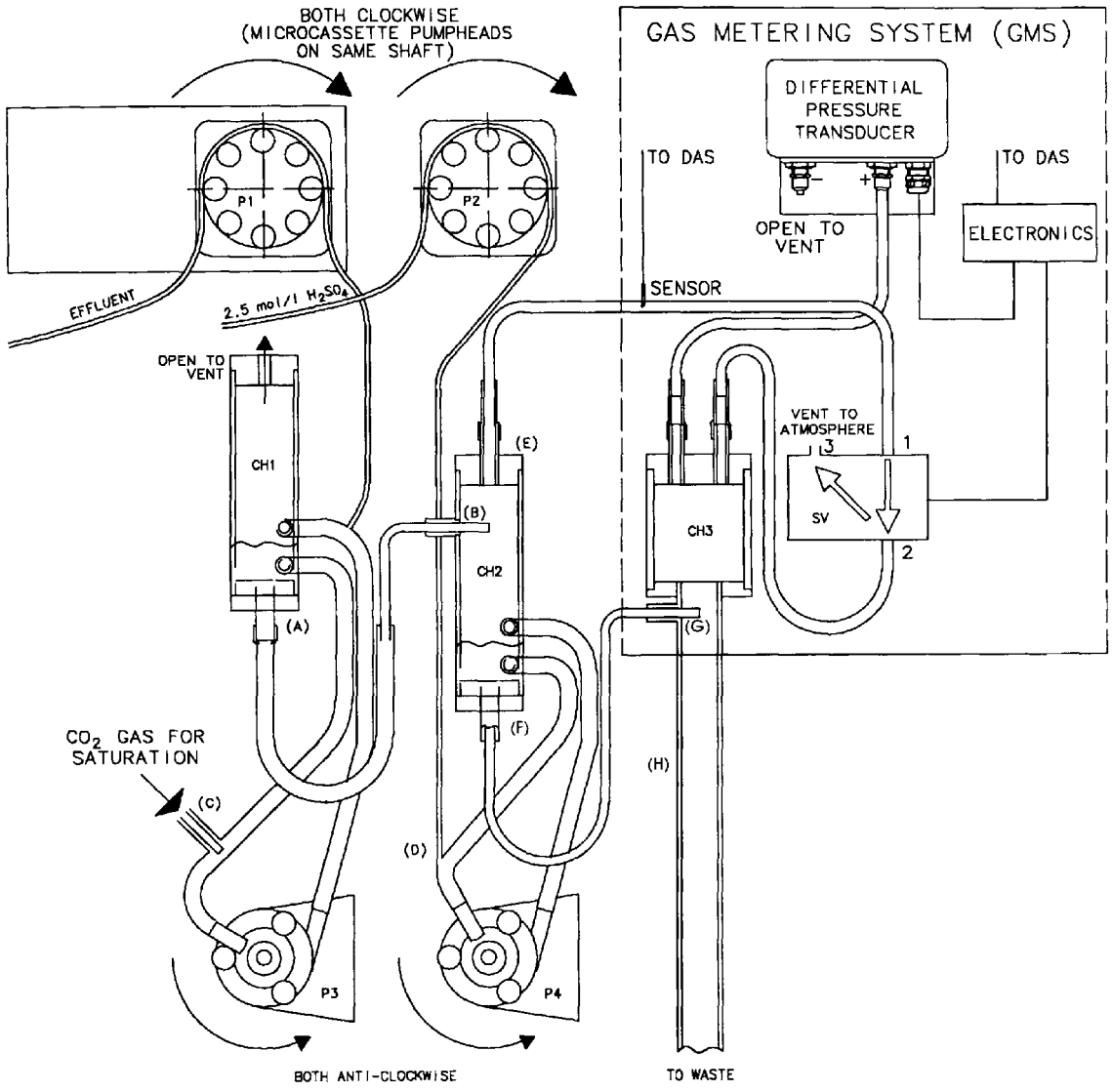


Figure 6.5 On-line pH measurement of an anaerobic filter during an organic overloading of 24.7 kgCODm^{-3}d^{-1}.

6.3 DESIGN AND CONSTRUCTION OF A PROTOTYPE BA MONITOR.

It was clear that constant flow of effluent from the saturation chamber to the acidification chamber was critical for the effective operation of the on-line BA monitor, so the BA monitor was fundamentally redesigned. The saturation and the acidification chamber were separated and positioned side by side (as illustrated in Figure 6.6 and plate 1).



(A) exit port to saturation chamber, **(B)** Input port to acidification chamber, **(C)** Input of CO_2, **(D)** Input port for sulphuric acid, **(E)** Gas port to gas metering system,**(F)** Exit port from the acidification chamber, **(G)** Overflow pipe, **(H)** Waste pipe, **(DAS)** data acquisition system, **(SV)** Solenoid valve, **(CH1)** Saturation chamber, **(CH2)** Acidification chamber, **(CH3)** Ballast chamber, **(P1)** Effluent pump, **(P2)** Sulphuric acid, **(P3)** Recycle pump mixing contents CH1, **(P4)** Recycle pump mixing the contents of **(CH2)**.
PATH 1 & 2 is normally open.

Figure 6.6 Prototype on-line bicarbonate alkalinity monitor.

The two chambers were connected by a manometer ('U' tube) overflow at the base of the saturation chamber port (A), to the acidification chamber at side port (B). The manometer overflow enabled the use of a wider bore tube so minimising blocking whilst maintaining a 'wet' system.

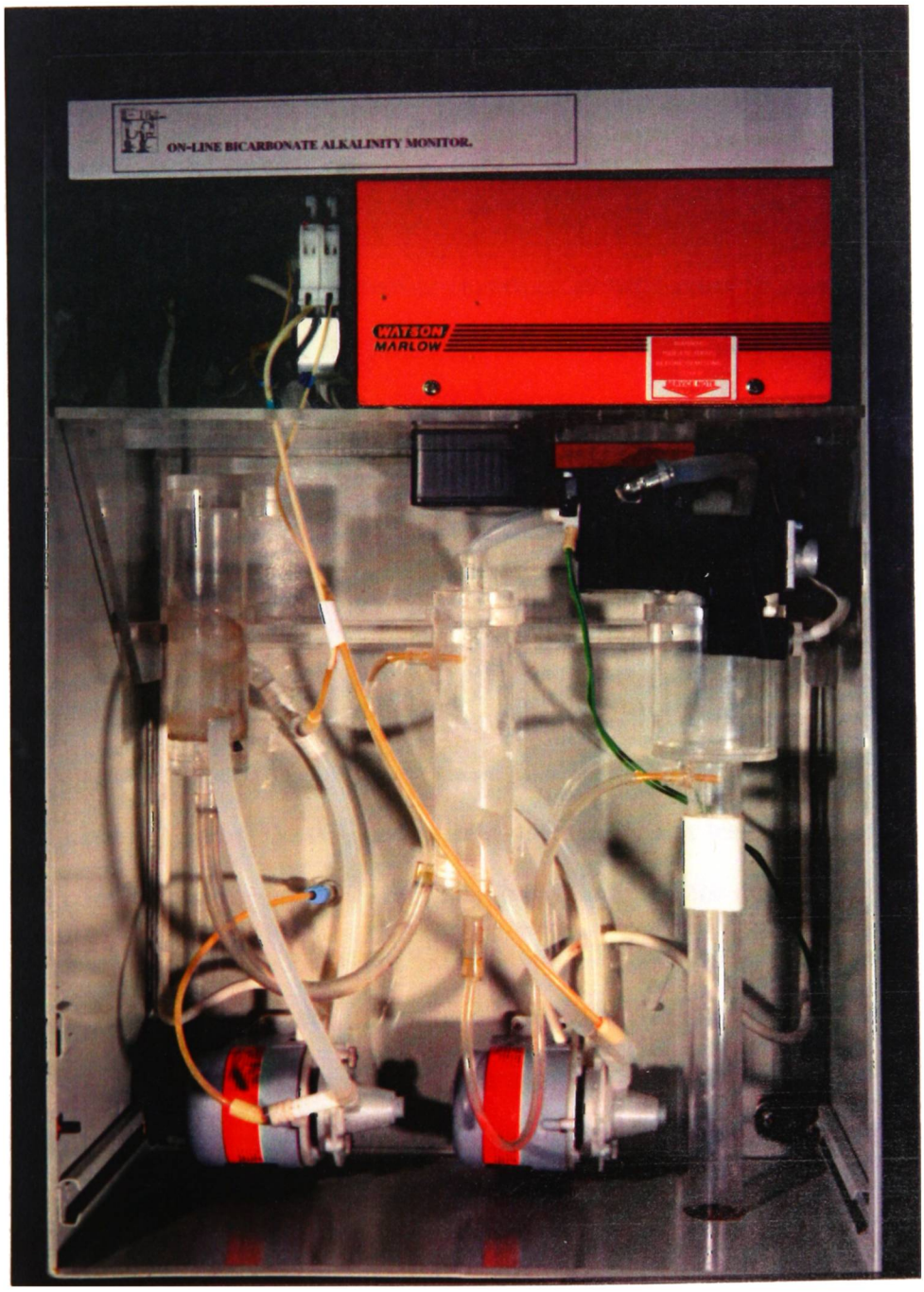


Plate 1 Prototype On-line BA monitor.

The construction of the overflow exit at point (B) was found to be critical to prevent film flow, which caused syphoning of the saturation chamber contents. The acidified effluent exited the acidification chamber through a second manometer connected at the base of the acidification chamber (port F). The outlet of this manometer (G) required the same construction as the outlet (B), to prevent syphoning of the whole system. The outlets (B) and (G) were constructed from rigid PVC tubing of i.d. 4 mm. Their construction also helped the production of small droplets minimising the pulsing effect. The manometers extended vertically to a distance greater than 50 mm beneath the exit points (A) and (F), preventing carry over of small gas bubbles and reduced pulsing. The saturation, acidification and ballast chambers were all constructed from extruded acrylic tubing because it was resistant to acid and easy to machine. The component parts of the saturation, acidification and ballast chambers are illustrated in Appendix 2. The relative height and orientation of the saturation and the acidification chambers were important to ensure constant flow, therefore each chamber was constructed with a fixing plate with two location pins. These locating pins pushed into location holes in the holding shelf (see Appendix 2 and part numbers 5 and 6) allowing removal of the individual chambers for cleaning as shown in plate 2.

The base of the ballast chamber was used as the fixing position for the waste pipe (I) to which the acidification outlet tube (G) was connected. The outlet nozzle of the saturation chamber (B) and (G) consisted of plastic tubing 20 in length (i.d. 5mm) inserted into extruded acrylic tubing (o.d 12mm) fixed to the side of the acidification chamber and the waste pipe respectively (see Appendix 2. part 2.3). Connection of the saturation exit port (A) to the entrance port (B) of the acidification chamber was achieved using 2 tubing diameters. PVC tubing (o.d 10 mm) was used to make up the 'U' tube section of the manometer which was connected to 7 mm i.d. polythene tubing which was pushed onto the 5 mm tubing of the nozzle. Connection of the exit port (F) of the acidification chamber and the outlet port (G) was made in the same way. The holding plate and the recycle pumps were attached to a mounting board (see Appendix 2 parts 0.1 to 0.3).

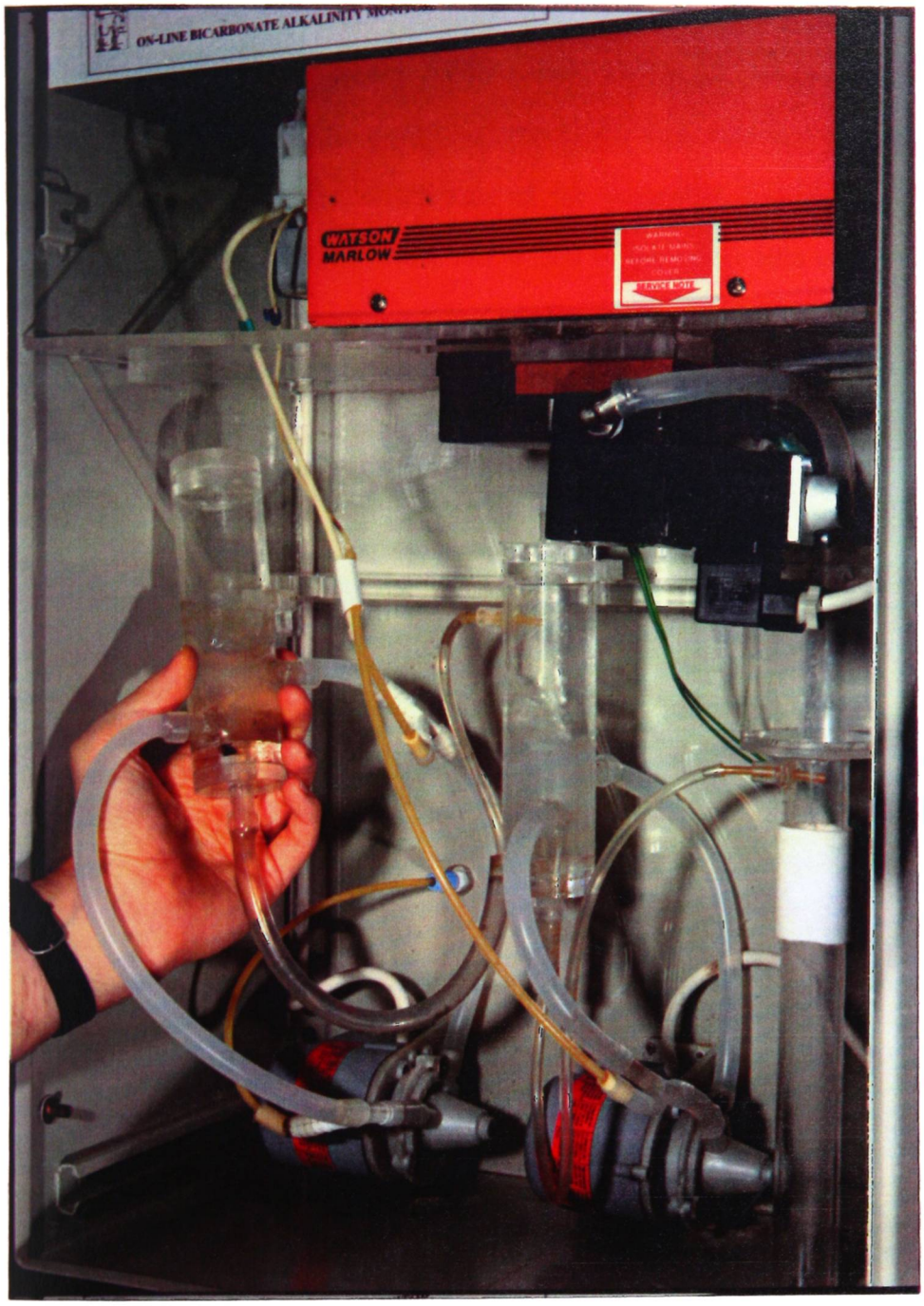


Plate 2 Removal of the saturation chamber for cleaning.

Silicon tubing (Watson and Marlow Ltd. Falmouth UK) was used for the connection of the recycle ports of both CH1 and CH2 to the 1020 recycle pumps (P3) and (P4) respectively. The input of CO_2 (C) for saturation entered the recycle tubing through a

3mm i.d tube which projected into the recycled effluent path, close to the recycle pump (P3). The suction of (P3) helped the production of small gas bubbles which are effective in saturating the effluent. A suitable weather-proof case of dimensions H600mm × W400mm× D250mm (Sarel Electric Ltd. Luton UK) was used for housing the apparatus. The peristaltic pump and the GMS were attached to a shelf fitted to the mounting board for the attachment of the peristaltic dosing pump and GMS. (see appendix 2 part 0.0). The GMS was bolted to the under side of the shelf as shown in plate 3.

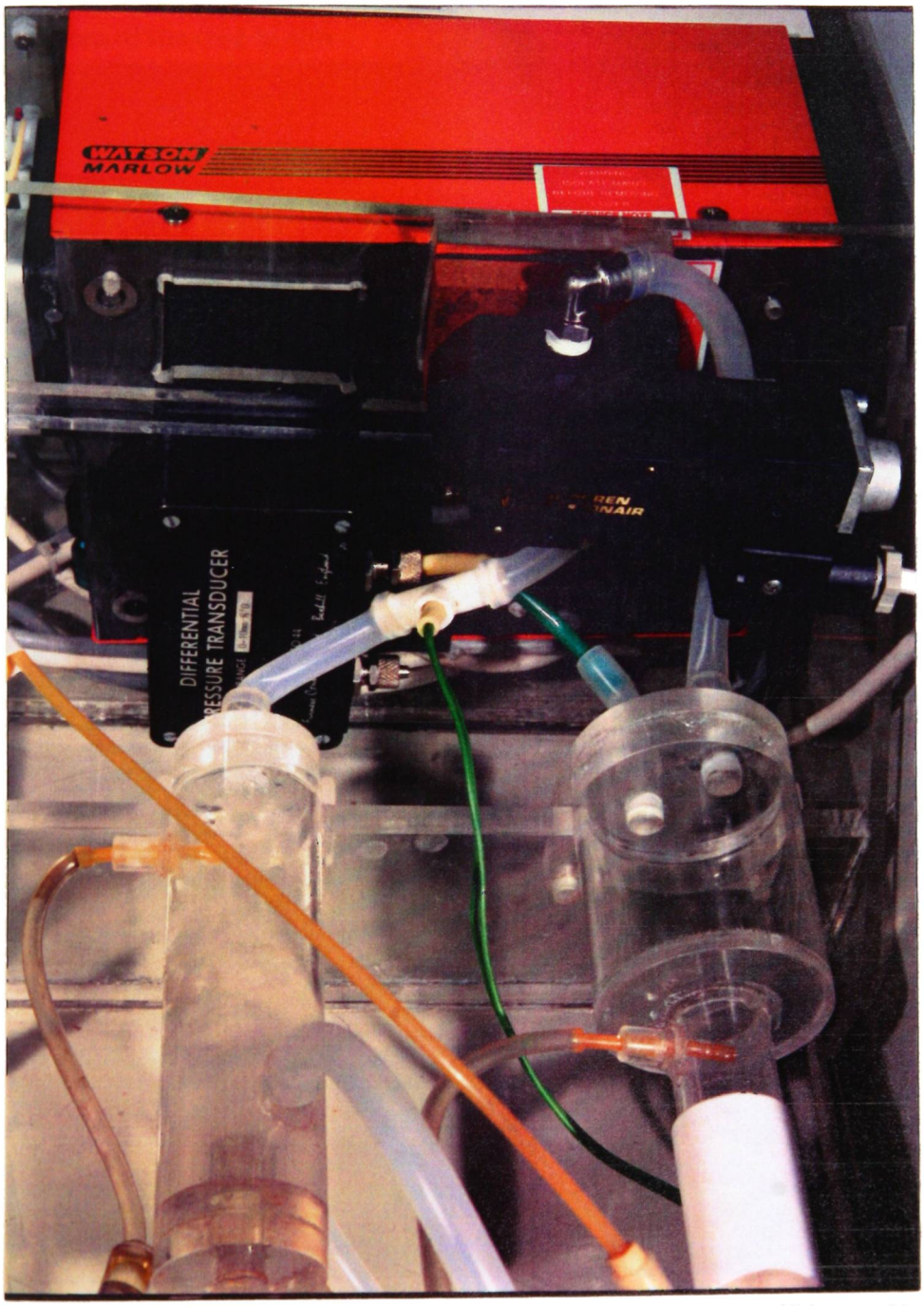


Plate 3 Mounting position of the GMS in the prototype BA monitor.

The solenoid valve was mounted on a vibration dampening pad to reduce resonance during operation. Severe vibrations had a small but significant effect on the performance of the differential transducer. The electronic control circuit was housed in a rack mounted box positioned above the dosing pump. The box ran on the steel runners that were allowing easy access for maintenance of the circuit control boards (see Plate 4). The mounting board was bolted to the back of the weather proof case at all four corners. Gas lines, power cables, output cable, effluent and acid tubing entered and exited at the rear of the case through waterproof bulkhead connections The waste pipe (I) exited the bottom of the case to sink.

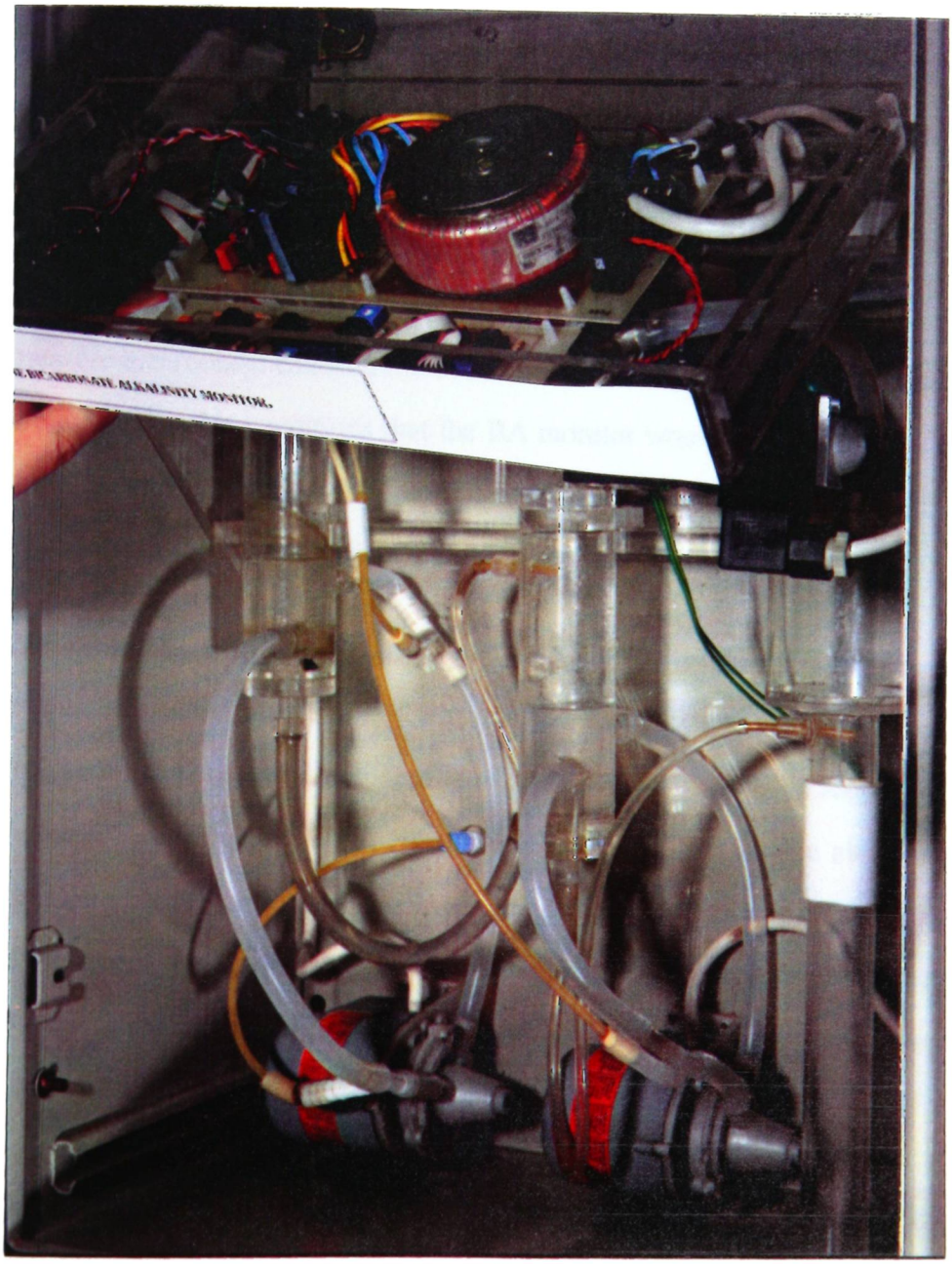


Plate 4 Electronic control circuitry for the BA monitor.

6.4. OPERATION OF THE BA MONITOR PROTOTYPE.

The effluent was fed to the saturation chamber at a flow rate of 9.5 cm^3 min^{-1} at point (C) (in Figure 6.6) and saturated by a constant flow of CO_2 gas (14 cm^3 min^{-1}) from a cylinder. Mixing of the saturated effluent was achieved by a 1020 recycle pump (P3) (EHIEM Berlin, Germany). The CO_2 saturated effluent passed through the exit port (A) to the acidification chamber at point (B), where it was mixed with 2.5 M H_2SO_4 by a second 1020 recycle pump (P4). The CO_2 gas liberated from the reaction between the bicarbonate in the effluent and the sulphuric acid passed through gas port (E) to the GMS as describe in section 4.3. The 5V pulses from the GMS control circuitry were received by the data acquisition system (DAS) and converted to a flowrate, calculated from a moving average of 5 minutes of raw data.

An experiment was designed to determine whether the redesigned BA monitor could measure bicarbonate concentration in effluents with high COD and fat levels. To simulate the worst possible conditions that the BA monitor would meet, it was used to determine the bicarbonate concentration in influent waste with a COD of 21,389 mgl^{-1}. Design 2 had blocked when the effluent COD approached 4500 mgl^{-1}.

The influent used to test the prototype BA monitor was dosed with sodium bicarbonate to give a concentration 500 $mgCaCO_3l^{-1}$. The waste was stored in a continuously stirred tank and maintained at a temperature of 37±1.2°C using a F1-15 recycling heater pump. Figure 6.7 shows that the BA monitor measured the bicarbonate alkalinity without any signs of blockage or foaming for a period of 45 hours. Effluent COD levels in the order of 21000 mgl^{-1} are unlikely to occur, so the probability of blockages occurring in the BA monitor when connected to the anaerobic digester were considered to be small.

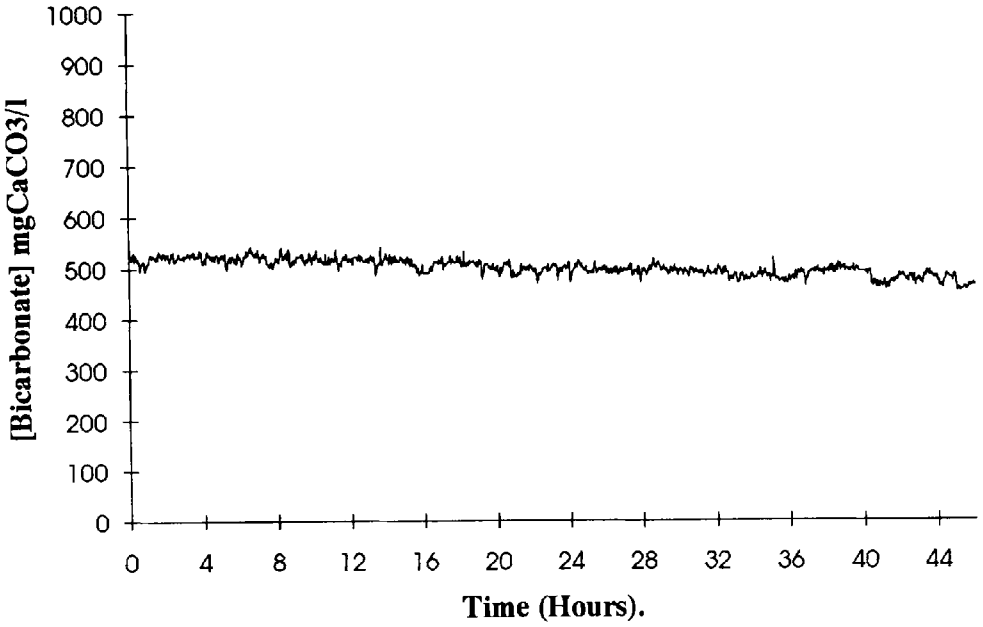


Figure 6.7 On-line bicarbonate determination of influent waste with a COD of 21,389 mgl^{-1} using the redesigned BA monitor.

6.5. CONCLUSIONS.

The on-line gas meter was shown to be effective as the gas sensor in the BA monitor, allowing on-line operation of the BA monitor. The redeveloped BA monitor can operate on wastewaters with COD levels of greater than 20gl-1 and a high fat content without blockage problems.

7. ASSESSMENT OF PRIMARY SENSOR CHARACTERISTICS OF THE PROTOTYPE BA MONITOR.

7.1. ACCURACY AND REPRODUCIBILITY.

The accuracy of the prototype BA monitor was determined using a series of standard bicarbonate solutions which were prepared immediately before use. Sodium bicarbonate (AnaLaR, BDH Ltd. Poole UK) was weighed and added to CO_2-free de-ionised water to make standard solutions of 5.0 to 50mM bicarbonate, corresponding to an alkalinity of 250 to 2500 $mgCaCO_3l^{-1}$ (Guwy *et al.*1994). Data from 1 hour of steady state operation of the BA monitor was averaged to obtain a representative measurement of the BA for each bicarbonate standard. The output from the BA monitor was adjusted to compensate for changes in pressure and temperature according to equation (25). Off-line measurements of bicarbonate were also performed at regular intervals using the standard titration method for bicarbonate determination (American Public Health Association, 1985). At least two sets of data at each bicarbonate concentration were collected on different days. The bicarbonate alkalinity monitor calibration results using the standard bicarbonate solutions are shown in Figure 7.1.

The calibration results of the BA monitor with standard bicarbonate solutions (250-2500 $mgCaCO_3l^{-1}$) and off-line determinations of alkalinity to pH 4.3 (American Public Health Association, 1985) are shown in Table 7.1. The standard deviation for both the on-line and the off-line measurements are also given. It can be seen that the two methods give comparable values. The accuracy of the BA monitor compared with the bicarbonate concentration by weight is better than 7.5% which is similar to accuracy given by titration to pH 4.3. It should be noted that the standards are solutions of pure sodium bicarbonate with no interfering substances, so that in this circumstance titration to pH 4.3 should give a true representation of bicarbonate content.

Table 7.1 Calibration of the Prototype BA monitor using standard sodium bicarbonate solutions.

Actual bicarbonate concⁿ by weight. ($mgCaCO_3^{-1}$)	Mean Bicarbonate measured concⁿ by on-line BA monitor. ($mgCaCO_3^{-1}$)	Mean Bicarbonate concⁿ measured by titration APHA (1985) ($mgCaCO_3^{-1}$)
230	(1.74) 236 [133]	(7.09) 238 [3]
230	(5.57) 229 [241]	(9.07) 232 [5]
500	(8.21) 521 [66]	(7.78) 530 [2]
500	(7.32) 517 [160]	(8.85) 512 [4]
500	(3.90) 489 [55]	(6.36) 492 [2]
700	(3.47) 731 [58]	(18.38) 737 [2]
700	(5.72) 726 [99]	(15.56) 716 [3]
1100	(8.06) 1073 [166]	(4.93) 1088 [5]
1100	(3.90) 1080 [44]	(10.61) 1084 [2]
1500	(15.80) 1528 [151]	(19.04) 1512 [3]
1500	(16.17) 1516 [175]	(29.57) 1518 [3]
1500	(16.14) 1507 [178]	(26.15) 1517 [3]
2000	(16.84) 1970 [172]	(9.06) 1966 [3]
2000	(25.59) 2003 [217]	(10.14) 1986 [5]
2000	(25.79) 1999 [217]	(16.02) 1994 [5]
2500	(34.86) 2569 [47]	(95.46) 2519 [2]
2500	(19.43) 2532 [49]	(21.92) 2547 [2]

( ) Standard Deviation [ ] Number of samples.

A linear regression analysis was performed on the on-line data using the off-line determination of bicarbonate concentration as the x-axis. Figure 7.1 is a plot of 17 data points, with at least two replicates at each bicarbonate concentration and demonstrates the reproducibility of the bicarbonate alkalinity monitor over the range 229 to 2569

$mgCaCO_3l^{-1}$. Each point is an average of at least one hour's data from the monitor, and a mean of at least 4 titrimetric determinations.

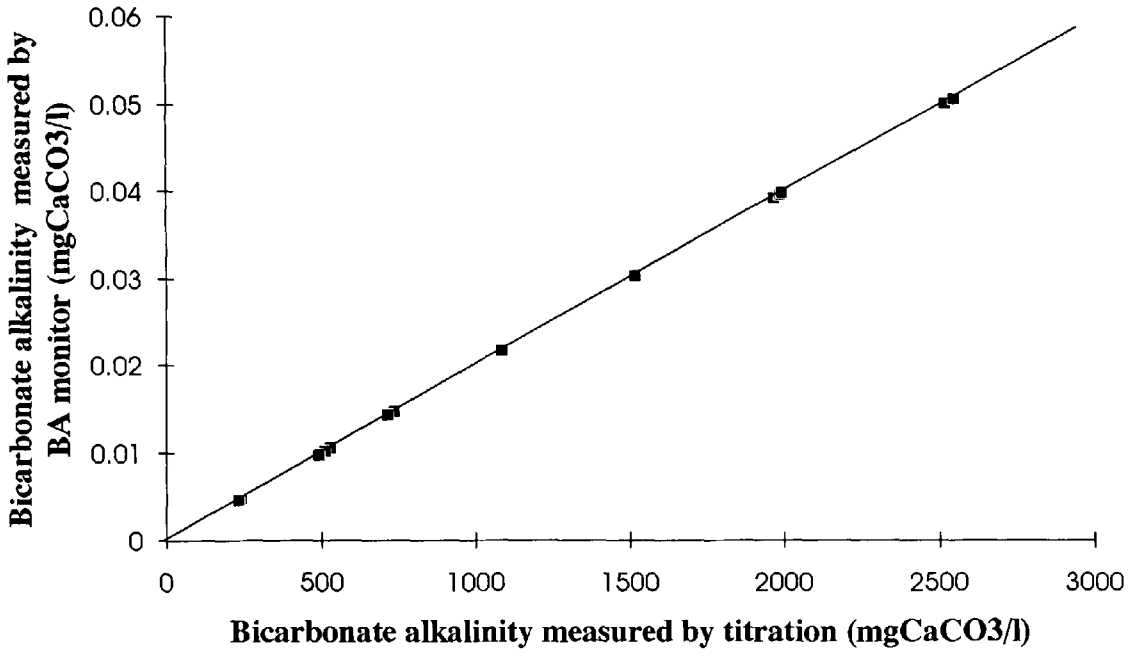


Figure 7.1 Correlation between measurements of bicarbonate alkalinity by the monitor and by titration to pH 4.3 (APHA, 1985).

Volatile fatty acids present in anaerobic and aerobic treatment systems interfere with the accuracy of titratmetric analysis of bicarbonate alkalinity (see section 2.3.2). Acetic and propionic acid, the main organic acids formed in the anaerobic process are effective buffers in the pH range close to their pK values, 3.7 to 5.7 and 3.9 to 5.9 respectively. Therefore their buffering capacity is a useless part of the alkalinity in the anaerobic digestion process which operates optimally in the pH range 6.5-7.5 (see section 2.3.2). However a portion of VFA buffering capacity is titrated using the titrametric method described by Jenkins *et al.* (1983). To determine the effect of VFA concentration on the accuracy of results from the bicarbonate alkalinity monitoring instrument, additional bicarbonate solutions were prepared which contained different concentrations of acetate and propionate. Each solution was also assayed using off-line methods of bicarbonate measurement described by Pauss *et al.* (1990), Jenkins *et al.* (1983) and Rozzi and

Brunnetti (1980). Direct comparison of the on-line BA monitor output with off-line methods using statistical analysis of variance is difficult because the on-line bicarbonate alkalinity values shown in Table 7.2 are averaged values of 30 data points of a moving average taken on a 5 minute basis.

Table 7.2 Comparison of results from different methods of bicarbonate alkalinity determinations using standard solutions of bicarbonate plus VFAs.

Standards			Methods			
Acetate (mgl^{-1})	Propionate (mgl^{-1})	Bicarbonate ($mgCaCO_3l^{-1}$)	BA monitor ($mgCaCO_3l^{-1}$)	Pauss *et al.* (1990) ($mgCaCO_3l^{-1}$)	Jenkins *et al.* (1983) ($mgCaCO_3l^{-1}$)	Rozzi & Brunnetti (1980) ($mgCaCO_3l^{-1}$)
		1500	1498 (3.4) [30]	1457 (9.5) [3]	1648 (6.3) [3]	1400 (7.1) [9]
200	100	1200	1258 (4.5) [30]	1350 (12.3) [4]	1390 (8.4) [4]	1230 (7.8) [12]
300	300	800	787 (2.1) [30]	770 (15.9) [3]	847 (13.4) [3]	778 (6.9) [9]
300	300	400	442 (3.9) [30]	465 (15.4) [3]	653 (7.9) [3]	380 (9.4) [9]

( ) = % Standard deviation. [ ] = Number of samples.

From these results it appears from the standard deviation of different methods that the BA monitor output is less variable than that of the off-line methods. Of the three off-line measurements the fixed end point titration method of Jenkins *et al.* (1983) yields the least accurate results. The accuracy of this method decreases as the VFA concentration increases relative to the bicarbonate concentration. This is because 20% of the VFAs are titrated as buffering capacity at a pH of 5.75, hence when the VFA concentration increases the contribution to the buffering capacity by subsequent titration is also increased.

The results shown in Table 7.2 using the methods of Pauss *et al.* (1990) and Rozzi and Brunnetti (1980) were not found to be as accurate as those reported in their papers. However, of the two, the back titration method reported by Pauss *et al.* (1990) was less susceptible to VFA interferences, but the method is time consuming and cumbersome. The inorganic carbon method outlined by Rozzi and Brunnetti is the most accurate of the methods previously reported and tested here, but the TOC analyser is more expensive, and more difficult to apply on-line to wastewater effluents than the Bicarbonate Alkalinity monitor. Interferences of phosphates and silicates, which are also present in anaerobic and aerobic treatment processes are also a problem in titrimetric determinations. Although not investigated here, the bicarbonate alkalinity monitor should be unaffected by the presence of silicates and phosphates. From Table 7.2 it can be seen that the BA monitor gave results which were at best 99.8% (with standard bicarbonate concentration 1500 $mgCaCO_3l^{-1}$) and at worst 90.4% (with standard bicarbonate concentration 400 $mgCaCO_3l^{-1}$, acetate 300 mgl^{-1}, propionate 300 mgl^{-1}) of the bicarbonate concentration by weight, in the range 400-1500 $mgCaCO_3l^{-1}$. The measurements obtained by the four different methods of bicarbonate alkalinity illustrate the problems associated with bicarbonate alkalinity determinations for anaerobic effluents. Although the simple fixed end-point titration method is quick and easy, accurate determination of the bicarbonate alkalinity in waste water streams containing VFAs is subject to significant errors. However the BA monitor is not effected by the presence of VFAs, silicates or phosphates as the measurement is based on the production of carbon dioxide gas, which is only produced as a result of bicarbonate ions present.

7.2. RESPONSE TIME.

An important primary sensor characteristic of any on-line instrument is its response time, the speed that an instrument responds to a step change in concentration i.e., the time needed for the sensor signal to respond to full scale change.

Full-deflection for the BA monitor is dependant on the hydraulic retention time of the effluent through the monitor. Full scale deflection can only occur when the acidification chamber is completely filled with the new concentration. The system behaves as two mixed systems separated by a plug flow section (the manometer). In addition there is a detention time associated with the sampling tubing from the digester to the monitor.

The response time of the bicarbonate alkalinity monitor could be calculated from the liquid volume and flow rate through the chambers. However in practice it was difficult to measure the liquid volumes of the BA monitor because of vigorous mixing in the chambers. In order to determine the response of the instrument to variations in bicarbonate concentration, experiments were performed by changing instantly the bicarbonate content of the standard solutions flowing through the instrument (concentration step changes). A single arrow in figure 7.2 shows the time of step change for all three experiments. The steady state mean of the bicarbonate concentration after the step change was determined together with the standard deviation. The response time was defined as the time taken after the step change to reach this mean ± two standard deviations and was found to be between 30 and 36 minutes. Experimental data relating to three concentration step change experiments are shown in Figure 7.2.

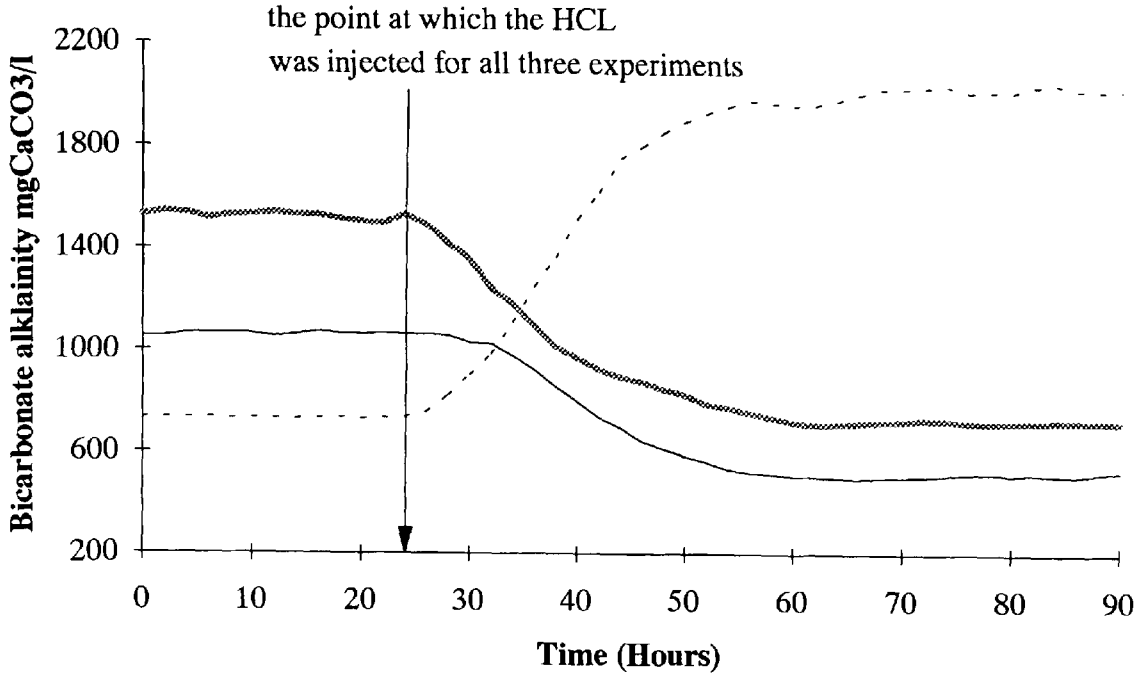
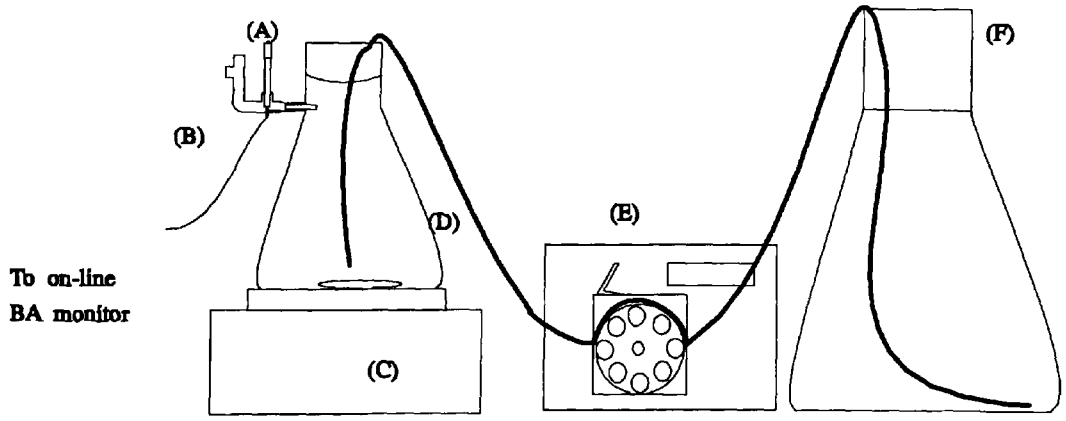


Figure 7.2 Bicarbonate signal during step changes of BA concentration for three standard bicarbonate solutions.

Before using the BA monitor on a real anaerobic digester, the response characteristics of the bicarbonate alkalinity monitor were compared to pH using a dynamic reactor system. The system consisted of a 2.0 litre continually stirred Erlenmeyer flask continually dosed with standard bicarbonate solutions.



(A) pH probe. (B) Effluent overflow unit. (C) Magnetic stirrer. (D) CSTR. (E) Dosing peristaltic pump. (F) Standard sodium bicarbonate solution.

Figure 7.3 Continually stirrer reactor apparatus for determining the response time of the BA monitor.

The BA monitor sample tube was positioned in the overflow pipe and positioned directly above the BA sample port was an a pH electrode that was connected to the I/O board for on-line measurement. The manometer overflow unit was adjusted so that the reactor volume contained 2 ±0.01 litres. The contents of the vessel were rapidly mixed by a magnetic stirrer (C) and flea set at 200 rpm to ensure complete mixing. The bicarbonate standards were pumped into the vessel by a 302F 55 rpm peristaltic pump (E), with a twin cassette 8 roller pump head (Watson and Marlow, Falmouth, UK). Standard solutions of sodium bicarbonate were pumped into a completely mixed vessel (liquid volume 2 ±0.01 litres), connected via a gravity overflow to the bicarbonate alkalinity monitoring device, with a pH electrode positioned in the overflow. To simulate the effect of a severe square pulse disturbance to an anaerobic digester known volumes of hydrochloric acid (1M) were rapidly injected in the vessel. The bicarbonate present in the CSTR vessel was destroyed proportionately.

Table 7.3 Condition of acid spike experiments to determine the response time of the BA monitor.

HCl Spike Experiments	[Bic] of standard. $mgCaCO_3l^{-1}$	Volume of 1 M HCl added. (cm^3)	Delivery rate of standard to the CSTR. $cm^3\ min^{-1}$
Experiment 1	1050	15.5	10
Experiment 2	1050	17	17
Experiment 3	966	27	17

Figures 7.4, 7.5 and 7.6 shows that the pH response to the acid shocks is rapid as expected. The first arrow on the Figures show the instant at which the acid spike is made and the second the full scale deflection of the BA monitor. The bicarbonate concentration determined by the on-line BA monitor responds within 28 to 32 minutes

for the 99% full scale step change. The pH responded instantly to the acid spikes in all three experiments.

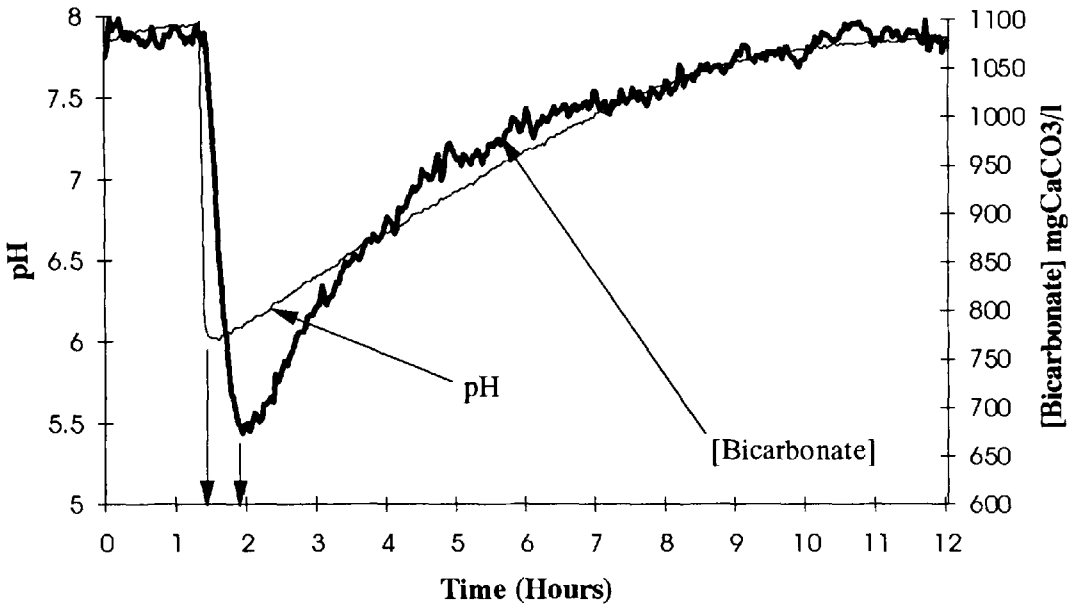


Figure 7.4 Comparison of responses of the BA monitor and pH electrode in a dynamic CSTR for experiment 1 (Acid added at 1.45 hrs).

The BA profile is steady with very little noise. The drop in bicarbonate for each of the experiments corresponds to the theoretical drop caused by the destruction of bicarbonate as a result of acid addition.

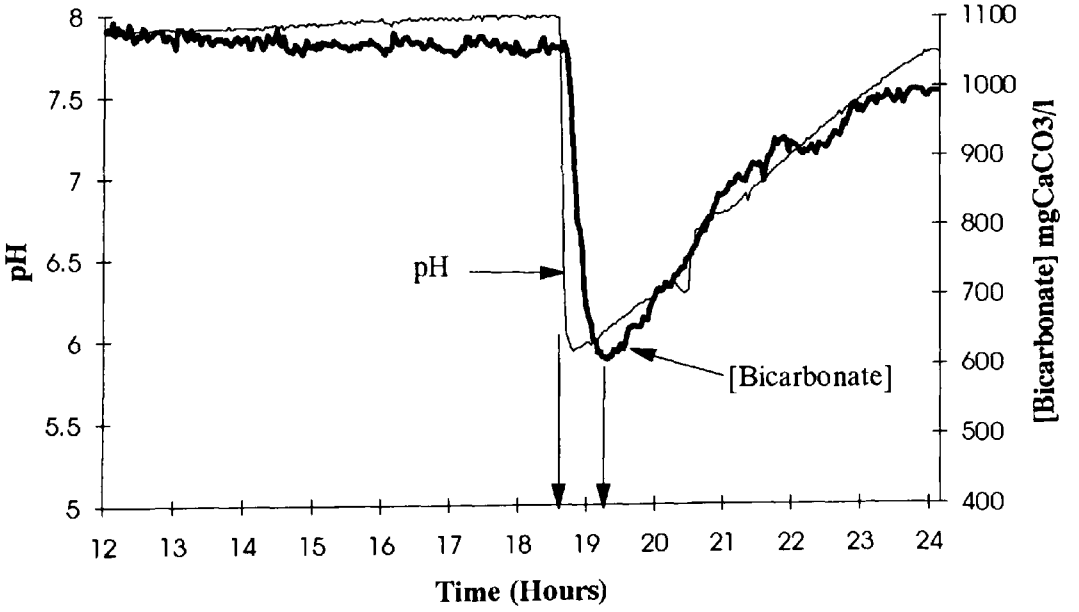


Figure 7.5 Comparison of responses of the BA monitor and pH electrode in a dynamic CSTR for experiment 2 (Acid added at 18.66 hrs).

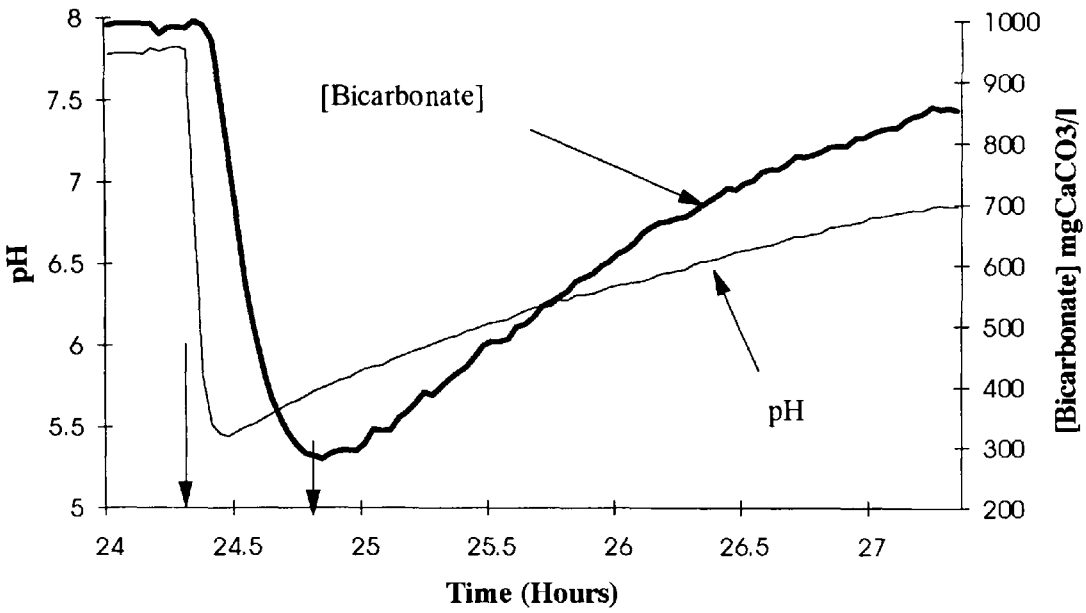


Figure 7.6 Comparison of responses of the BA monitor and pH electrode in a dynamic CSTR for experiment 3 (Acid added at 24.8 hrs).

The 'acid spike' experiments 1 to 3 show that the BA monitor is reliable and accurate method of determining bicarbonate alkalinity on-line, and that the pH responds rapidly. However pH probes are known to foul when in prolonged contact with anaerobic digester effluent and the reliability and accuracy of the measurement can be severely effected (see section's 2.4.4). The BA monitor however is not subject to fouling and therefore an ideal alternative to pH monitoring.

7.3. CONCLUSIONS.

The prototype BA monitor was shown to have an accuracy of ±7% and a response time of 30 minutes and for bicarbonate standards containing VFA concentrations similar to those expected in an unstable anaerobic digester in the bicarbonate concentration range 5-50mM. The prototype BA monitor provides a rugged, reliable and relatively low cost method for continuous on-line instrument for monitoring the bicarbonate/carbonate species in wastewater treatment such as anaerobic digestion (Guwy *et al.* 1994).

8. MONITORING ANAEROBIC INSTABILITY USING THE IMPROVED ON-LINE BICARBONATE ALKALINITY MONITOR.

Development of the improved BA monitor from the initial testing (shown in Figure 6.2 and Figure 6.4) of the BA design 2 had taken approximately 5 months. The improved BA monitor was connected to a 10 litre anaerobic filter reactor which was operating on simulated ice-cream waste (see section 3). Gas production, hydrogen concentration, pH and carbon dioxide percentage were measured on-line, whilst VFA and COD were determined off-line. The gas analysers were positioned in series and received biogas pumped periodically by computer controlled pumps previously described in section 3.7. Samples for COD and VFA analysis were collected directly from the digester every hour using the auto sampler described in section 3.10. The BA monitor was connected to a port in the overflow tube in close proximity to the pH probe and auto sample port. The anaerobic filter had been operating at a volumetric organic loading rate Bv = 5 to 6 $kgCODm^{-3}d^{-1}$, (influent flow rate 10 cm^3min^{-1}, hydraulic retention time 0.7 days) for more than 30 days.

Table 8.1 Parameters measured and methods of analysis.

Parameter measured.	**Method of Measurement.**
Off-line pH	Combined Electrode
Individual VFA concentration.	Gas Chromatography
Off-line Bicarbonate and VFA Alkalinity	$pH_{5.75}$ Jenkins (1983)
On-line Bicarbonate Alkalinity	BA monitor
On-line Carbon Dioxide percentage	ADC CO_2 analyser
On-line Hydrogen gas concentration	GMI Exhaled H_2 monitor
Off-line Methane percentage	Gas Chromatography
Off-line Chemical Oxygen Demand	Sealed tube digestion
On-line Gas production	Electrode gas meter
On-line pH	Combined Electrode

Treatment efficiency measured as COD destruction averaged 73%, with a biogas yield between 0.24 - 0.33m^3kg^{-1}COD added. The pH of the influent was maintained for these experiments by the addition of NaOH (0.55gl^{-1}). The parameters measured and the methods of determination are shown in Table 8.1.

8.1. RESULTS AND DISCUSSION OF THE ORGANIC OVERLOAD EXPERIMENTS 1 AND 2.

In order to assess the effectiveness of the BA monitor as an instrument for monitoring and controlling stability in anaerobic digestion a series of overload experiments were performed. Two different organic overloads were applied to the digester, the conditions for each overload are shown in Table 8.2.

Table 8.2 Conditions of organic overload experiments 1 and 2.

Experimental Overload	**1**	**2**
Influent concentration. change. (mgCODl^{-1})	3500 - 14879	4272 - 16460
Percentage COD change	426%	385%
Organic loading rate (kgCOD$m^{-3}day^{-1}$)	5.04 - 21.425	6.15 - .23.70
Hydraulic Retention Time (Days)	0.69	0.69
Duration of overload (Hours)	8	8

The overloads were initiated by removal of the influent pipe from the influent storage tank containing the 'normal' strength feed and placing it in a stirred 25 litre vessel containing the overload strength waste. The hydraulic loading rate was kept constant before, during and after the overload. The overload strength waste was pumped into the reactor for eight hours, after which the influent pipe was returned to the influent storage tank containing the normal strength waste. Results from the organic overload of experiment 1 and 2 are illustrated in Figures 8.1a to 8.5a and Figures 8.1b to 8.5b respectively. The start and end of the organic overload are shown as arrows in these Figures.

In experiment 1 the effluent chemical oxygen demand (COD) increased from an average value of 980 $mgCODl^{-1}$ before the overload to 4200 $mgCODl^{-1}$ at the end of the overload. This corresponded to an increase in the total effluent volatile fatty acid concentration, which rose from 70 ppm to 860 ppm. It can be seen from Figure 8.1a that the increase did not occur immediately, but approximately 2 hours after the start of the overload, similarly the response to the end of the overload is delayed by 2 hours.

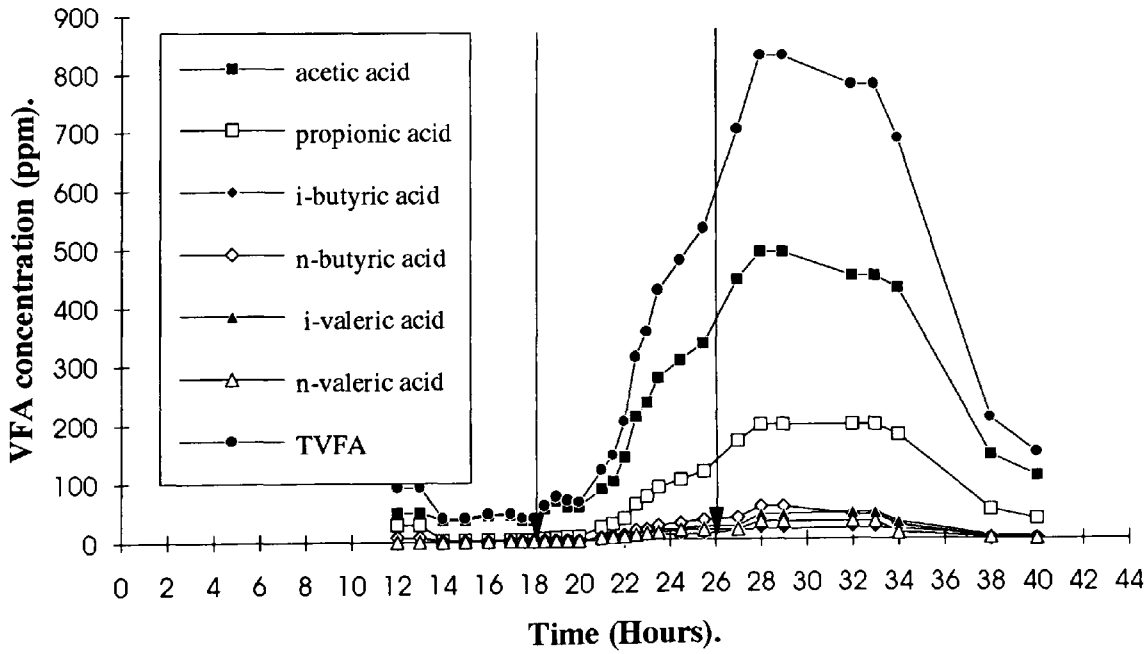


Figure 8.1a VFA concentration during organic overload experiment 1.

It is also interesting to note that the rate of increase of the TVFA concentration is as rapid as the propionic acid. An increase in propionic acid is widely considered to be the first sign of bacteria instability. The rapid increase in the partial pressure of hydrogen caused by the slow growth rate of the methanogens compared to that of the acid-forming bacteria will result in a greater rate of build up of propionic acid compared to acetic acid because acetogenesis from propionate is only thermodynamically possible ($\Delta G^{o'}$ is -ve) when the pH_2 is low. However, in experiment 1 and 2 the rate of acetic acid production is greater than the propionic acid as can be seen from Figure 8.1a and 8.1b.

In experiment 2 the TVFA concentration rose from 95 ppm to 920 ppm an increase of 825 ppm compared to a rise of 795 ppm for overload experiment 1. This may correspond to the greater increase in COD load in experiment 2, however the difference in the TVFA concentration between the two experiments is very small. The delay in the response of approximately 2 hours was also apparent before and after the end of the overload.

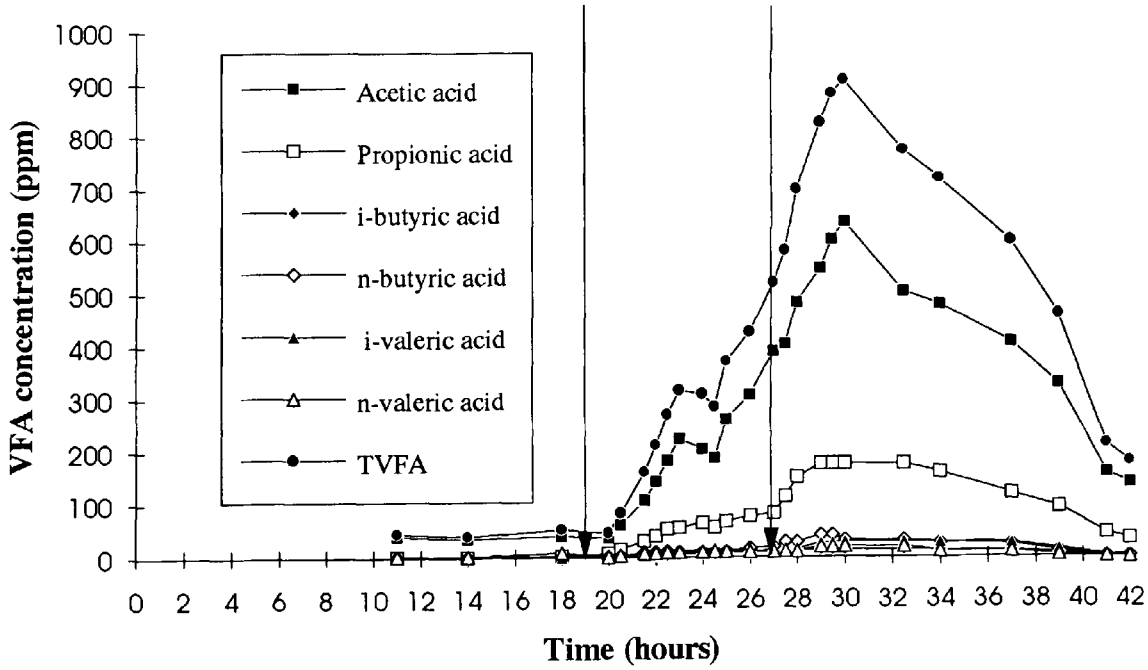


Figure 8.1b VFA concentration during organic overload experiment 2.

From Figure 8.2a it can be seen that the bicarbonate alkalinity during experiment overload 1 starts to fall at time 19 hours, 1 hour after the start of the overload. This was caused by the accidental syphoning dilute perchloric acid (approximately $100cm^3$) from the electrode gas meter into the digester during sampling biogas for off-line gas analysis. The on-line pH measurement also shows a small drop at this point (see Figure 8.3a) as does the gas production (see Figure 8.4a). The effect of the syphoned acid on the measurement of bicarbonate concentration, pH and gas production was short, lasting approximately 1 hour.

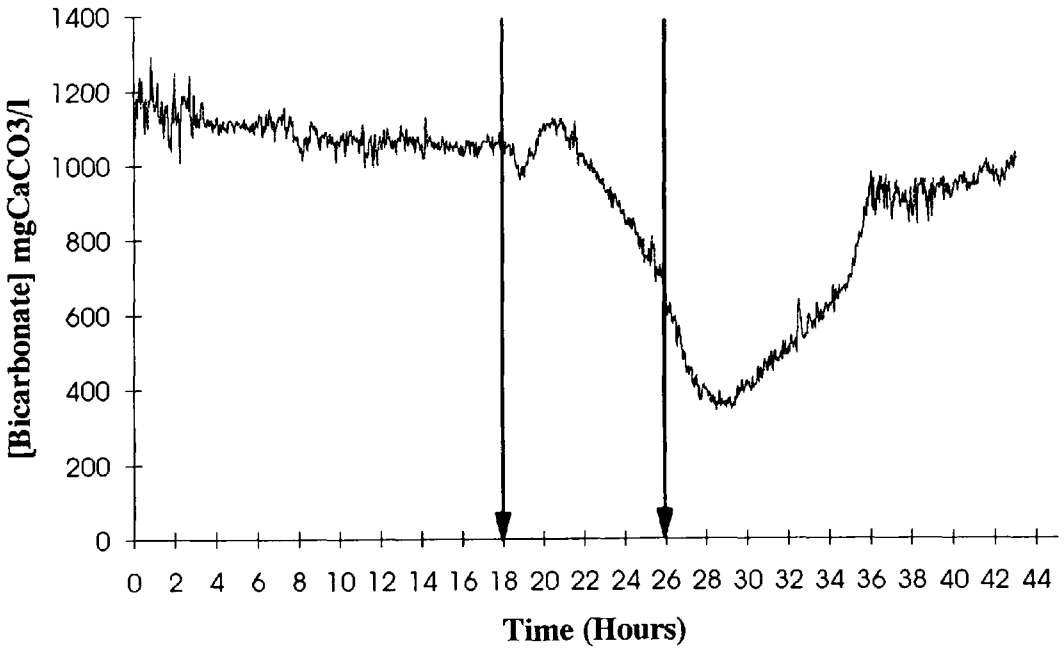


Figure 8.2a On-line bicarbonate alkalinity as measured by the prototype BA monitor during organic overload experiment 1.

The bicarbonate concentration measured on-line by the BA monitor in experiment 1 shows a typical response profile of an organic overload. The bicarbonate concentration began to decrease 2.5 hours after the overload start and reached a minimum concentration of 430 $mgCaCO_3l^{-1}$ three hours after the overload end (see Figure 8.2a). The reduction in bicarbonate (see Figure 8.1a) can be explained by the increase in volatile fatty acids (VFA) resulting from imbalance between the acetogenesis and

methanogenesis during overload. The bicarbonate ions present in the liquor neutralise the VFAs that build up producing carbon dioxide (see chapter 2). In the overload experiments here, only the organic content of the ice-cream feed was increased; the di-ammonium hydrogen orthophosphate, urea and sodium bicarbonate concentrations remained constant, and therefore the cations in the system are kept constant. Hence the amount of bicarbonate alkalinity derived from added organic substrate is very small and therefore the alteration of the ion balance due to the overload can be neglected and the change in bicarbonate alkalinity is theoretically equivalent to the change in volatile fatty acid concentration, on a molar basis (Weiland and Rozzi 1990).

Therefore monitoring the bicarbonate alkalinity concentration should allow the indirect evaluation of total volatile fatty acid. Calculation of the TVFA expressed as $mgCaCO_3l^{-1}$ from the values shown in Figures 8.1 revealed an increase of 663 $mgCaCO_3l^{-1}$ that corresponded to 703 $mgCaCO_3l^{-1}$ actual decrease in bicarbonate concentration measured by the BA monitoring experiment overload 1. Hence there is a good correlation between the actual change in TVFA concentration and the associated change in bicarbonate concentration measured using the BA monitor (see section 9.3)

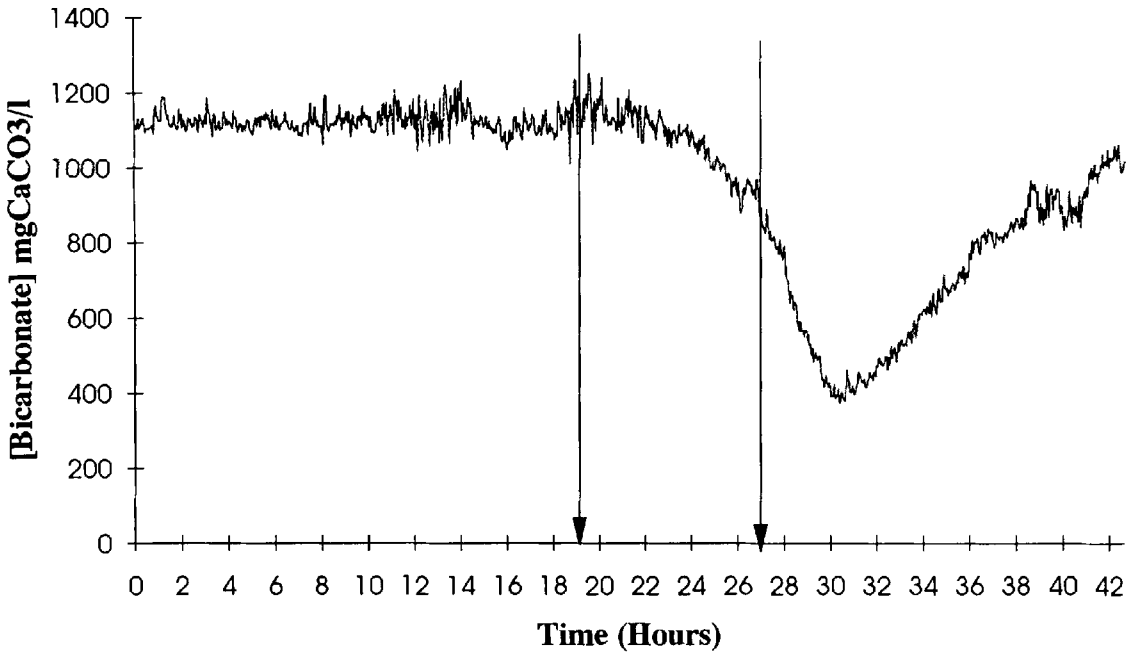


Figure 8.2b On-line bicarbonate alkalinity as measured by the prototype BA monitor during organic overload experiment 2.

The BA monitor profile of experiment 2 was similar to that for experiment 1. From Figure 8.2b it can be seen that the bicarbonate alkalinity starts to decrease 2.5 hours after the initiation of the overload as in experiment 1. This delay is due to a combination of three factors, the biological system response, the hydrodynamic properties of the digester and the response time of the BA monitor itself. The full response time of the BA monitor was already known to be 30 minutes and therefore a delay 2 hours is caused by the response of the biological system plus the mixing properties of the reactor. This 2 hour delay is confirmed by the response of pH in both experiments 1 and 2.

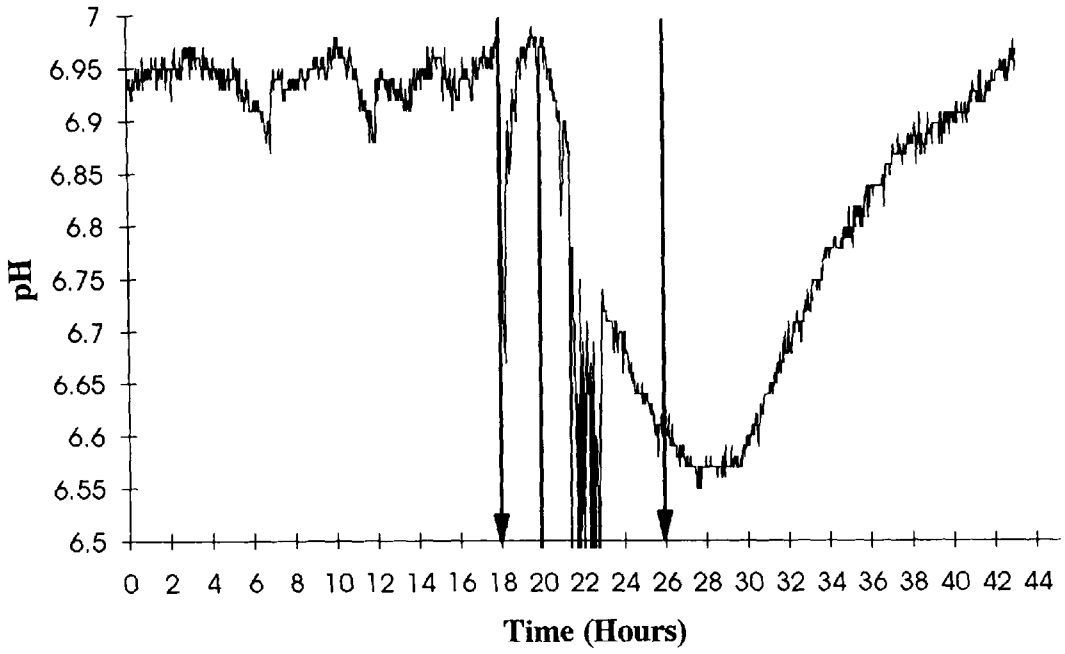


Figure 8.3a On-line pH during organic overload experiment 1.

From Figure 8.3a it can be seen that the pH measurement is interrupted at time 21 hours, this was attributed to a trapped air bubble or fat build up at the pH bulb/effluent interface. Normal on-line measurement was resumed and the maximum point of pH deflection was recorded 2 hours after the end of the overload. Similarly the pH profile for experiment 2 (shown in Figure 8.3b), the maximum deflection point occurred 2-3 hours after the overload end. The pH response to the end of overload in experiment 2 sluggish compared to that of the bicarbonate alkalinity. However in the 'acid spiking' experiments performed on a CSTR fed with standard bicarbonate the pH responded rapidly (see Figure 7.4 to 7.6). This may be an indication that the porous junction of the pH probe has become partially blocked with fats or solids during use on the synthetic ice-cream waste.

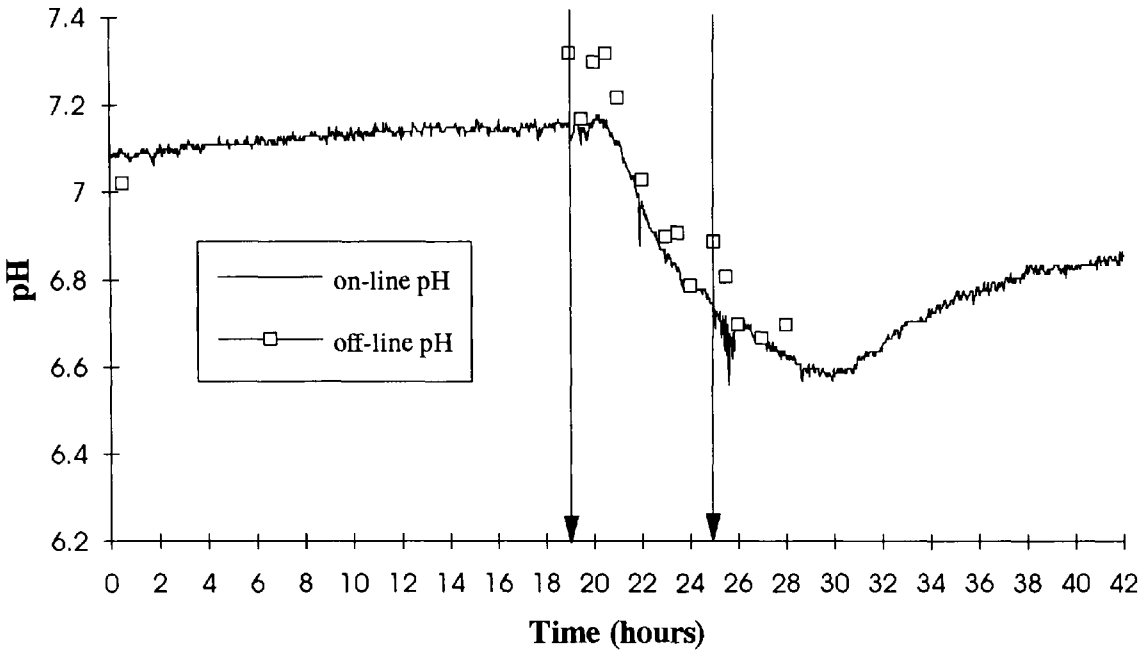


Figure 8.3b On-line pH during organic overload experiment 2.

Initially from the results of the overload experiments it appeared that on-line pH measurement is an accurate way of detecting digester instability, comparable to that of TVFA and on-line bicarbonate measurements. However comparison with off-line pH measurements reveals differences in recorded values. The off-line measurements are assumed to be more accurate than the on-line measurements because before each analysis the pH response was checked by immersion into calibration buffers. However off-line pH measurements are also subject to inaccuracies, because dissolved carbon dioxide escapes from the liquid into the atmosphere during sampling. Therefore to check the accuracy of the pH probe, it was removed from its housing at the end of the overload for inspection and calibration check. On removal the probe bulb was seen to be completely caked in fats and suspended solids suggesting that the accuracy of the probe would have been severely impaired. This was confirmed by immersion of the probe into calibration buffers which showed a discrepancy of greater than 0.5 pH units at pH 7 and 4. However with a suitable cleaning mechanism pH could be used to monitor trends in performance.

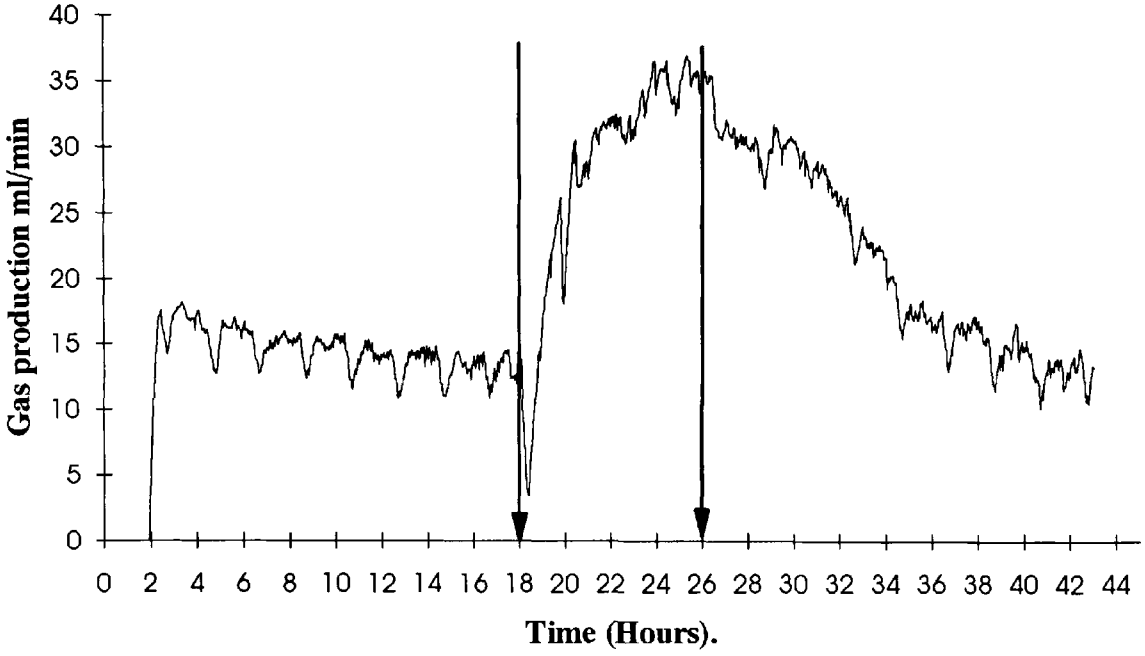


Figure 8.4a Gas production during organic overload experiment 1.

The profile of the biogas flowrate for experiments 1 and 2 drops at regular intervals (see Figures 8.4a and 8.4b respectively), this is because every 2 hours biogas was removed for the analysis of carbon dioxide and hydrogen percentages. From Figure 8.4a the gas production rate is seen to increased rapidly after the start of the overload and reached a maximum flowrate at time 28 hours that coincided with the end of the overload. The gas production rate during the organic overload in experiment 2 is similar, rising rapidly from 13 to 40 cm^3 min^{-1} compared to 15 to 30 cm^3 min^{-1} in experiment 1. It is interesting to note that in both cases the biogas production rate reaches a maximum before the end of the overload.

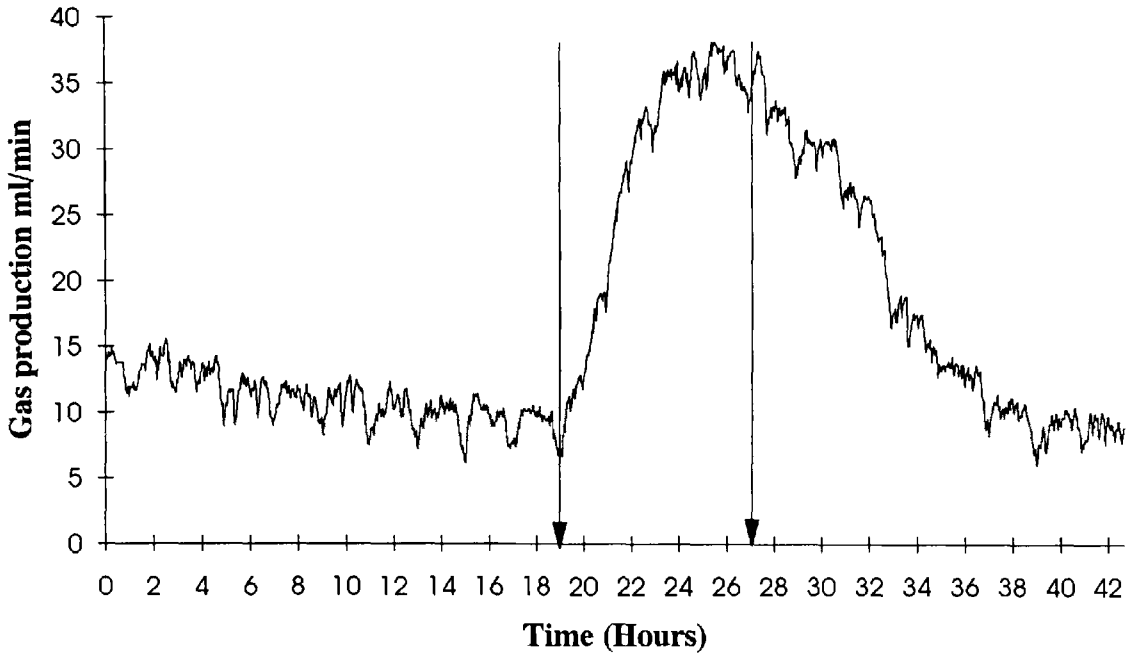


Figure 8.4b Gas production during organic overload experiment 2.

Gas production is not generally considered as good control or instability variable as changes are a result rather than the cause of instability (Hickey *et al.* 1990). The results from this overload suggest that the gas production response is as rapid as VFA concentration and bicarbonate alkalinity, the parameters most frequently proposed in control processes. However it is important to realise that an increasing gas production may not equate to instability and without information of the methane /carbon dioxide composition and the bicarbonate concentration it is difficult to state whether digester performance has changed.

The on-line percentage carbon dioxide in the biogas in experiments 1 and 2 responded quickly to the start of the overload shown in Figure 8.5a and Figure 8.5b respectively. The percentage CO_2 was lower in experiments 1 and 2 during steady state than would normally be expected in an anaerobic digester. The reason for this is probably due to the reaction of hydroxide ions (used to neutralise the influent) with carbon dioxide in digester liquor effectively reducing the percentage CO_2 in the gas headspace. In experiment 1 the maximum increase in carbon dioxide occurs approximately 1 to 2 hours

after the end of the overload. The increase in carbon dioxide percentage is partly the result of reduced methanogenic efficiency.

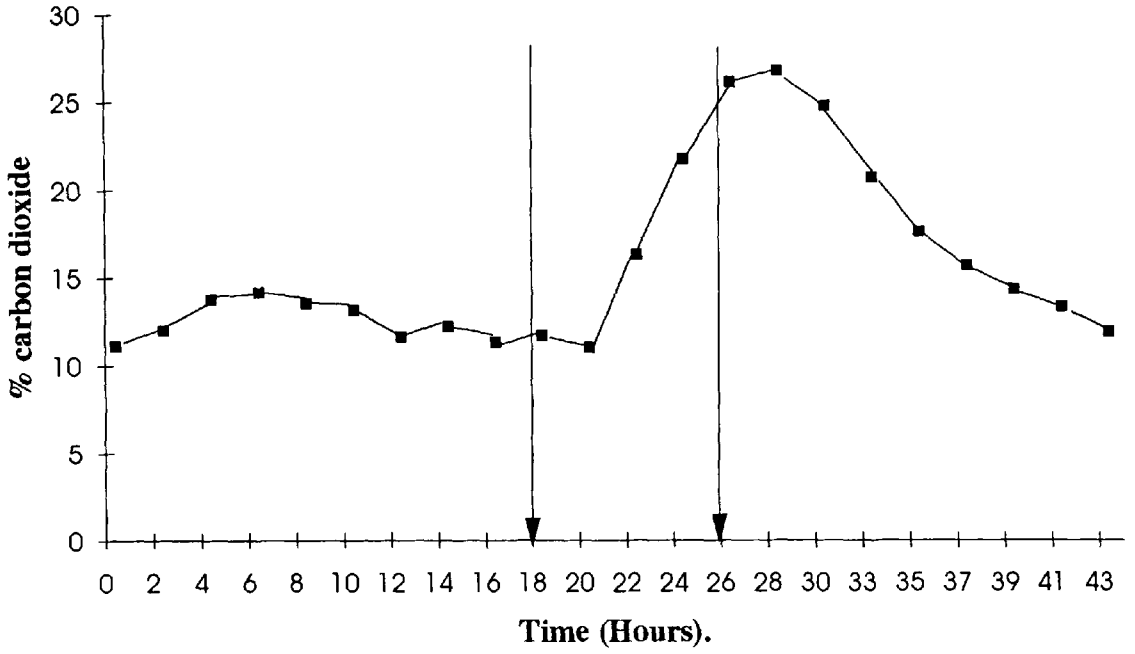


Figure 8.5a Percentage carbon dioxide during organic overload experiment 1.

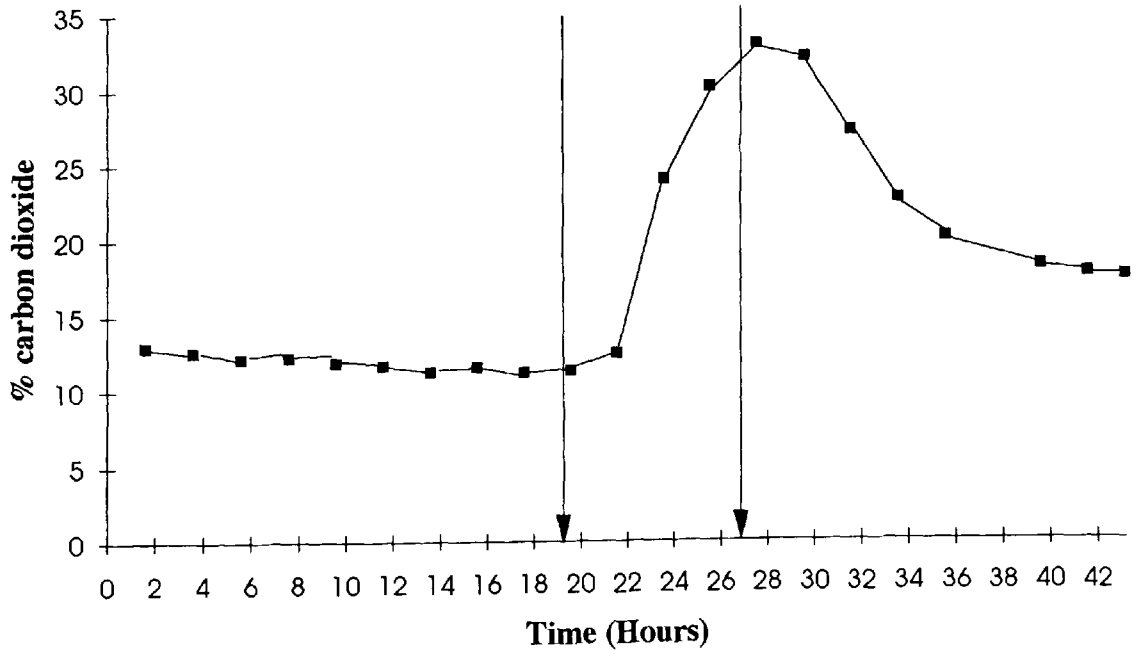


Figure 8.5b Percentage carbon dioxide during organic overload experiment 2.

However the largest proportion of the carbon dioxide increase is due to bicarbonate destruction by the increase in volatile fatty acid concentration. The maximum deflection in percentage carbon dioxide occurs after the end of the overload in both experiments because the bicarbonate ions are still begin destroyed.

Mixing is important in anaerobic processes as it promotes uniform distribution of substrates and prevents the localised build up of inhibitory substances such as VFAs. There are two main types of mixing in dynamic processes; firstly plug-flow in which increments of influent pass through the system and are discharged in the same sequence and secondly completely mixed systems where the retention of the influent is based on a probability distribution. Usually biological processes are not 100% mixed or 100% plug flow but somewhere in between. However for process control purposes it is far easier if the process is completely mixed so that changes in control variables can be applied to the reactor as a whole and not just one localised region. Taking the organic overload experiments 1 and 2 as examples, the BA monitor, on-line pH, and off-line measurements of COD and VFA were all taken from the same point (the overflow unit). If there is little dispersion in the system, i.e. tending towards the plug flow, any changes occurring at the base of the reactor nearest to the input will not be transferred to the overflow unit immediately. This has obvious ramifications in the control of the process, in so much that there will be a delay in the appropriate control action, which in severe cases could result in process failure. Similarly it is difficult here to assess the response time and suitability for process control of the various liquid phase parameters unless the system is completely mixed. The assumption that a digester is completely mixed is common to most mathematical models attempting to compare the different parametric response. Hence to improve the interpretation of parameter response for future experiments, the digester's mixing characteristics were investigated.

8.1.1 Lithium tracer study.

Levenspeil (1962) described a pulse input method that has been widely used in stimulus-response investigations. The method involves 'instantaneous' injection ('spike') of concentrated tracer chemical to the reactor. The concentrated tracer used in this study was $LiCl_2$ primarily because of its absence at background levels. Low lithium concentration was used as it is toxic to anaerobic bacteria. However provided the input concentration is not higher than 1.0 gl^{-1} the specific methanogenic activity is unaffected (Smith *et al.* 1991). Therefore a 5 gl^{-1} standard solution of lithium chloride was prepared using anhydrous $LiCl_2$ crystals (AnaLaR BDH Ltd.) A 10 cm^3 volume standard was injected into the influent port of the reactor at point (A) marked in Figure 3.1. The hydraulic retention time and the organic loading rate were the same as at steady state operation during the organic overload experiments 1 and 2. At the instant the tracer was injected into the digester a sample was taken from the reactor at point (X) (see Figure 3.1) by the auto-sampler already described in section (3.10). Samples were taken at 7.5 min intervals for first 5 hours after which the sample interval was increased to 30 minutes. The lithium content of each sample was analysed using Flame Photometry as describe in section (3.11).

The $[Li^+]$ exit distribution plot (Figure 8.6) suggests that the digester was not completely mixed and there was no change in lithium concentration for 1.9 hours. These results are consistent with the 2 hour delay in the measurement of the liquid phase parameters for the organic overload experiments 1 and 2.

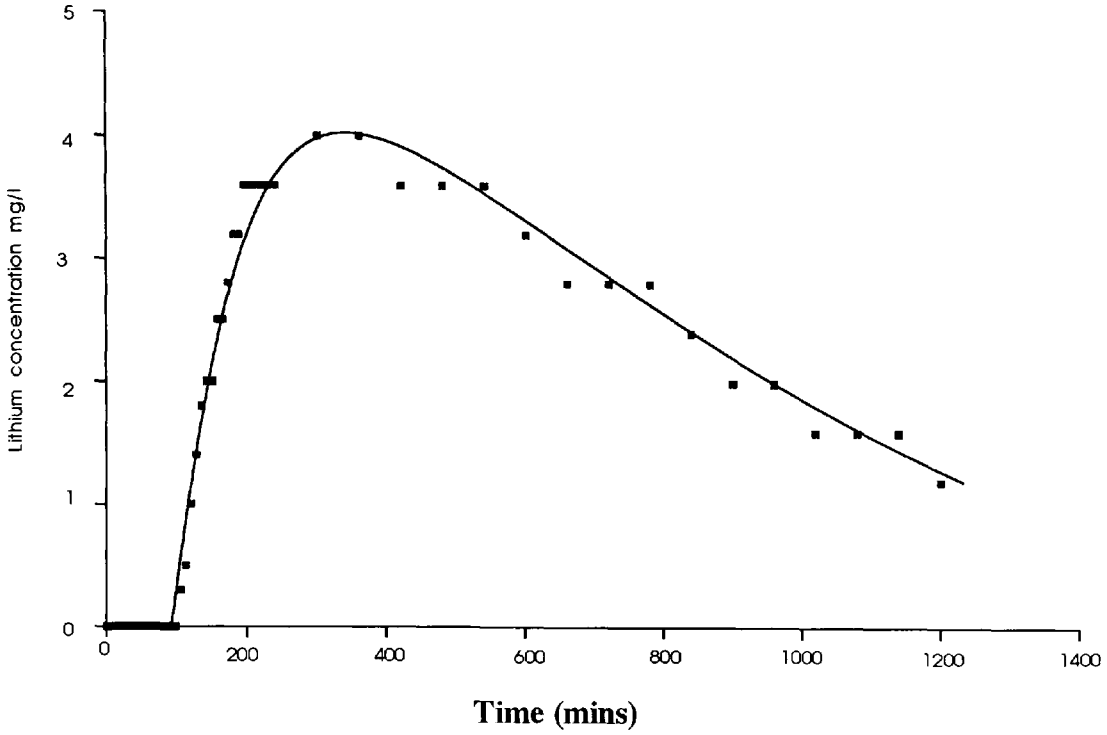


Figure 8.6 Exit distribution plot for an anaerobic filter reactor without recycle applied.

8.2. RESULTS AND DISCUSSION OF THE ORGANIC OVERLOAD EXPERIMENTS 3 AND 4.

In experiments 3 and 4 the effluent was recycled at 20 cm^3 min^{-1} increasing the upflow velocity 0.073 mh^{-1} in an attempt to mix the reactor contents. The conditions for two organic overload experiments that were applied to the digester are shown in Table 8.3.

Table 8.3 Conditions of organic overload experiments 3 and 4.

Experimental Overload.	**3**	**4**
Influent concentration change ($mgCODl^{-1}$).	4600 - 9230	4558 - 12010
Percentage COD change.	100%	163%
Recycle rate cm^{-3} min^{-1}	20	20
Organic loading rate ($kgCODm^{-3}d^{-1}$).	6.624 - 13.29	6.56 - 17.29
Hydraulic Retention Time (days).	0.69	0.69
Duration of overload (Hours).	8	8

The digester and instrument operation was unchanged from experiments 1 and 2 except that the biogas was recycled constantly through the gas analysers, instead of intermittently which allowed continuous measurements of the biogas composition. During the overload experiments 3 and 4 the electrode gas meter became unreliable and therefore the gas flowrate measurements for the remaining experiments are omitted.

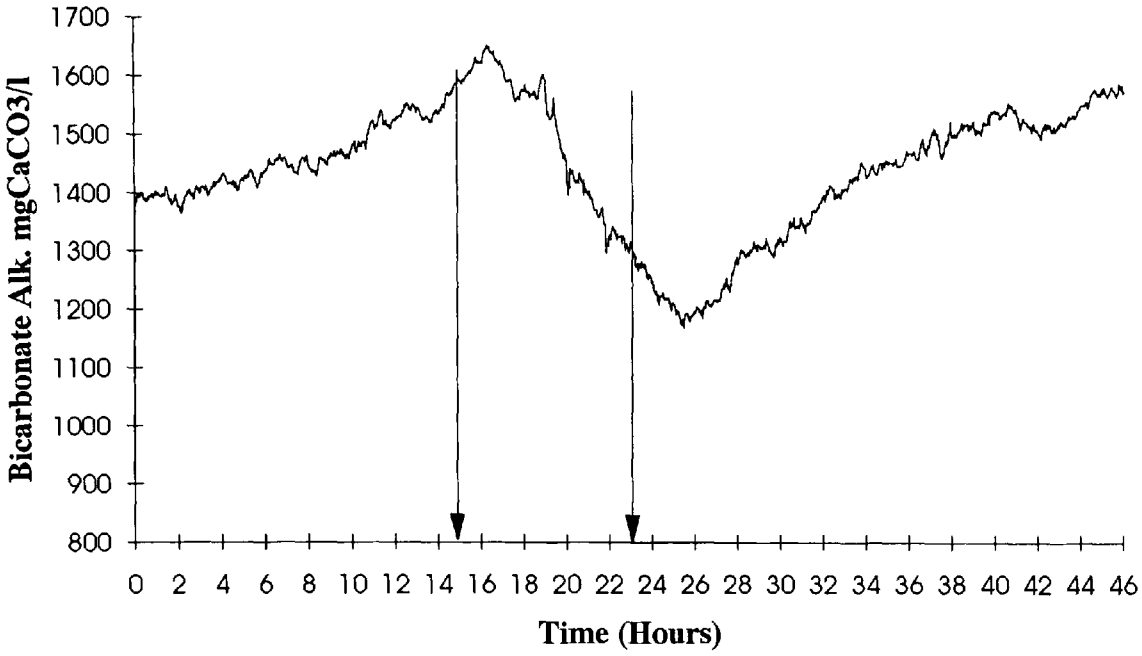


Figure 8.7a On-line bicarbonate alkalinity as measured by the prototype BA monitor in organic overload experiment 3.

From Figure 8.7a it can be seen that the anaerobic bacteria are not at steady state, as the bicarbonate alkalinity steadily rises in the 15 hours before the overload. The bicarbonate concentration continues to rise even after the organic overload was started. This suggests that the reactor is still not completely mixed even with the addition of a recycle loop. After approximately 1.5 hours the bicarbonate alkalinity drops from 1640 to 1180 $mgCaCO_3l^{-1}$ with the start in recovery occurring about 2 hours after the end of the overload. From these two transitions it can be seen that the recovery of the anaerobic bacteria is slower than its initial response to an increase in organic loading. However the bicarbonate alkalinity rises steadily after the end of the overload to the bicarbonate level at the start of the overload.

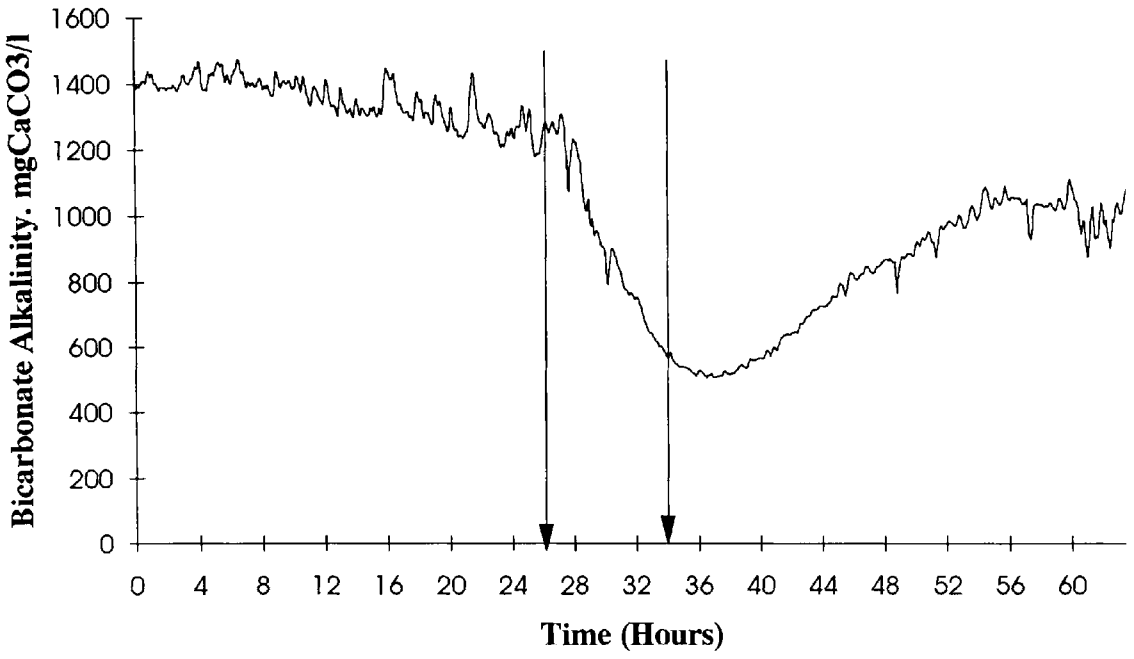


Figure 8.7b On-line bicarbonate alkalinity as measured by the prototype BA monitor during organic overload experiment 2.

Figure 8.7b shows that the bicarbonate concentration before the start of the overload in experiment 4 is relatively constant. Although the bicarbonate concentration is lower at the initiation of the overload than in experiment 3, the anaerobic digester can be regarded as being in steady state operation. The bicarbonate drops from 1249 to 510 $mgCaCO_3l^{-1}$ approximately 2 hours after the start of the overload. This constitutes a reduction of 739 $mgCaCO_3l^{-1}$ that is 60% greater than the reduction of bicarbonate in experiment 3 yet the increase in organic load for experiment 4 compared to experiment 3 is only 32% greater. This illustrates the problems of predictive feed forward control using the organic input to the reactor. The initial value of BA in experiment 4 is not reached in the 26 hours after the overload as shown in Figure 8.7b in contrast to the BA in experiment 3 in Figure 8.7a. This is possibly related to the greater fall in BA observed in experiment 4 which may have been caused by the larger increase in the loading rate (see Table 8.2).

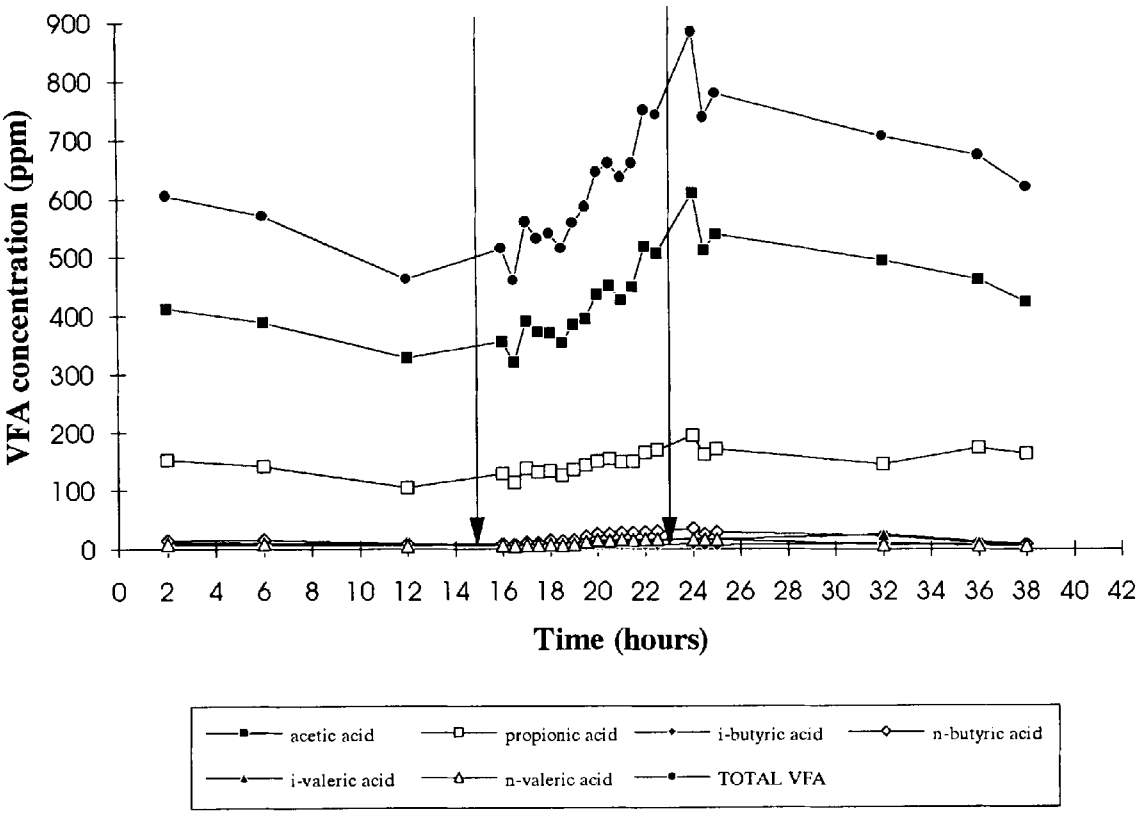


Figure 8.8a VFA concentration during organic overload experiment 3.

The volatile fatty acid data for experiments 3 and 4 show a close correspondence to the bicarbonate alkalinity response. Figure 8.8a show that the volatile fatty acid concentration falls from 605 to 463 mgl^{-1} in the duration before the overload. This corresponds to the increase in bicarbonate alkalinity during the same time period. It is probable that the anaerobes are able to utilise the VFAs available to leave a surplus of bicarbonate ions. The point at which the VFA concentration starts to increase is unclear, however the delay after the end of the overload is approximately 1 hour.

From Figure 8.8b it can be seen that the VFA data of experiment 4 show a similar response with an increase from 330 to 1370 mgl^{-1}, an increase of 1040 mgl^{-1} that corresponds to a change of 730 expressed as $mgCaCO_3l^{-1}$. This compares very closely to the change in bicarbonate that was 739 $mgCaCO_3l^{-1}$, hence the correspondence between the indirect measurement of volatile fatty acid concentration using the BA monitor and the actual measurement of VFA is again good. A higher VFA and lower BA are obtained

in experiment 4 than in experiment 3, this is probably due to the greater increase in step loading rate in experiment 4.

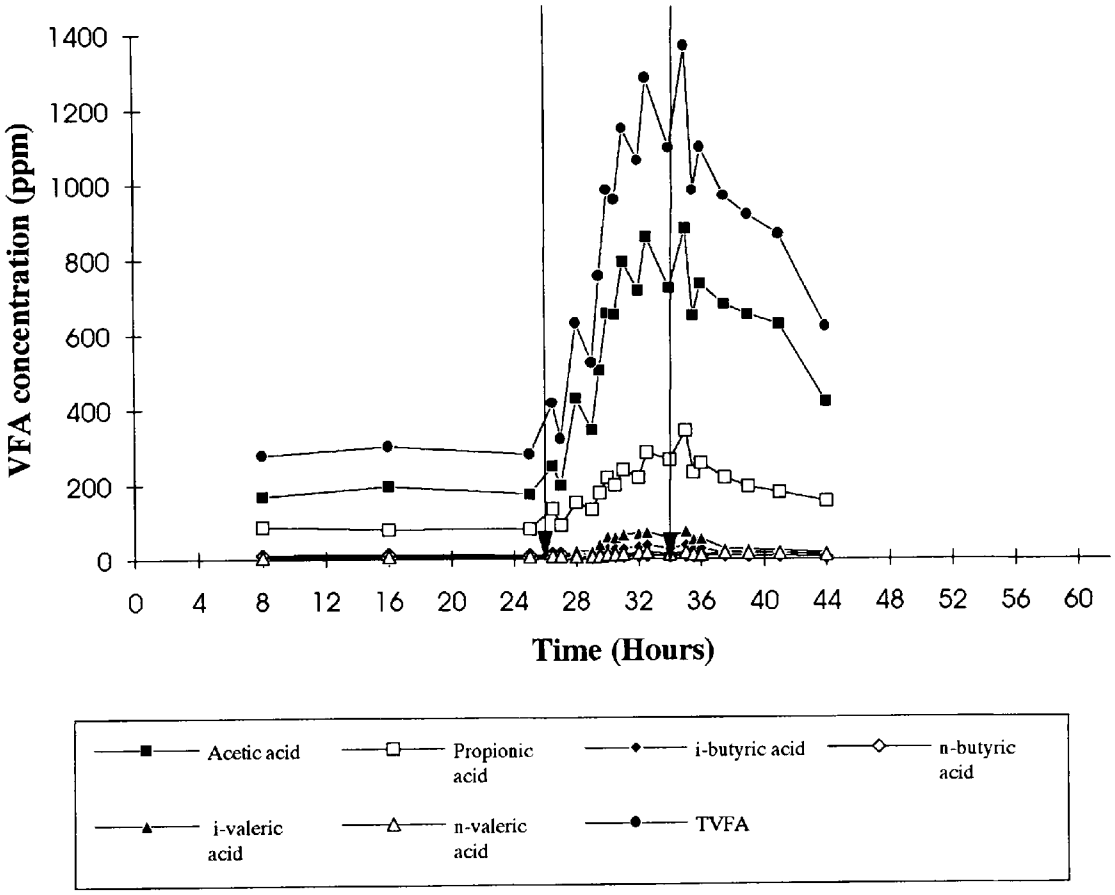


Figure 8.8b VFA concentration during organic overload experiment 4.

Figure 8.9a shows the output of the on-line pH probe which is interrupted by spikes at regular intervals. The spikes are caused as liquid is taken from the reactor by the autosampler, the exact reason is uncertain. The response of the pH to the overload is not immediate as with the bicarbonate alkalinity and the volatile fatty acid concentration strengthening the hypothesis that the reactor is still not a completely mixed system. After the delay the pH drops from 7.1 to 6.2, however the recovery after the end of the overload is slow unlike the bicarbonate alkalinity and the VFA concentration. This highlights the unsuitability of using pH (an exponential measurement) as a process control parameter.

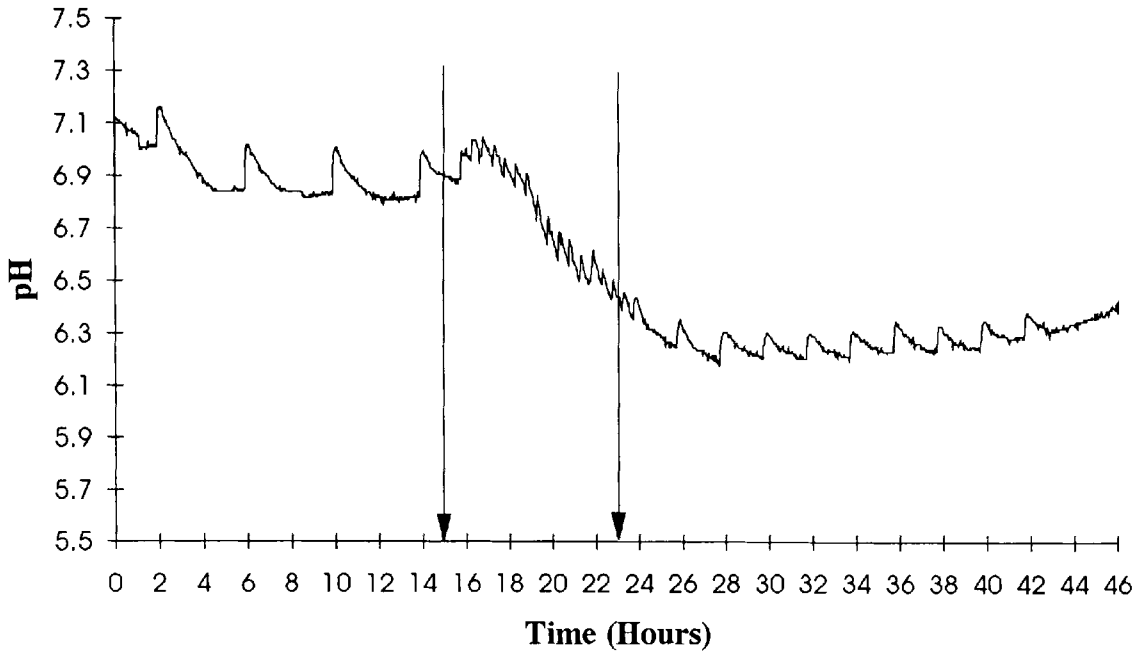


Figure 8.9a On-line pH during organic overload experiment 3.

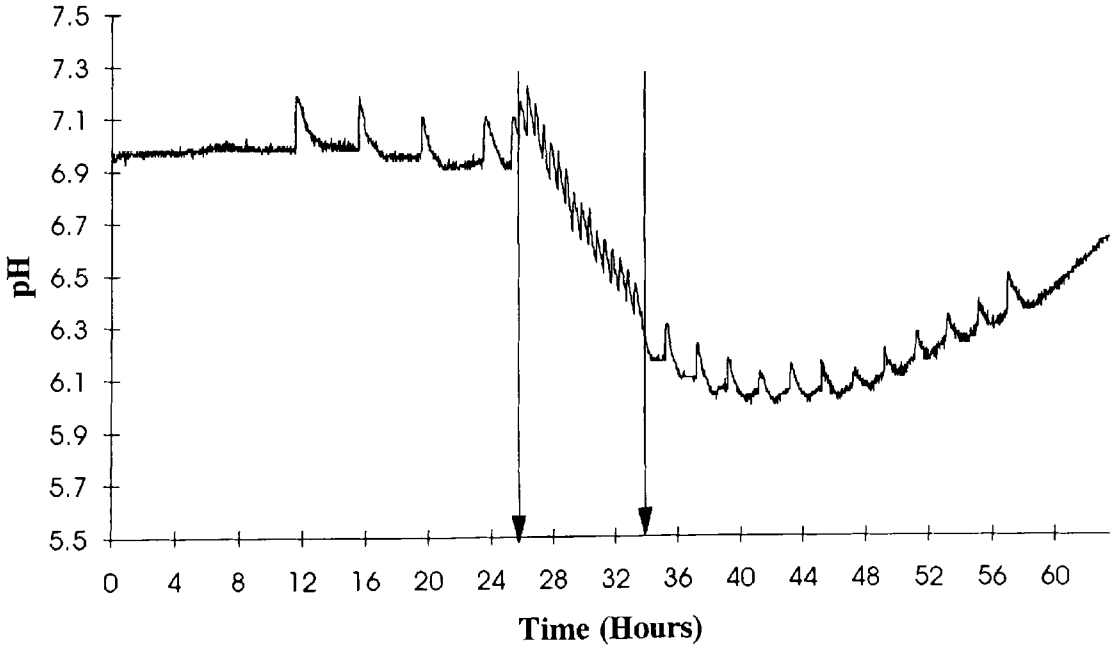


Figure 8.9b On-line pH during organic overload experiment 4.

There does not seem to be any delay in pH response to the initiation of the overload in experiment 4, but the sluggish response to the end of the overload is apparent (see Figure 8.9b). The pH drops from 7.0 to 6.1 corresponding to a change of 0.9 units.

Therefore there is very little difference between the pH reductions for experiment 3 and 4, whereas the difference between the reduction of BA in experiments 3 and 4 was 270 $mgCaCO_3l^{-1}$ which constitutes a difference of 39%. Therefore the pH measurement can fail to differentiate between shocks of differing severity.

The on-line percentage carbon dioxide in the biogas in experiments 3 and 4 are shown in Figure 8.10a and 8.10b respectively. The carbon dioxide increases from 21.5 to 29% after approximately 1.5 hours, the maximum deflection occurring after the end of the overload.

The response of carbon dioxide in experiment 4 is clearer, with an initial delay in response of about 1 hour before the carbon dioxide percentage rose linearly to its maximum of 41% which occurred approximately 1.2 hours after the end of the overload. The increase in carbon dioxide percentage is greater for experiment 4 than that of experiment 3 because more bicarbonate alkalinity is destroyed as a result of greater concentration probably caused by greater increase in organic overload. In addition the acidogenic bacteria will produce more CO_2 in experiment 4 than experiment 3 as there is greater concentration of long chain fatty acids available. The maximum deflection occurred after the end of the overload in both experiments corresponding to the delay of bicarbonate alkalinity and volatile fatty concentration.

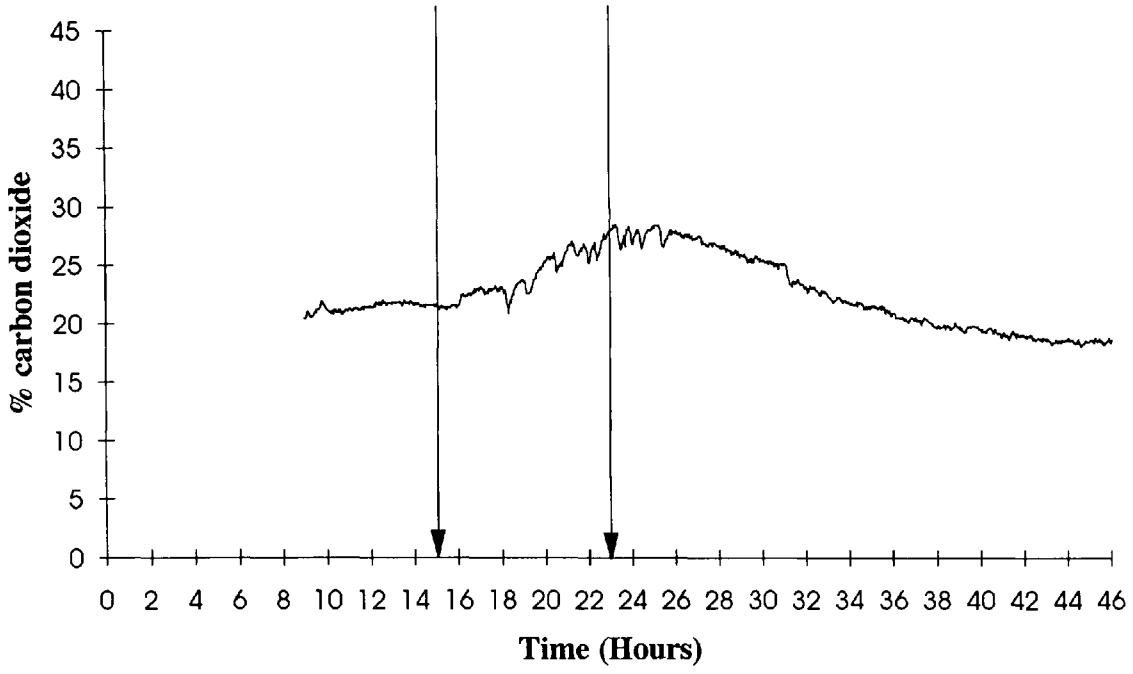


Figure 8.10a Percentage carbon dioxide during organic overload experiment 3.

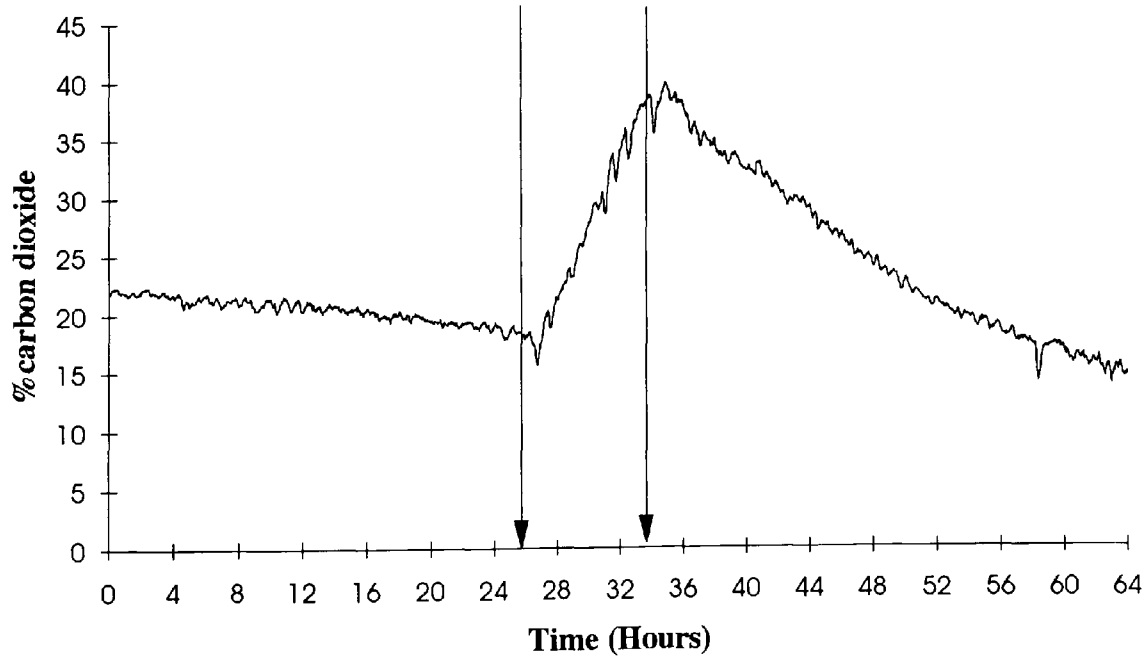


Figure 8.10b Percentage carbon dioxide during organic overload experiment 4.

A second lithium tracer study was performed on the reactor as described previously. It can be seen from the tracer exit distribution plot (Figure 8.11) that there is still a delay time of 30 minutes before any change in the [Li+] concentration was measured. This delay would be transmitted to measurements made in the liquid phase and will effect the gas measurement according.

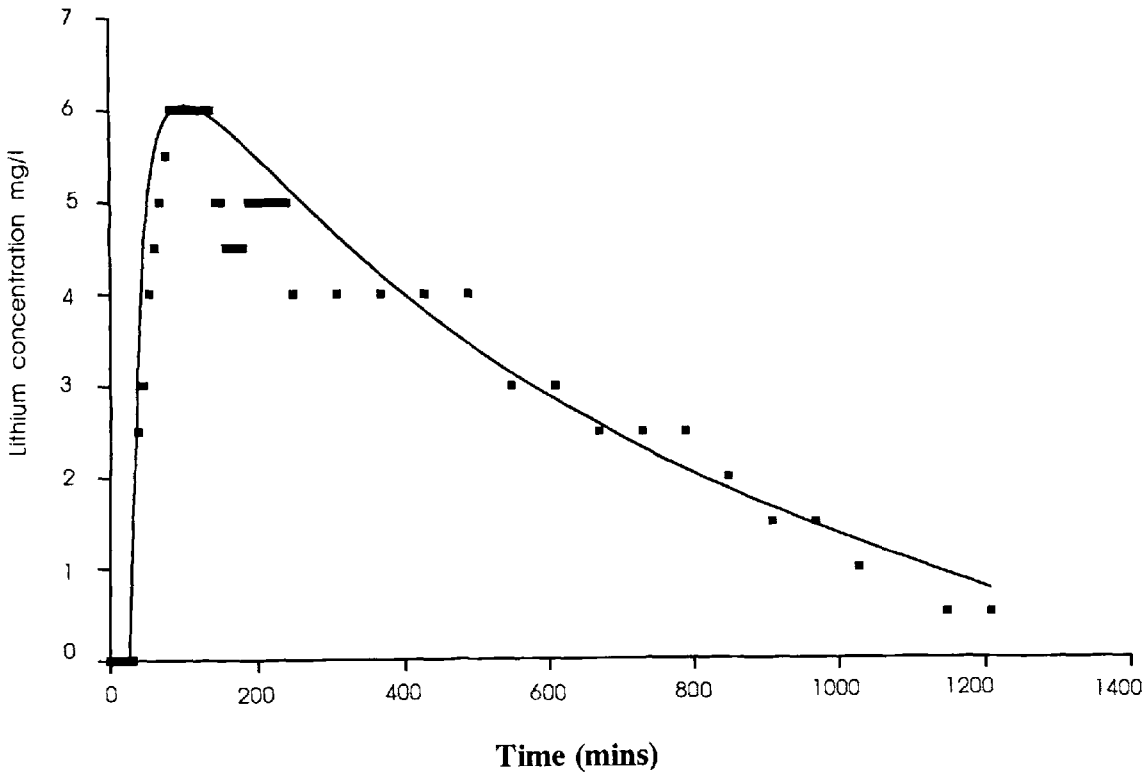


Figure 8.11 Exit distribution plot for an anaerobic filter with a recycle applied.

8.3. CONCLUSIONS.

The overload experiments described in this chapter showed that bicarbonate alkalinity measured by the on-line BA monitor was an effective way of monitoring instability in anacrobic digesters. The experiments also confirmed that on-line pH measurement using a 1180-1170 combination pH electrode drift by as much as 0.2 pH units due to fats and

proteins build up at the junction point of the electrode. Biogas production measurement was sensitive to the initiation of organic overloads and could give a valuable indication of changes in the feed input.

9. ON-LINE MEASUREMENT OF BICARBONATE ALKALINITY DURING OVERLOADING OF A MODIFIED LABORATORY ANAEROBIC FILTER.

9.1. ALTERATIONS MADE TO ANAEROBIC FILTER REACTOR.

Examination of the reactor contents revealed that a large excess of biomass had formed a blanket at the bottom of the reactor. The biomass blanket volume was approximately one third of the wet volume of the reactor. It was postulated that this blanket could be responsible for the poor mixing in the digester. Therefore the anaerobic digester was modified by draining the excess biomass from the reactor through the influent port (A in Figure 3.1). To ensure that air did not enter the reactor head space, the gas port (D) shown in Figure 3.5 was connected to a nitrogen line. After the removed of most of the excess biomass (3.2 litres) the reactor was fed with half the normal strength (2200 $mgCODl^{-1}$) ice-cream waste and allowed to acclimatise for a period of 8 days, during which the influent strength was slowly increased to a level of 4595 $mgCODl^{-1}$.

9.2 LITHIUM TRACER STUDY.

A third tracer studied was carried out to assess whether the removal of biomass had increased the mixing in the digester. Again the tracer study was performed with a recycle rate of 20 cm^3 min^{-1}, a HRT of 0.694 and a influent strength of 4365 $mgCODl^{-1}$. The lithium concentration was determined as before using flame photometry and the results plotted as an exit distribution curve. The exit distribution plot (see Figure 9.1) is typical of a completely mixed system with a delay time of only 7.5 minutes before a change in $[Li^+]$ is measured.

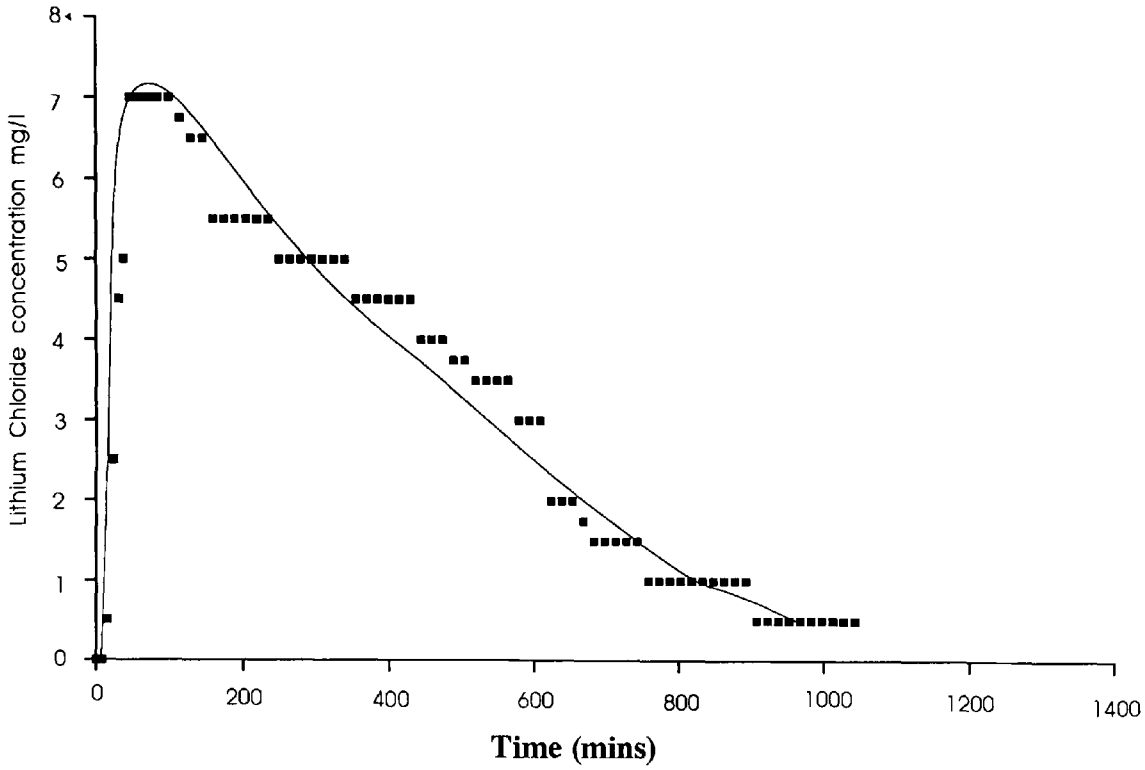


Figure 9.1 Lithium concentration exit distribution plot for the modified anaerobic filter.

9.3 PERFORMANCE OF THE MODIFIED DIGESTER.

A series of experiments were designed to investigate the performance of the BA monitor on the modified (completely mixed) anaerobic filter as outlined below;

9.3.1 Bicarbonate shocks (experiment 5 and 6).

Two step changes were performed, altering the concentration of the sodium bicarbonate in the feed while maintaining the organic concentration at 4500 $mgCODl^{-1}$.

5) 4 hours of baseline feed with 2.5 gl^{-1} of bicarbonate in the feed followed by a 8 hours step decrease of 2.0gl^{-1} sodium bicarbonate in the feed.
6) 4 hours of baseline feed with 2.5 gl^{-1} of bicarbonate in the feed followed by a 8 hours step increase of 3.0gl^{-1} sodium bicarbonate in the feed.

Three 25 litre batches (1, 2 and 3) of simulated ice-cream waste were prepared as described in section 3.3. However a different amount of sodium bicarbonate was added to each batch, 2.0 gl-1 was added to batch 1, 3.0 gl-1 to batch 3 (the shock wastes) and 2.5 gl-1 to batch 2 (the 'normal' waste). The anaerobic filter was fed with the 'normal' strength influent containing 2.5 gl^{-1} $NaHCO_3^-$ for 22.5 hours before the influent tube was switched to batch 1 to produce the first bicarbonate step decrease (experiment 5). After 4 hours the influent tube was returned to the 'normal' influent for a further 11 hours before a step increase in bicarbonate was administered (experiment 6). The initiation of the step increase in experiment 6 was performed by two computer controlled peristaltic pumps. The pump delivering the normal influent (batch 2) was switched off at the same time as a pump delivering influent from batch 3 was switch on. The reverse action was applied 8 hours later to end the increase.

The results of both bicarbonate step changes are illustrated in Figure 9.2. It is clear that the reactor is virtually completely mixed as the bicarbonate in experiment 5 begins to fall after 30 minutes (the response of the BA monitor) of the start of the step decrease in bicarbonate. The BA response to the step decrease is almost linear, indicating that the anaerobic system behaves as a pure integrator to the change in concentration of bicarbonate input to the reactor. At the end of the step change the bicarbonate concentration starts to rise again after a time of 30 minutes which is consistent with a completely mixed reactor. Before the start of bicarbonate experiment 6 there was an electronic malfunction which can be seen as a straight line starting at time 44 hours, however the fault was rectified before the initiation of step increase in bicarbonate alkalinity. Again the BA responded linearly to the BA step change.

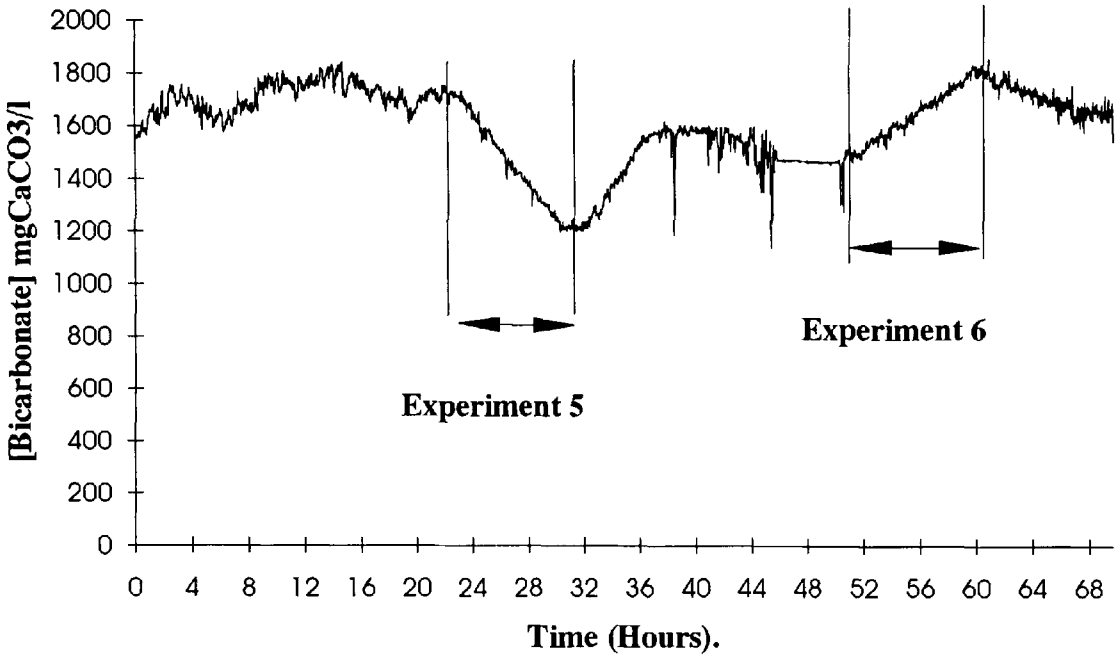


Figure 9.2 Bicarbonate step changes on an anaerobic filter reactor.

The percentage carbon dioxide and gas production rate were also monitored on-line for these BA step change experiments as shown in Figure 9.3.

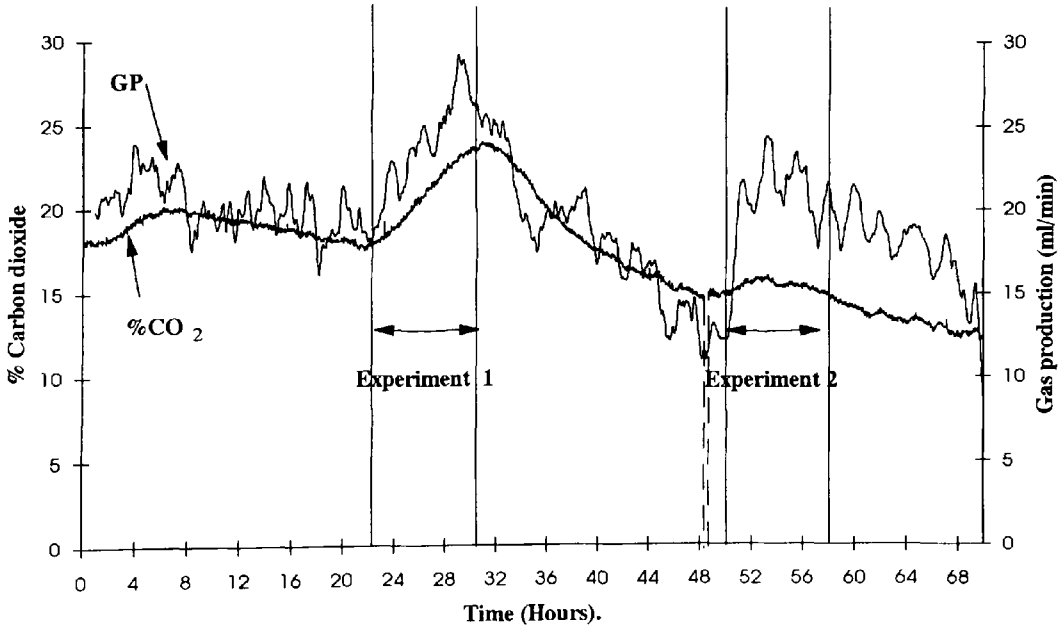


Figure 9.3 Gas production and percentage carbon dioxide during bicarbonate step changes.

It is clear from Figure 9.3 that the percentage carbon dioxide in the biogas increases as a direct result of the application of experiment 1 to the system. Its response is immediate to the change in bicarbonate input concentration and reaches a maximum value at the end of the step decrease, 8 hours later. The increase infers that the reduction of bicarbonate alkalinity in the influent is sufficient to provide process instability. If the anaerobes do not utilise the VFA, bicarbonate will be destroyed by the surplus. Therefore the reduction of the bicarbonate input into the digester means that the VFA concentration will increase and as a consequence the pH will decrease and the anaerobes may become inhibited. Hence the increase in carbon dioxide percentage may not solely be the result of the physico-chemical effect of bicarbonate destruction.

During experiment 6 the percentage carbon dioxide remains constant whereas the gas production increases to the steady state level. The increased gas production is a result of restored bacterial activity due to increased buffering capacity which neutralises excess VFAs in the system.

From the bicarbonate step changes it is evident that the bicarbonate buffering capacity is crucial in maintenance of anaerobic process stability. The bicarbonate step changes in experiments 5 and 6 also showed the extent of 'steering' that could be exerted on the system. through the controllable bicarbonate alkalinity input, to counterbalance the effect of fluctuations in the organic load which are difficult practically to manipulate.

9.3.2. Organic overload experiment 7.

The organic overload experiments 7 and 8 were performed to evaluate the response of the BA monitor on the modified reactor with recycle (Hawkes *et al.* In Press). These experiments would also allow comparison of gas and liquor phase parameters which were made difficult in organic overload experiments 1 and 2 discussed in section 8.1 by

the presence of a 2 hour detention time. The conditions of the organic overload experiments 7 and 8 are shown in Table 9.1.

Table 9.1 Conditions of organic overload experiments 7 and 8.

Experimental Overload	**7**	**8**
Influent concentration change (mgCODl^{-1}).	4670 - 9130	4468 - 12470
Recycle rate (cm^3 min^{-1})	20	20
Percentage COD change.	95%	179%
Organic load rate (kgCOD/m^3/day).	6.73 - 13.15	6.43 - 17.97
Hydraulic Retention Time (Days).	0.69	0.69
Duration of overload (Hours).	8	8

The prototype BA monitor output (see Figure 9.4) was subject to 'spikes' which occurred at time 12, 24 and 46 hours this was due to blockage of the effluent peristaltic tube with large slugs of fatty material which had accumulated in the overflow pipe. It was this that caused the noisy response of the BA monitor and not blockage within the BA monitor itself. However the response to the overload is clear, less clear is the presence of a delay in response caused by the mixing characteristics of the anaerobic filter. In the following figures the arrows represent the beginning and ending of the overload.

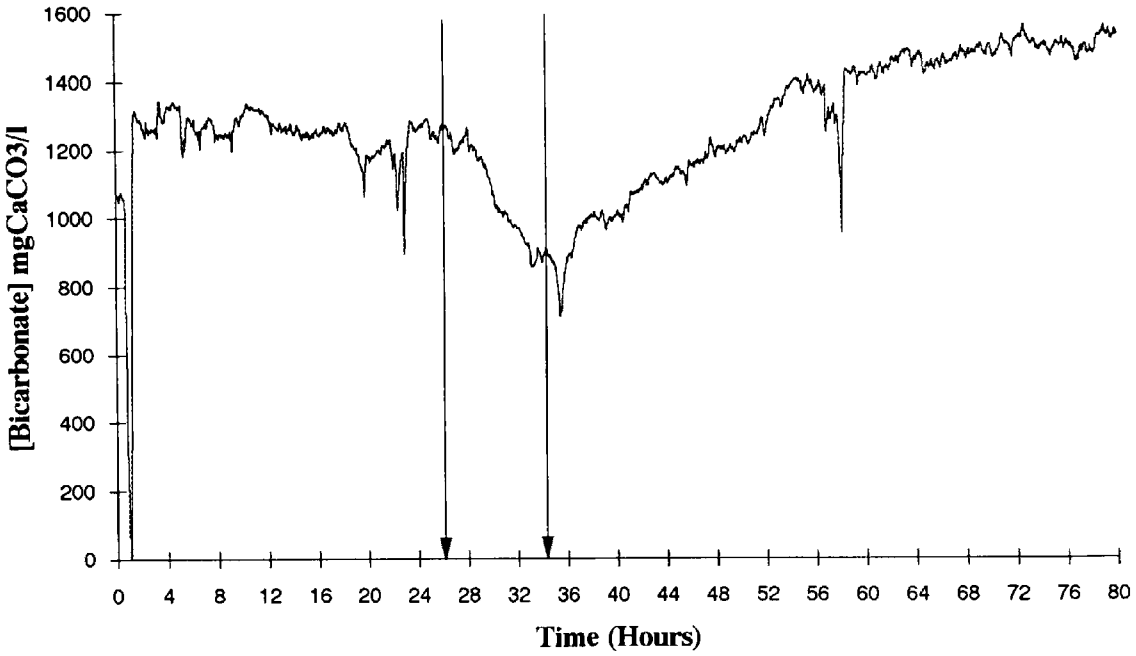


Figure 9.4 On-line bicarbonate alkalinity as measured by the prototype BA monitor for organic overload experiment 7.

Figure 9.5 showing the pH output was subject to a blockage at the eight hour mark, however the response to the overload is more definite than in organic overload experiments 1 and 2 described in section 8. In fact the pH values begin to fall at the instant the overload was applied. Therefore, the modifications to the filter (i.e., recycle and removal of biomass blanket) improved digester mixing and reduced liquid phase parametric response times. So, it was possible to make a more accurate comparison between the gaseous measurements of hydrogen and carbon dioxide levels with the liquid phase parameters.

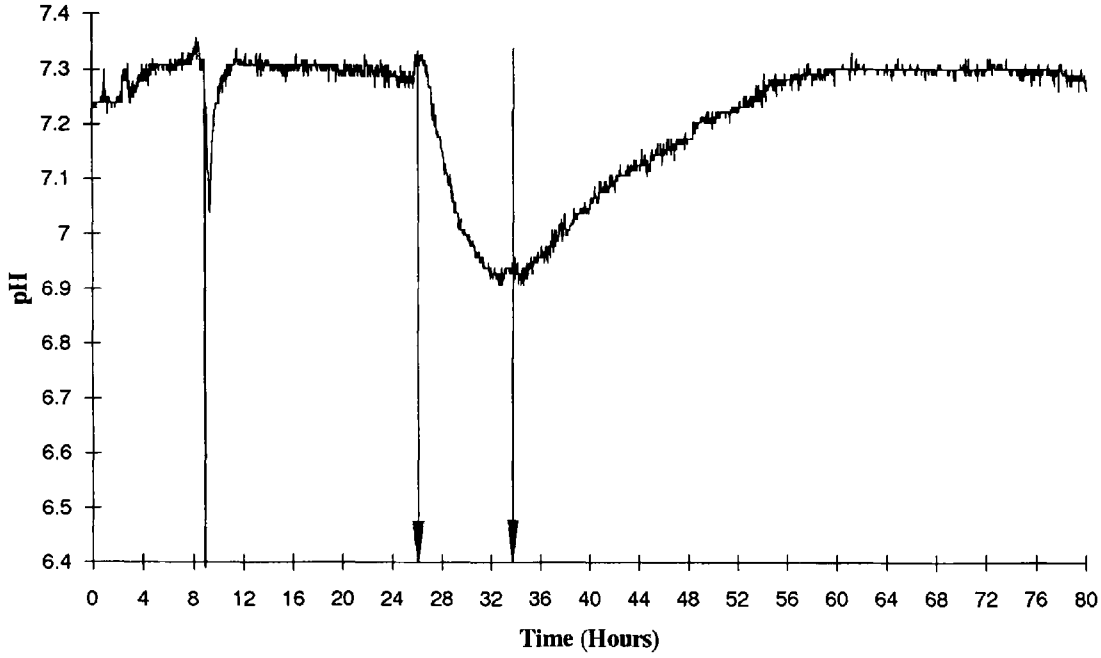


Figure 9.5 On-line pH for organic overload experiment 7.

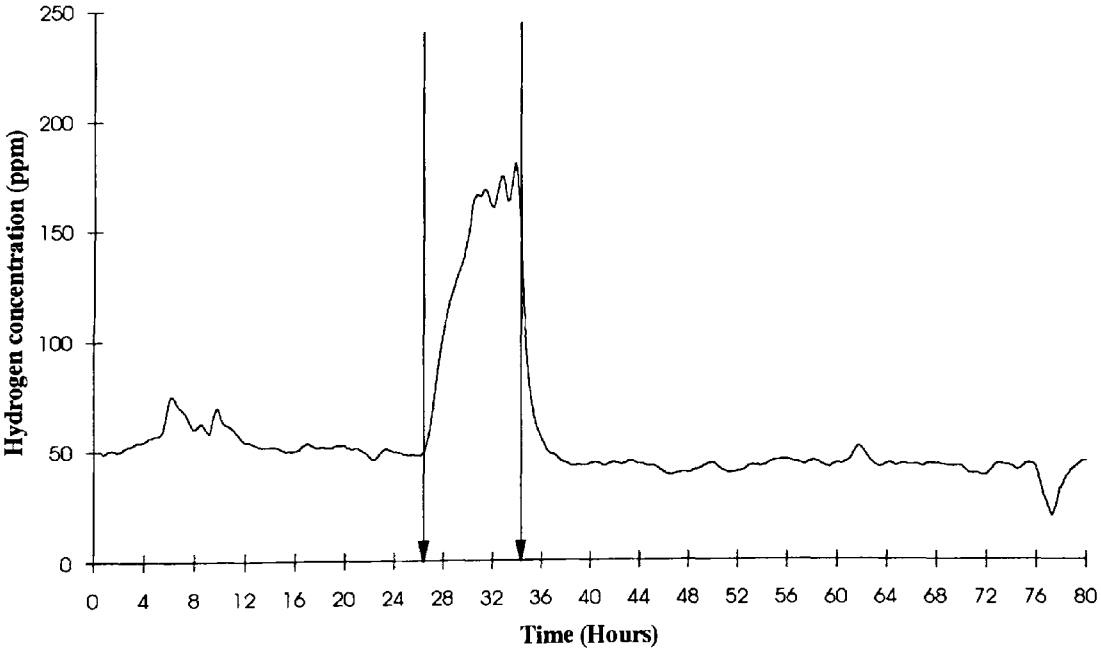


Figure 9.6 Hydrogen concentration in the biogas during organic overload experiment 7.

The hydrogen concentration in the biogas is very responsive to changes in process stability as can be seen in Figure 9.6. During the anaerobic degradation of organic matter nicotine adenine di-nucleotide (NAD^+) is reduced and must be re-oxidised in order that the process can continue. Therefore protons are reduced to hydrogen and utilised by the lithotrophic methanogens via the 'interspecies hydrogen transfer system'. However during overloading of the anaerobic system the slow growth rates of the methanogens compared to the acidogenic bacteria causes the hydrogen to increase in the system (see section 2.2.6).

This results in an increased production of propionic acid which is confirmed in Figure 9.8 showing the VFA concentration. At the end of the overload the hydrogen concentration falls dramatically due to the very low residence time (Gujer and Zender, 1983). The results of experiment 7 support previous work by Whitmore and Lloyd 1986, Hickey *et al.* 1987, Collins and Paskins 1987, Mosey and Fernandez 1989 and Hickey *et al.* 1989, showing that hydrogen is a good instability indicator. However, because of the complex dynamics of hydrogen in an anaerobic system and its dependency on the waste type and condition, it is unsuitable as a stand alone control variable. Switzenbaum *et al.* (1990) reported that changes in hydrogen concentration are not always apparent and therefore unreliable as a control variable. Although in this experiment the increase is clearly due to the increase in organic load and the subsequent instability of the process, the hydrogen concentration varied considerably prior to the overload without any corresponding changes in any of the other parametric variables. Powell and Archer (1989) suggested that anaerobic process control based on hydrogen monitoring should include the determination of a liquor phase parameter such as bicarbonate or VFA concentration. The results obtained here during the overload and in steady state periods prior to the shock would support this proposal.

The changes in carbon dioxide percentage (see Figure 9.7) also occur immediately after the overload start which contradicts the general opinion that the carbon dioxide percentage changes as a result of instability and is therefore not useful as an early

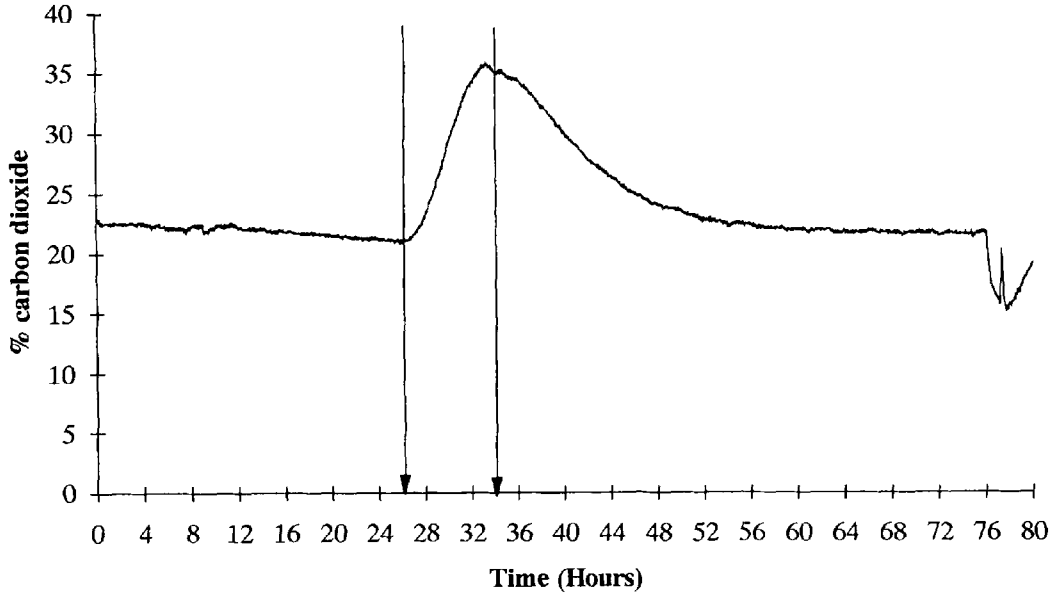


Figure 9.7 Percentage carbon dioxide during organic overload experiment 7.

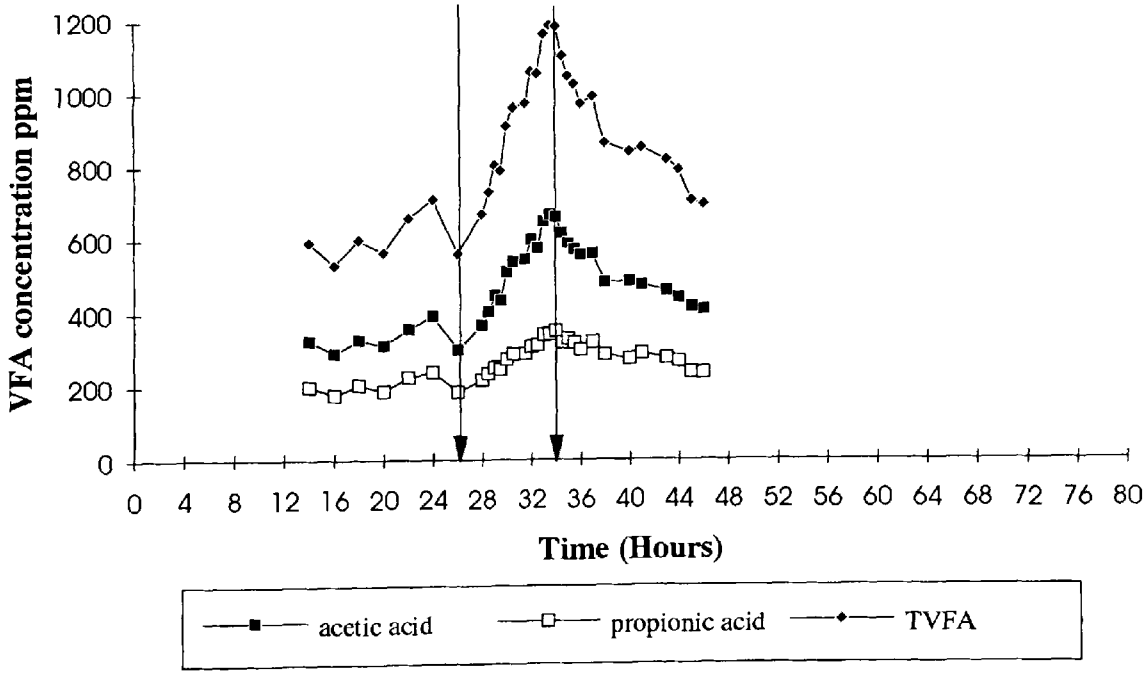


Figure 9.8 Volatile fatty acid concentration during organic overload experiment 7.

warning variable. Comparison of carbon dioxide percentage with hydrogen and VFA concentrations (which are considered to be the best instability parameters and respond

rapidly to changes in process stability) shows that the % carbon dioxide is equally suited to early warning of impending instability.

9.3.3. Organic overload experiment 8.

The influent COD strength for experiment 8 was trebled for eight hours (4468 to 12470 $mgCODl^{-1}$) corresponding to a loading rate increase of 6.4 to 18 $kgCODm^{-1}day^{-1}$. The effluent COD during the overload experiment is plotted in Figure 9.9.

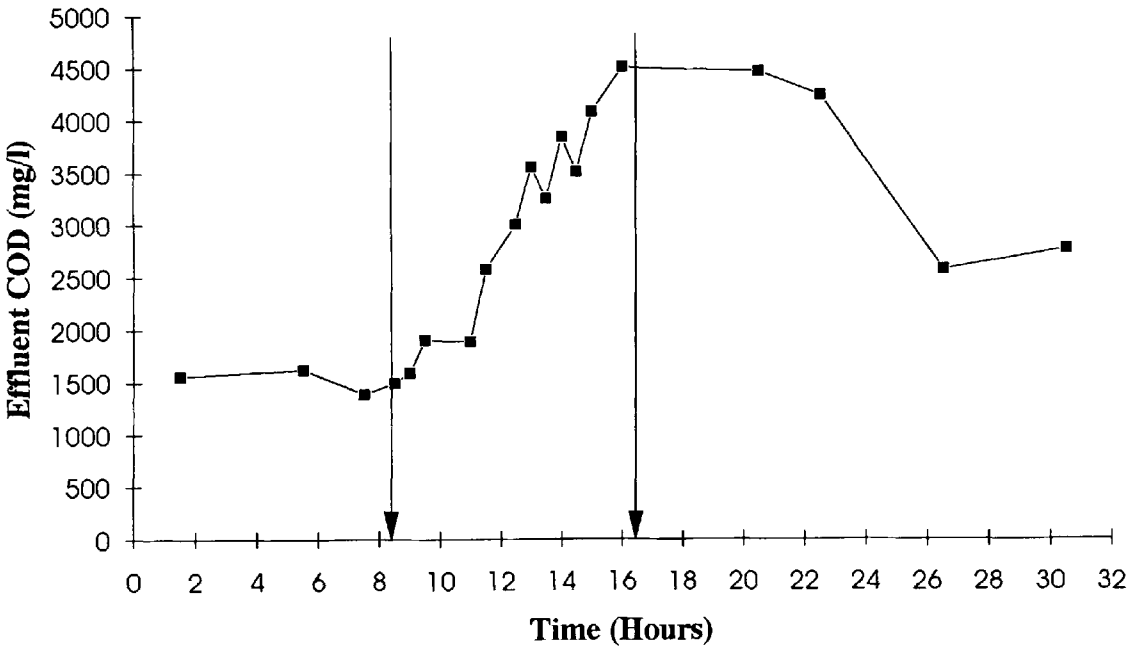


Figure 9.9 Effluent COD during experiment 8.

The COD results are typical of those experienced during an organic overload and the percentage COD removal decreased from 66% to 40%. It can be seen from Figure 9.10 that the decrease in COD removal coincides with a decrease in bicarbonate alkalinity. The bicarbonate alkalinity began to drop about one hour or more after the initiation of the shock and decreased almost linearly until about 30 minutes after the end of the overload. This result indicates that the response of the biological system in the liquid

phase is almost immediate, since the reactor is completely mixed and the response time of the bicarbonate analyser is 30 minutes. This observation is confirmed by the data related to volatile acids (acetic, propionic and the sum of acetic, propionic, n- and iso-butyric acids and n- and iso-valeric acids given as TVFA) which are reported in Figure 9.11.

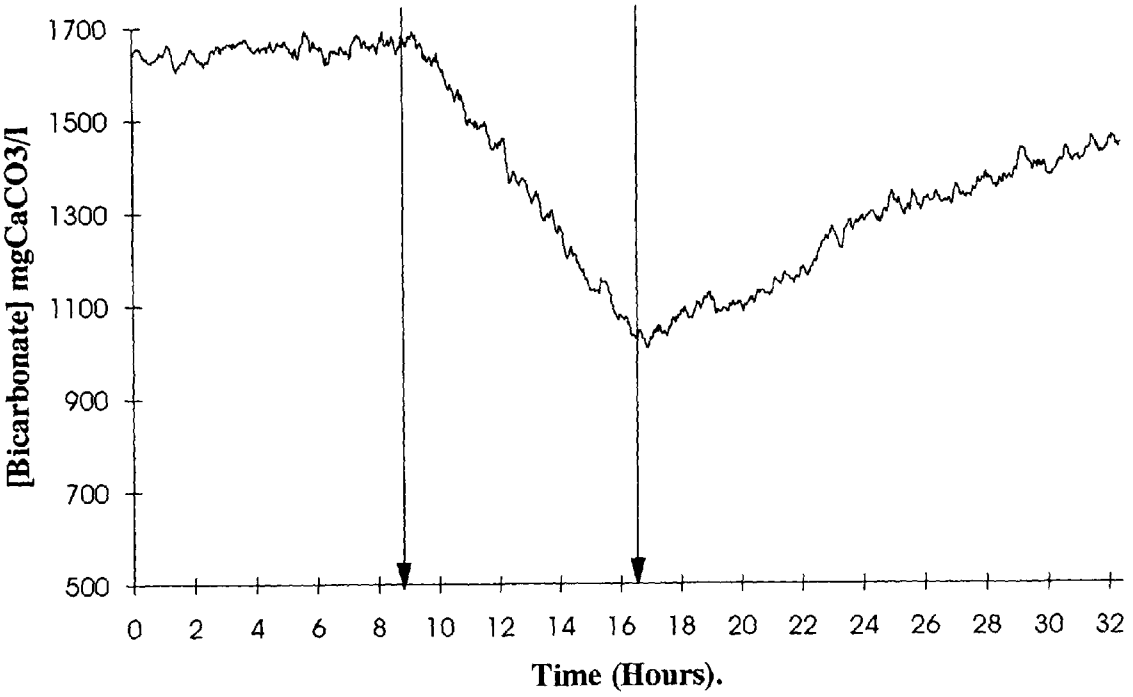


Figure 9.10 On-line bicarbonate alkalinity as measured by the prototype BA monitor for organic overload experiment 8.

The propionic and acetic acid concentrations responded rapidly to the overload which confirms that the reactor stability has been upset. During an overload there should be a greater rate of increase in propionic acid compared to that of acetic acid, however the rate of increase in acetic acid and propionic acid were very similar. Comparing Figure 9.11 with Figure 9.10 it can be observed that the changes in bicarbonate alkalinity are inversely related to the TVFA concentration, as in the previous experiments 1,2,3,4 and 7.

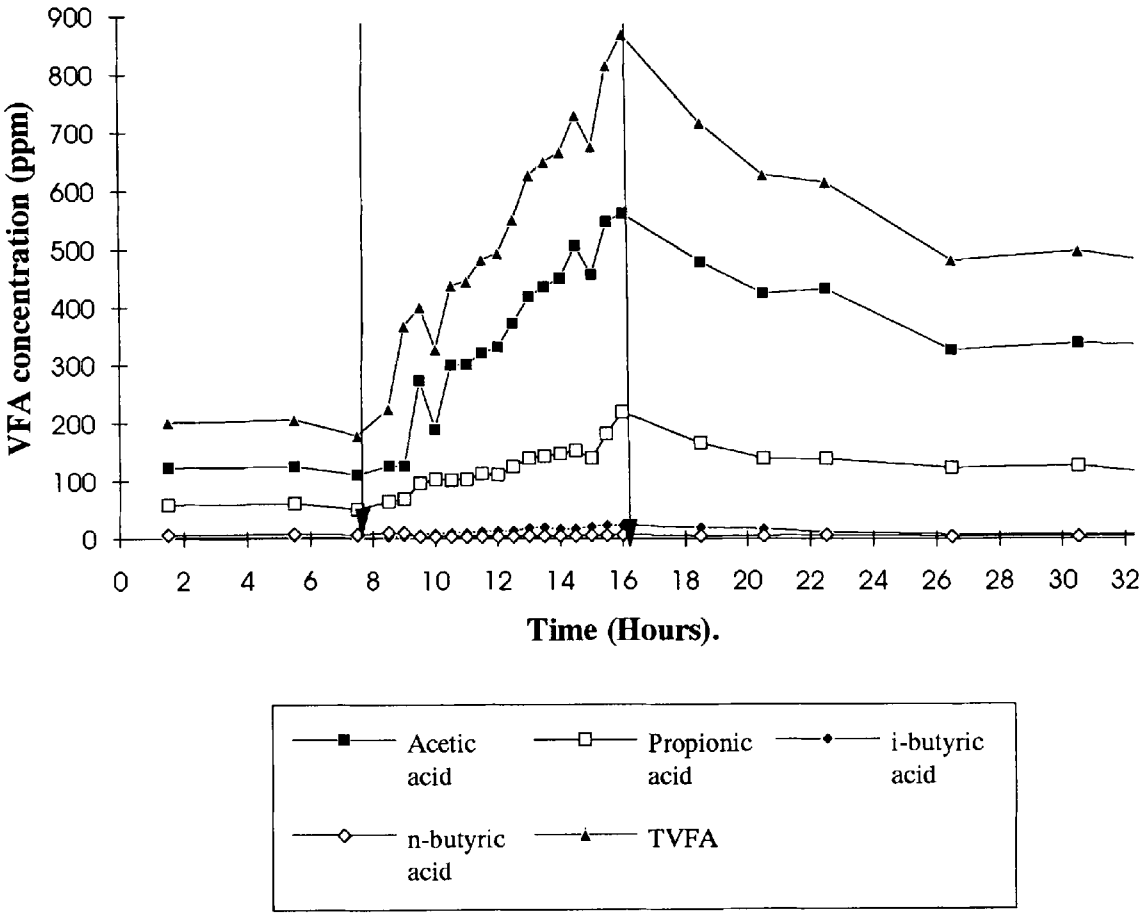


Figure 9.11 Volatile fatty acid concentration during organic overload experiment 8.

This correspondence is shown in Figure 9.12 where the change in the bicarbonate alkalinity measured before the overload and during overload/recovery ($\Delta BA = BA_{steady\ state} - BA_{transient}$) and corresponding figures for the increase in volatile fatty acids measured ($\Delta VFA = VFA_{transient} - VFA_{steady\ state}$) are plotted on a molar basis. In this figure, data related to bicarbonate alkalinity have been shifted 0.5 hours backwards in order to account for the response time of the bicarbonate analysing device. It can be seen that the timing and extent of ΔBA and ΔVFA compare well. During the period of higher stress (at the end of the overload) the measured ΔVFA was consistently lower than ΔBA, while before and for the first 8 hours of the step overload the two values were much closer. Possibly there are organic acids other than acetic, propionic, n- and i-butyric and

n- and i-valeric acids formed during the overload period which affect the bicarbonate concentration but are not detected by the GC method used.

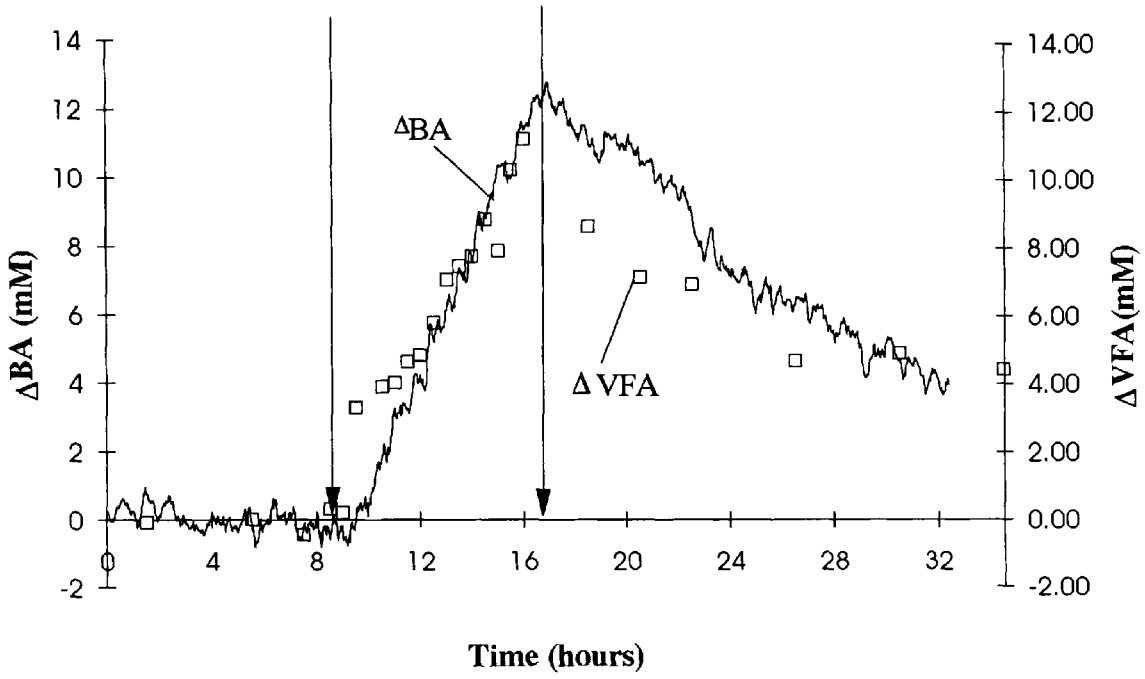


Figure 9.12 $\Delta BA = BA_{steady\ state} - BA_{transient}$ and $\Delta VFA = VFA_{transient} - VFA_{steady\ state}$ plotted against time (overload indicated by arrows).

In order to check the validity of the correspondence between ΔBA and ΔVFA, data for three overload experiments are reported in Figure 9.13. It can be seen that a definite correspondence exists. It must be taken into account that this use of ΔBA in indirect determination of ΔVFA cannot be applied if the potential alkalinity of the wastewater is appreciable, as happens in effluents containing proteins or salts of organic acids (McCarty, 1964, Anderson and Yang, 1992). In this case the correspondence between Δ BA and ΔVFA would not hold during overloads and subsequent transients.

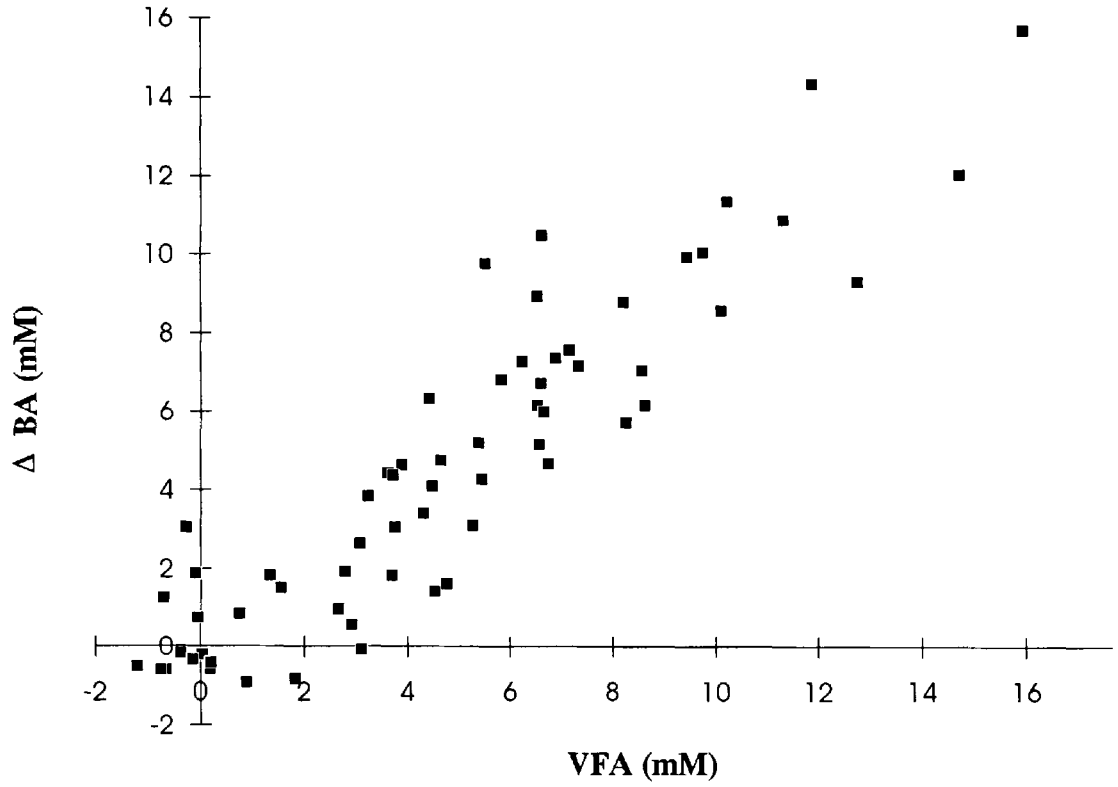


Figure 9.13 Relation between ΔBA ($BA_{steady\ state}$-$BA_{transient}$), and ΔVFA ($VFA_{transient}$ - $VFA_{steady\ state}$) as defined for three overload experiments 4, 7 and 8.

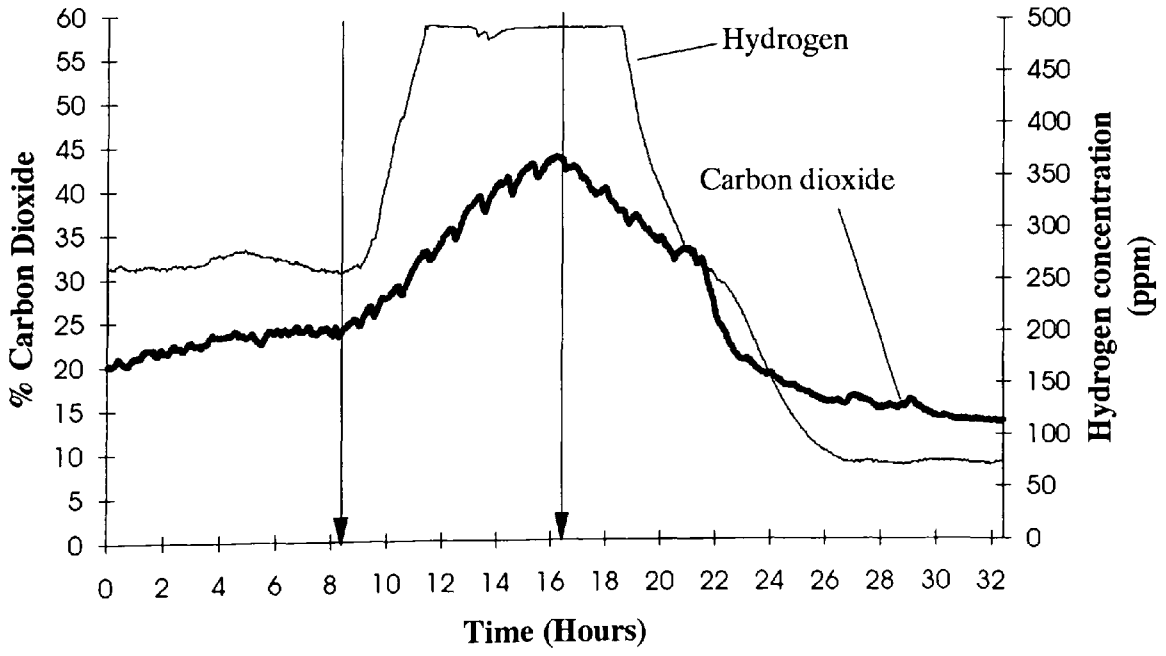


Figure 9.14 Changes in hydrogen and carbon dioxide in the gas phase.

In Figure 9.14 the biogas concentrations of CO_2 and H_2 are plotted. The hydrogen concentration is relatively high before the overload as normal steady state values were approximately 60 to 100 ppm as shown in Figure 9.6. It can be seen that the change in H_2 concentration during the step load exceeded the concentration measurable by the data acquisition program used under these conditions. However the maximum reading on the hydrogen meter was recorded at 896 ppm at the end of the overload, after which the concentration fell rapidly. After the overload, hydrogen concentration drops below the steady state level before the overload. This inconsistency has proved to the biggest problem with the use of hydrogen as a control variable.

In order to have a more quantitative estimation of the response times of the parameters given in the above figures, the time intervals needed to obtain a variation of three times the standard deviation of the steady state value (calculated over thirty minutes preceding the overload for on-line measurements) were calculated for CO_2, BA, and pH. The limit of plus or minus three standard deviations chosen to evaluate change from steady state is that which would normally be applied in the implementation of control procedures. For hydrogen however, the standard deviation of the steady state data was small, hence + or - 3 three standard deviations gave a response time of the same order as that of the hydrogen monitoring instrument (eight minutes). This does not accord with the observed rate of change hydrogen (see Figure 9.14.) which shows a response time of approximately 35 minutes. A similar response time of 30 minutes is observed for hydrogen concentration gas in experiment 7. Data for two overload experiments 7 and 8 are reported in Table 9.2. The value of three times the standard deviation as a percentage of the steady state mean of each parameter is also shown. In the case of VFA, it can be seen from figure 9.11 that the response time was approximately 60 minutes compared to approximately 180 minutes in experiment 7. Direct comparison with the response times found by other workers (Barnes *et al.* 1983, Moletta, 1988, Cayless *et al.* 1989, Jones 1992) is not possible because of the different experimental conditions.

Table 9.2. Response Time of gas and liquid phase parameters to organic overload measured on-line.

	2 fold overload		3 fold overload	
	Response time (min)	% Deviation from steady state mean	Response time (min)	% Deviation from steady state mean
CO_2	44	3.0	16	4.7
H_2	30	-	35	-
pH	70	0.8	46	0.3
Bicarbonate Alkalinity	54	4.5	68	2.2

It should be noted that the response times in Table 9.2 were obtained with instruments which themselves had different response times. It should also be noted that the rate of gas production was approximately 13 cm^3min^{-1} biogas before the overload, rising to a maximum of approximately 18 cm^3min^{-1} during the eight hour period, giving a gas residence time in the headspace of about two hours. Delays in gas composition changes are related to mass damping by the headspace volume, as observed by Denac *et al.* (1988). In the experience of the author, on-line measurements of H_2 show drift, need frequent re-calibration, and would be difficult to implement as the basis for a control strategy. The carbon dioxide concentration changes in the biogas give a good indication of the onset of instability, but they are not so tightly correlated to parameters in the liquid phase, especially after the overload is terminated. Frequent fouling of pH probes in ice-cream wastewater was experienced; the response of pH electrodes was found to be unreliable during this work.

In Figure 9.15, pH measured on-line and off-line during the overload is plotted, as well as the values calculated by entering the experimental values of bicarbonate concentration

and carbon dioxide concentration into the bicarbonate equilibrium equation, combined with the pH equation of Capri and Marais (1975):

$$pH = -Log_{10} \frac{k_{a1} \cdot k_H \cdot P_{CO_2}}{\gamma \cdot [HCO_3^-]} \qquad (30)$$

where k_{a1} is the first equilibrium constant for HCO_3^-, k_H is Henry's constant and γ is the activity coefficient for monovalent ions, calculated using the Güntelberg approximation derived from the Debye-Hückel equation (Sawyer and McCarty, 1978).

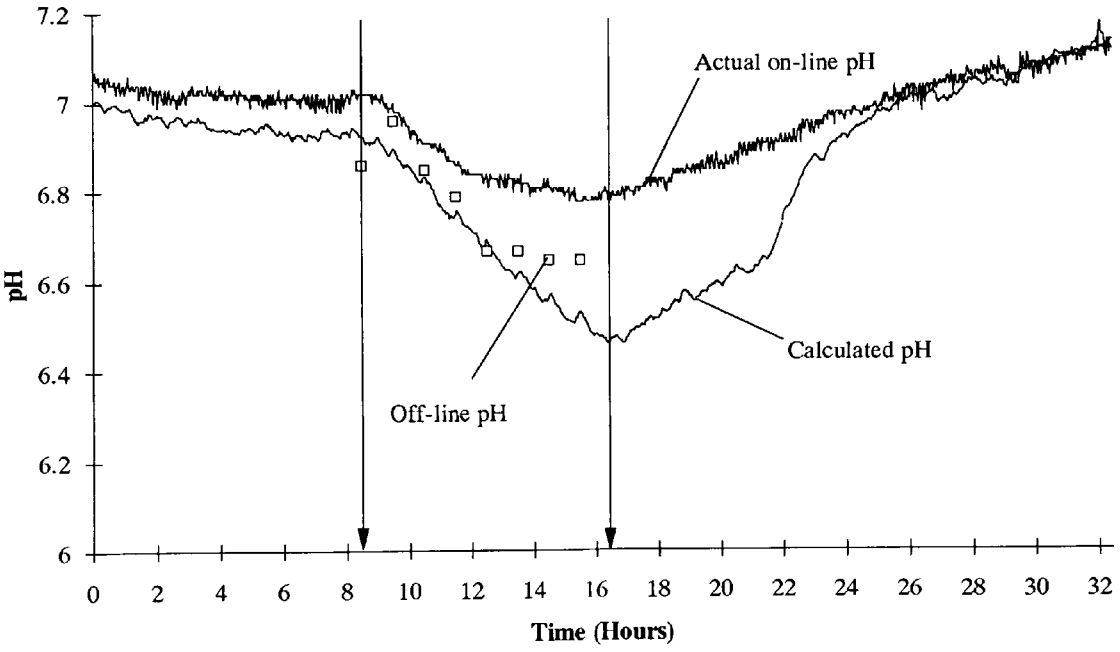


Figure 9.15 pH values from on-line measurements (probe sited in the effluent stream from the reactor) and off line measurements (in samples of effluent) during the step overload in experiment 8 (indicated by arrows). Also shown is pH calculated from on-line bicarbonate alkalinity and carbon dioxide measurements.

It can be seen that the comparison between the calculated and the off-line pH value is better than the on-line values with the off-line pH measurement. The reason for this was probably due to fouling of the on-line electrode by fats and proteins in the anaerobic

effluent. Therefore, in those conditions where the correct operation of pH probes is problematic. The use of the bicarbonate alkalinity measuring device could allow the indirect measurement of proton concentration with an accuracy acceptable in most cases (errors of the order of 0.1 units). This degree of accuracy can be proven quite easily from the bicarbonate equilibrium equation: assuming errors of the order of 10% on bicarbonate alkalinity and CO_2 measurements (available instruments are more accurate than this), the error in the calculated pH is equal to 0.087 units only. This accuracy is better than that obtained using standard electrodes and voltmeters.

9.4. CONCLUSIONS.

Changes in bicarbonate alkalinity measured by the BA monitor proved to be as rapid as acetic acid, propionic acid and TVFA measurements during the overload experiments 7 and 8. A clear relationship between the change in bicarbonate concentration (ΔBA) and the change in total volatile fatty acid concentration (ΔTVFA) during steady state operation and overload conditions was established. The measurement of BA using the BA monitor and carbon dioxide by on-line infra red measurement allowed the indirect measurement of proton concentration. Measurement of hydrogen in the biogas using the on-line exhale hydrogen analyser also showed a rapid response to incoming organic overloads. However significant changes in the hydrogen concentration in the biogas occurred without any associated changes in stability. Over a operation period as short as 6 months sufficient biomass build up can occur in the digester to severely effect the mixing characteristics. Lithium tracer studies showed that removal of the biomass sludge blanket from the bottom of the reactor increase the mixing in the filter.

10. SUGGESTIONS FOR FURTHER RESEARCH.

10.1. USING THE BA MONITOR FOR CONTROLLING WASTEWATER PROCESSES.

The BA monitor described in thesis offers a large potential for further research and industrial development. Control of treatment processes especially anaerobic digestion, is vital if they are to be successful in the industrial market place.

Bicarbonate alkalinity has be shown to be a useful instability parameter by McCarty 1964, Pohland and Engstrom 1964, and as a result of the work presented here bicarbonate concentration can be monitored on-line. Therefore the next stage of development of the BA monitor is its use in a control strategy.

One of simplest form of feedback controller is the Proportional-Integral-Derivative (PID) device. The development of an anaerobic process mathematical model using the data collected the BA monitor and the other process parameters will enable simulations to "tune in" the PID. The resulting parameters could be transferred to the real-time application when a satisfactory performance is achieved and only finer tuning is required. The simplest form of sampled incremental PID controller is the following

$$dNa(t) = P_p\,[e(t)-e(t-1)] + hP_i e(t) + P_d[e(t) - 2e(t-1) + e(t-2)]/h \qquad (31)$$

Where dNa(t) is the incremental amount of bicarbonate to be injected into the system at the next sampling time, e(t), e(t-1), e(t-2) is the error between the output variable and the desired set-point at time t, t-1, t-2. These time instants are separated by the sampling interval h. The three PID parameters are P_p, P_i, P_d . The result of equation (31) is the incremental dosing signal, which has to be summed up to the previous one to form the signal going into the process, thus;

$$Na(t) = Na(t-1) + dNa(t) \quad (32)$$

Equation (32) provides the required dosing signal to drive the bicarbonate metering pump. So the overall closed-loop system could be as follows;

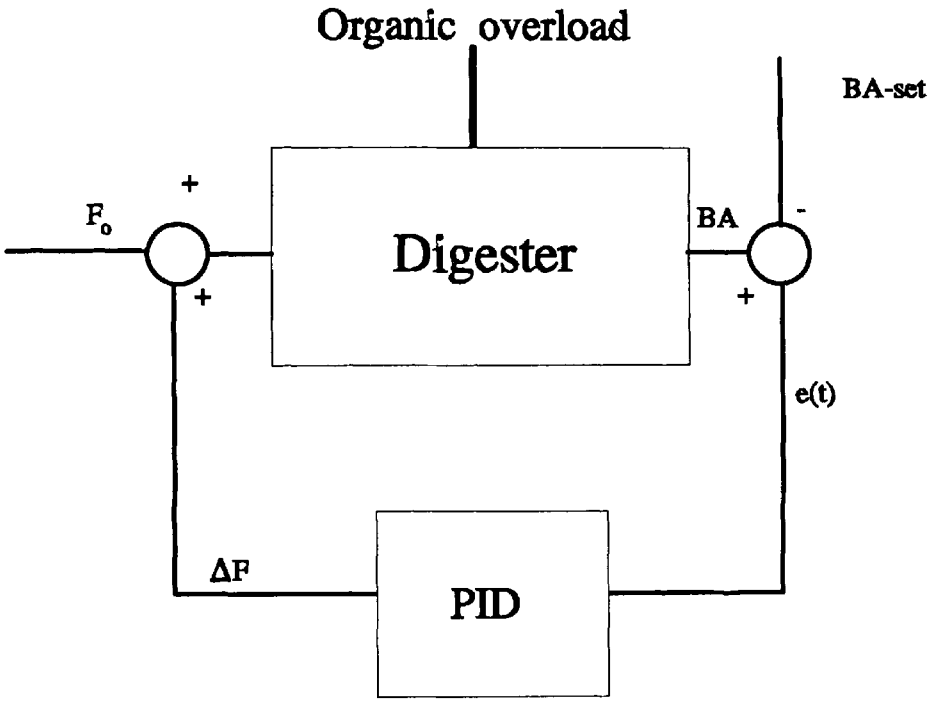


Figure 10.1 Schematic representation of a possible BA feedback controller.

If an appropriate value of bicarbonate alkalinity is chosen for steady state operation of anaerobic digestion, for example 1000 $mgCaCO_3l^{-1}$, any deviation from this set point will result in a correcting action on a bicarbonate dosing pump, normally delivering a flow F_O. Therefore if a perturbation such as an organic overload causes deviation of the BA output from the desired BA-set value, the resulting non zero error e(t) will cause the PID controller to deliver a non zero ΔF corrective command to the dosing pump driver.

The PID controller can be connected to an anaerobic digester to establish whether the BA monitor can be used to control the stability of a reactor. This would be a novel contribution to research in the field of anaerobic wastewater treatment.

The BA monitor could be used with a PID controller to investigate:

a) if failure of the anaerobic process could be prevented.

b) whether the efficiency of COD removal could be increased, with BA control.

An alternative approach would be to utilise a neural network to control the anaerobic process. Neural networks work, with their parallel approach, should be capable of combining one or more sensors required to detect instabilities in the anaerobic digestion process. Once the neural network is trained it should be capable of rapid recognition of instability such as an organic overload. Neural network simulations for the classification of data presented in this thesis have already been used to build a neural network based on bicarbonate measurement using the BA monitor (Wilcox *et al.* In Press).

The application of the BA monitor is not limited to anaerobic digestion process, it is also ideally suited to aerobic processes particularly nitrification. The overall empirical equation for the process of nitrification is as follows;

$$NH_4^+ + 1.83O_2 + 1.98HCO_3^- \rightarrow 0.98NO_3^- + 0.021C_5H_7NO_2 + 1.88H_2CO_3 + 1.04H_2O \quad (33)$$

For 1g of NH_3-N converted approximately 7.14g of bicarbonate alkalinity are destroyed, therefore in wastewater systems with low or high NH_3 concentrations bicarbonate ions are essential to maintain the optimum pH.

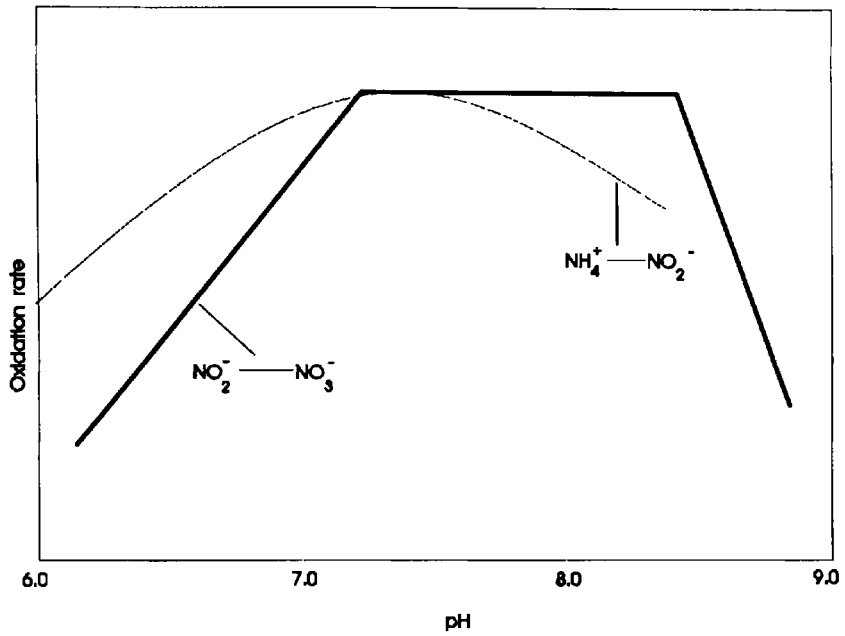


Figure 10.2 The effect of pH on ammonia oxidation. (taken from Phosphorus and Nitrogen Removal from Municipal Wastewater ed., Sedlak, R.).

It can be clearly seen from Figure 10.2 that the oxidation rates of both nitrate and ammonia are reduced if the pH is not maintained between 7 and 8.5. As bicarbonate alkalinity is responsible for almost all the buffering capacity in this pH range the control of pH is intrinsically linked to the bicarbonate concentration.

11. CONCLUSIONS

Pilot scale studies of an anaerobic filter showed that the bicarbonate alkalinity responded only marginally slower than propionic acid to the organic overload. Off-line bicarbonate measurements were shown to be subject to less fluctuations than either off-line pH or % carbon dioxide measurements. Direct on-line measurement of bicarbonate alkalinity by measuring the carbon dioxide yield from a sample stream, after addition of excess acid was shown to an effective method for standard solutions and anaerobic effluents.

A new low flow gas meter was developed that was capable of measuring on-line gas flows of 0.1 to 14cm^3min^{-1} with an accuracy of ±5% and a response time of 1 minute. The on-line gas meter was effective as the gas sensor in the BA monitor, allowing on-line operation of the BA monitor.

Redesign of the chamber configuration of the BA monitor meant that it could operate on wastewaters with COD levels of greater than 20gl-1 and a high fat content without blockage problems. Subsequent calibration of the newly developed BA monitor gave an accuracy of ±7% and a response time of 30 minutes and for bicarbonate standards containing VFA concentrations similar to those expected in an unstable anaerobic digester in the bicarbonate concentration range 5-50mM.

Overloading experiments on an anaerobic filter showed that bicarbonate alkalinity measured by the on-line BA monitor was an effective way of monitoring instability in anaerobic digesters. Changes in bicarbonate alkalinity measured by the BA monitor proved to be as rapid as acetic acid, propionic acid and TVFA measurements during the overload experiments 7 and 8. A clear relationship between the change in bicarbonate concentration (ΔBA) and the change in total volatile fatty acid concentration (ΔTVFA) during steady state operation and overload conditions was established. The experiments also confirmed that on-line pH measurement using a 1180-1170 combination pH

electrode drift by as much as 0.2 pH units due to fats and proteins build up at the junction point of the electrode.

The overloading program illustrated that the measurement of hydrogen in the biogas using the on-line exhale hydrogen analyser also showed a rapid response to incoming organic overloads. However significant changes in the hydrogen concentration in the biogas occurred without any associated changes in stability.

The on-line BA monitor is a better alternative to existing measurements of bicarbonate alkalinity where VFA concentration exceeds 300ppm. The prototype BA monitor provides a rugged, reliable and relatively low cost method for continuous on-line instrument for monitoring the bicarbonate/carbonate species in wastewater treatment such as anaerobic digestion. The measurement of bicarbonate alkalinity using the BA monitor and carbon dioxide by on-line infra red measurement allowed the indirect measurement of proton concentration. The BA monitor could be used to control the performance of a reactor in an expert system, the implications of which are large.

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APPENDIX 1

Calculation of Chemical Oxygen Demand.

If a effluent sample was diluited by 1 in 10 with distilled water.

For example 3.4cm^3 of FAS (0.0296mols) were required to react with the residual Dichromate in an effluent sample.

Therefore, Moles FAS = $\frac{\text{Volume titrated} \times \text{Concentration of FAS}}{1000}$

$$= \frac{3.4 \times 0.0296}{1000} = 1.0064 \times 10^{-4}$$

The equation for the reaction between the Fe (II) and dichromate is as follows:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \leftrightarrow 6Fe^{2+} + Cr^{3+} + 7H_2O$$

Therefore, moles FAS : moles dicromate = 6 : 1

Therefore, the number of moles of residual dichromate is;

$$\frac{1.0064 \times 10^{-4}}{6} = 1.677 \times 10^{-5} \text{moles}$$

5cm^3 M&B COD reagent used in the seal tube test contains 2.8×10^{-5} M of $K_2Cr_2O_7$

Thus,

$K_2Cr_2O_7$ used = $K_2Cr_2O_7$K(initial) - $K_2Cr_2O_7$ (final)

$= 2.8\times10^{-5} - 1.677\times10^{-5}$

$=1.123\times10^{-5}$moles

From the oxygen equivalent equation:

$$K_2Cr_2O_7 + 4H_2SO_4 \leftrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$

Therefore, 3 moles of (O) are equivalent to 1 mole of $K_2Cr_2O_7$

So, the COD of the sample is ;

$$1.123\times10^{-5} \times 3 = 3.368\times10^{-5} \text{ moles}$$

However the COD is expressed as $mg(O)l^{-1}$

So, the COD of the sample is equal to;

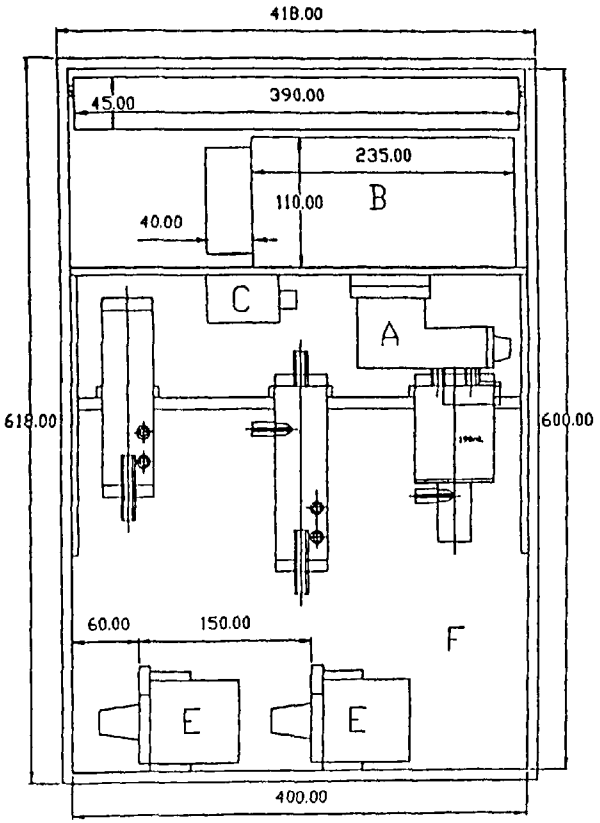
$$3.368\times10^{-5} \times 1000 \times 16(\text{Mr } O_2) \times 1000 \times 10 \text{ (dilution factor)} = 0.538 \text{ mg(O)}l^{-1}\text{moles}$$

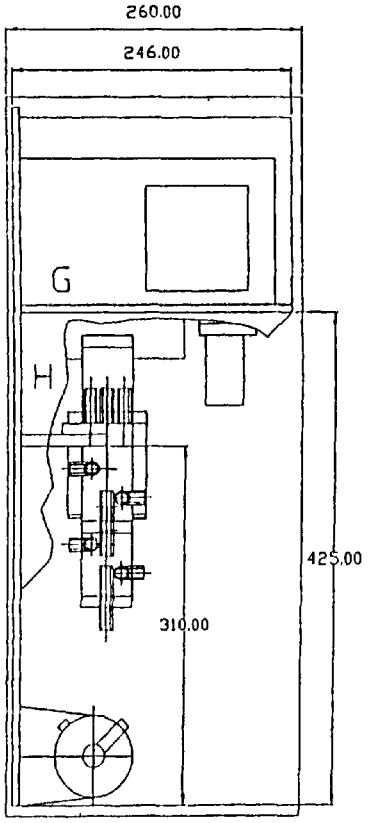
Therefore a value of 0.539 mg O for $2.5cm^3$ sample gives a COD of;

$$215 \text{ mgCOD}l^{-1}$$

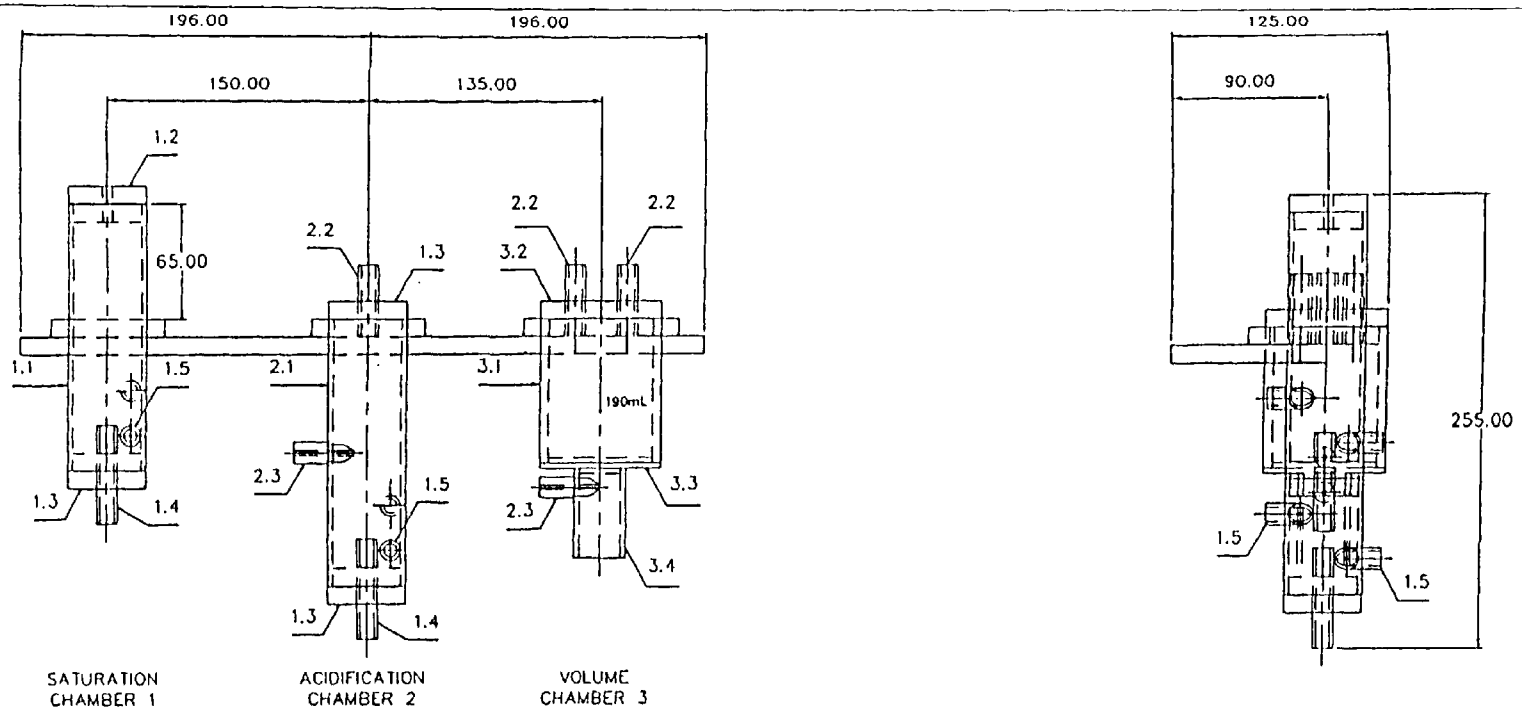
APPENDIX 2

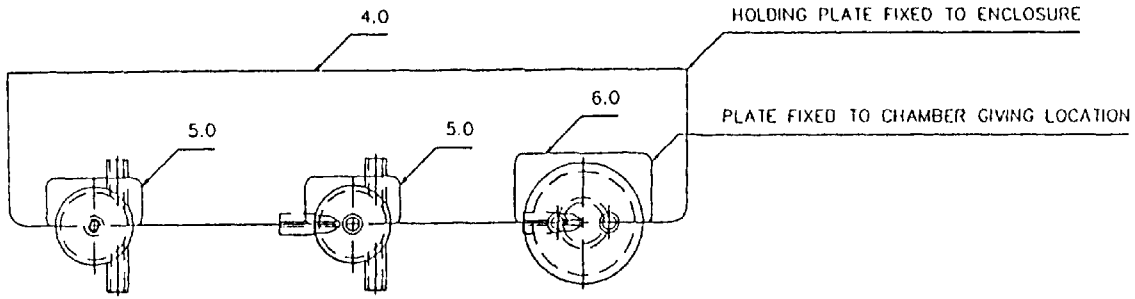
Engineering diagrams of the BA monitor construction.





PART	DESCRIPTION	DRG No.
A	3-WAY SOLENOID VALVE	—
B	FEED PUMP	—
C	TRANSDUCER	—
D	ELECTRONIC COMPONENTS	—
E	RECYCLE PUMP	—
F	MOUNTING BOARD	0.1
G	SHELF	0.2
H	SHELF SUPPORT	0.3
I	ANALYSER ASSEMBLY	0.4





PART No.	COMPONENT DESCRIPTION
6.0	ø70mm LOCATING PLATE
5.0	ø45mm LOCATING PLATE
4.0	HOLDING PLATE
3.4	EFFL. DISPOSAL PIPE
3.3	ø70mm LOWER CAP
3.2	ø70mm UPPER CAP
3.1	VOLUME CYLINDER
2.3	EFFL. NOZZLE CONNECTOR
2.2	GAS LINE CONNECTOR
2.1	ACIDIFICATION CYLINDER
1.5	MIXING PUMP CONNECTOR
1.4	EFFLUENT CONNECTOR
1.3	ø45mm LOWER CAP
1.2	ø45mm UPPER CAP
1.1	SATURATION CYLINDER

3rd ANGLE	DIMENSIONS IN MM		SCALE	1:4	POLYTECHNIC OF WALES
	TOLERANCES±0.5 UOS		DRAWN	C.FIELDEN	
			CHECKED		TITLE: ANALYSER ASSEMBLY
	MATERIAL	ACRYLIC	APPROVED		DRG No. 0.4
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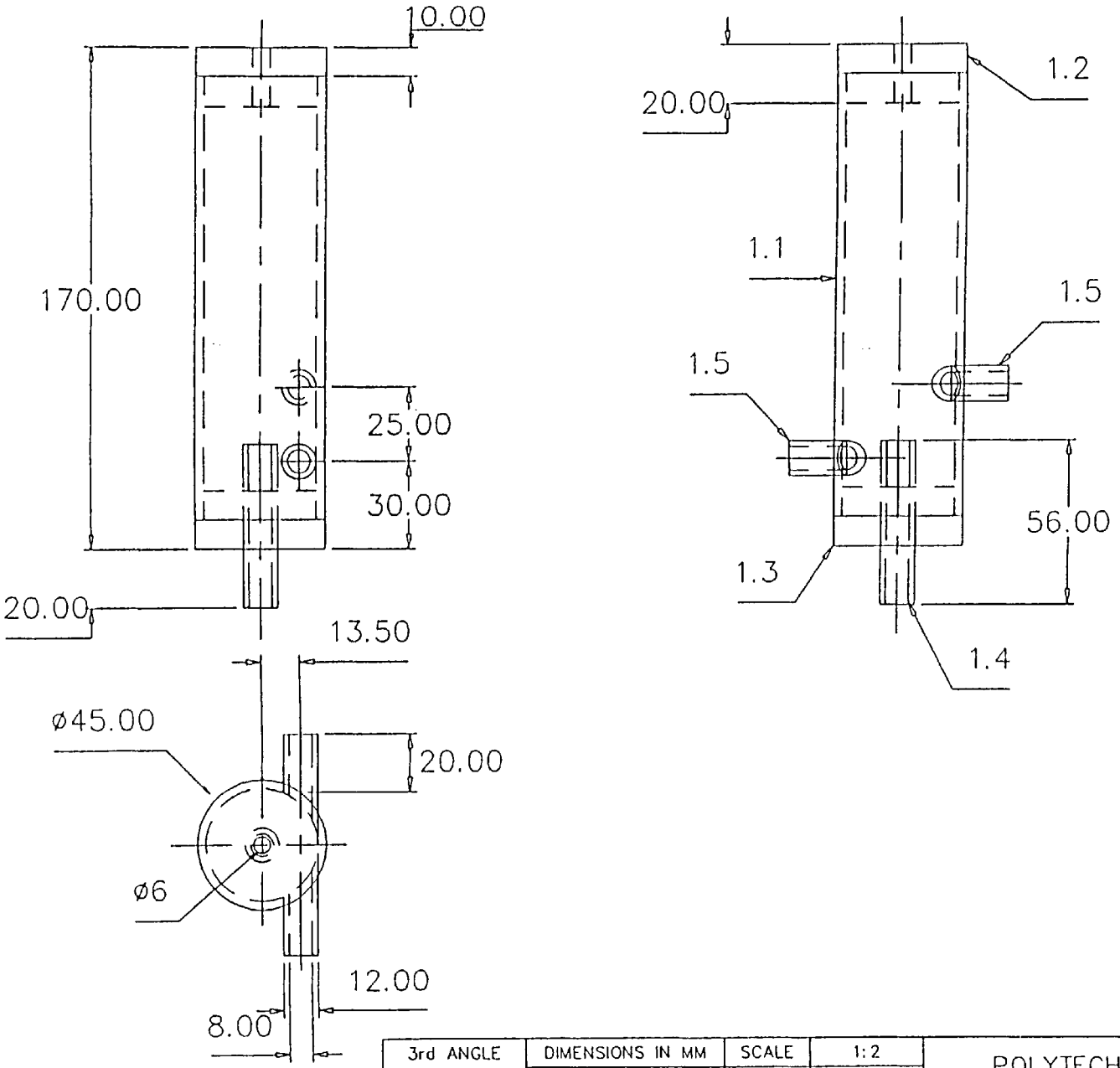

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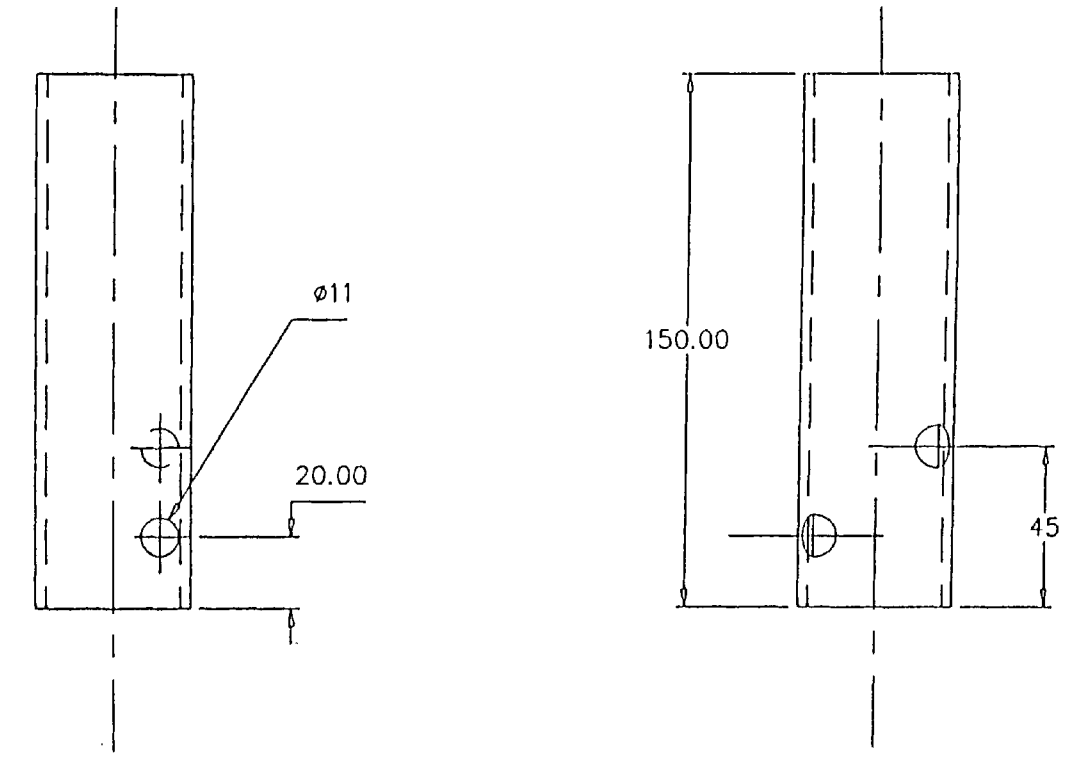

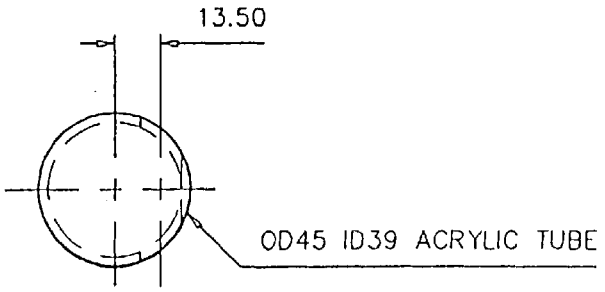

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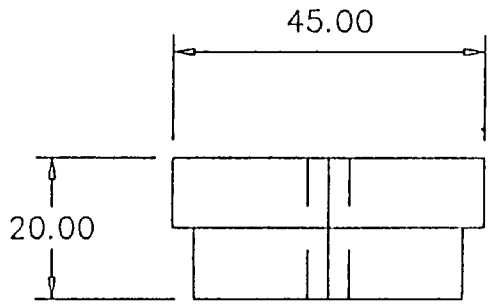

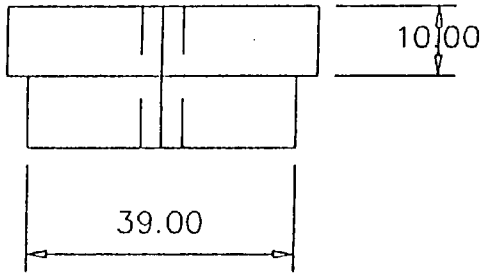

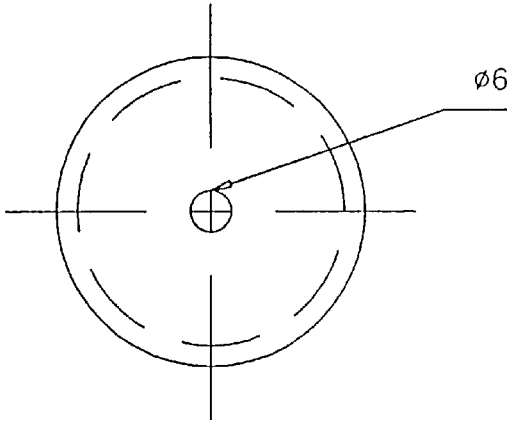

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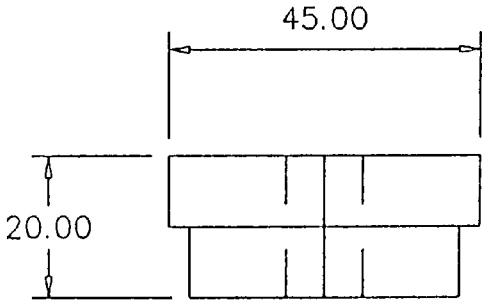

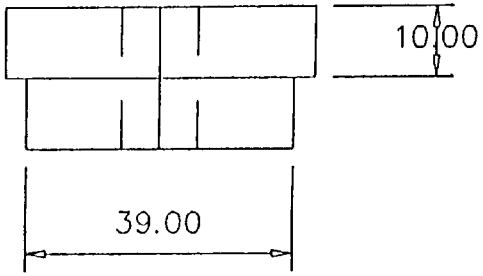

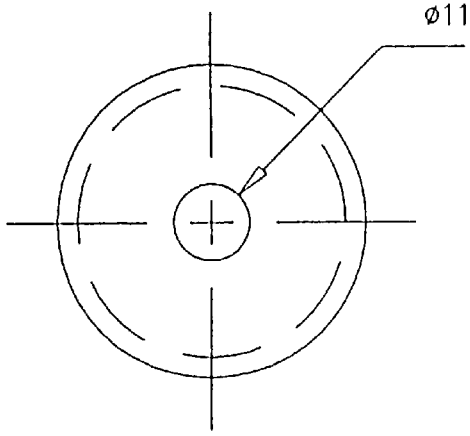

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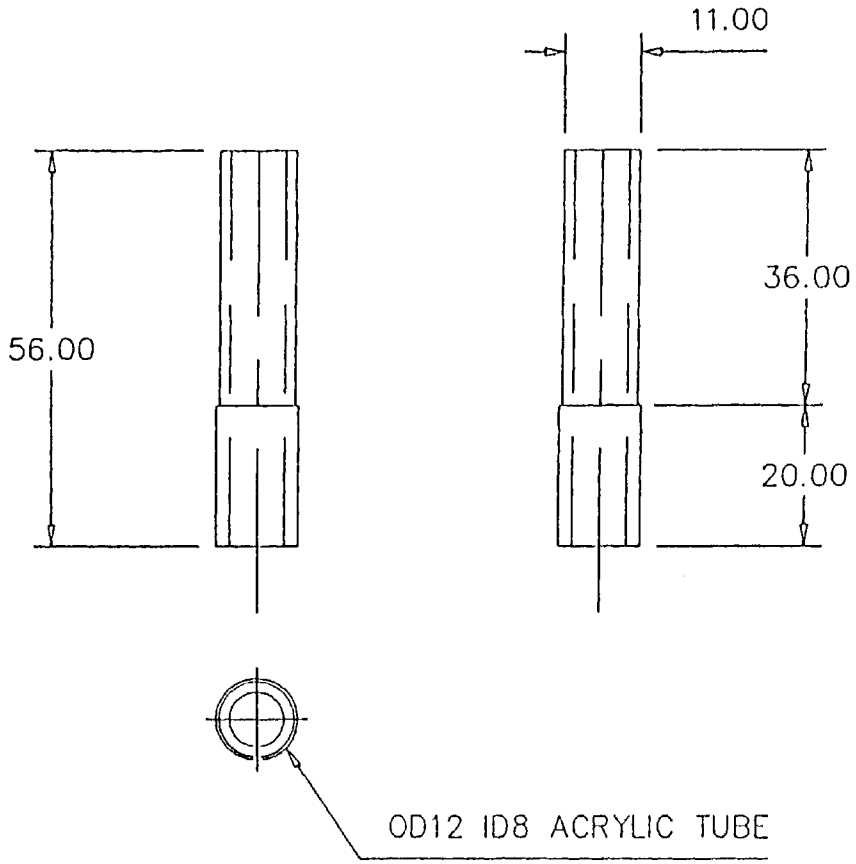

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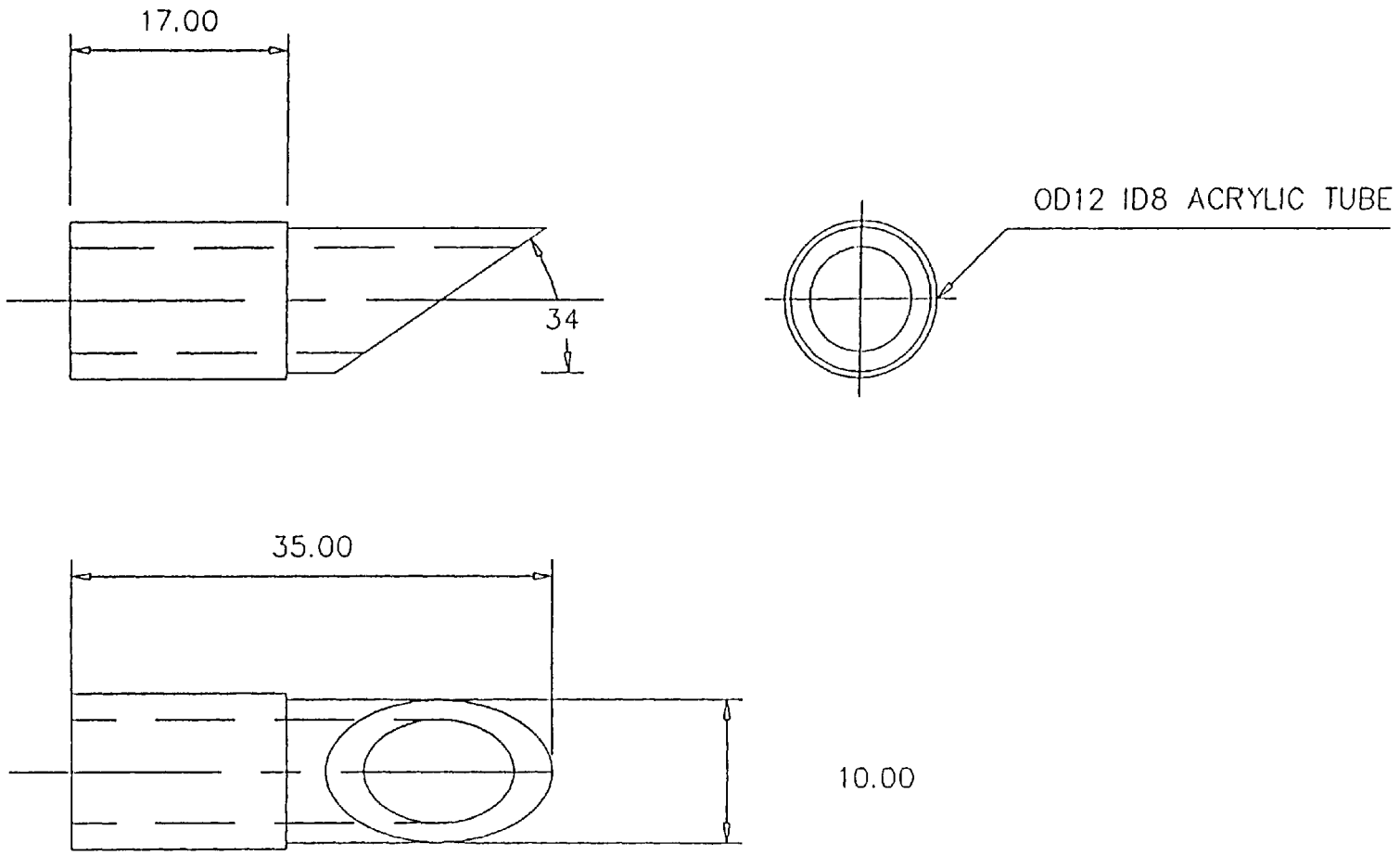
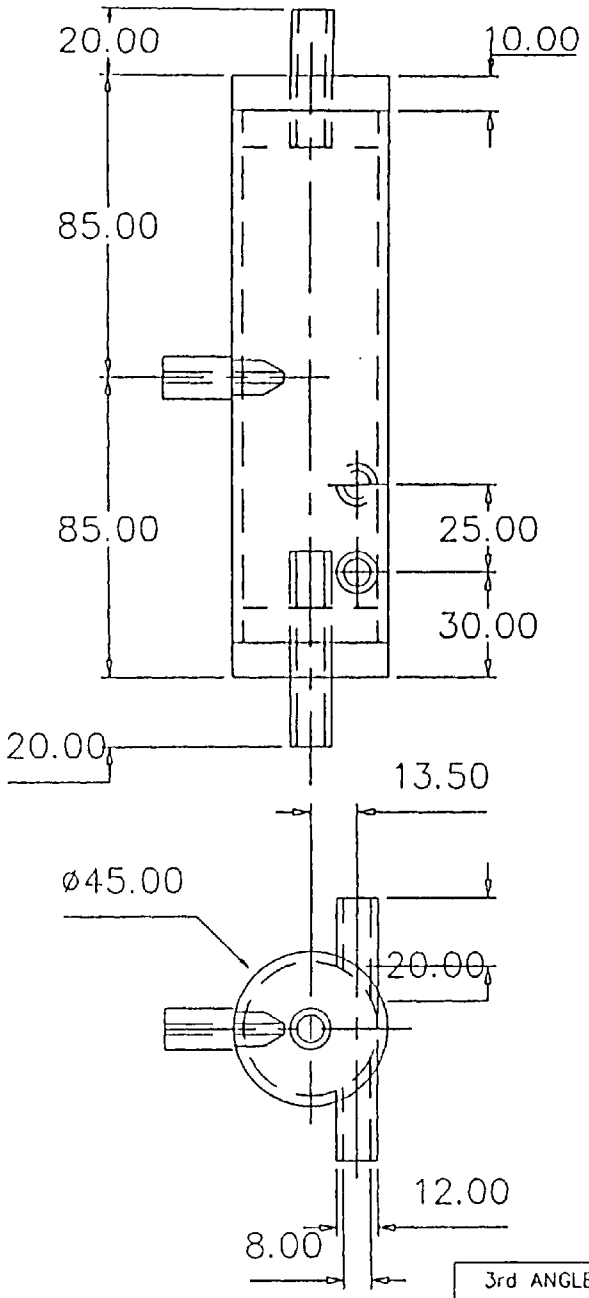
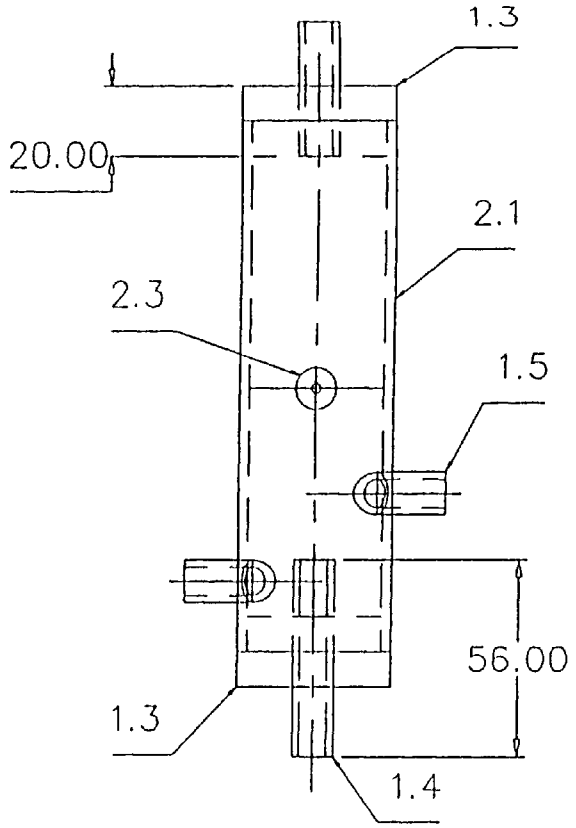
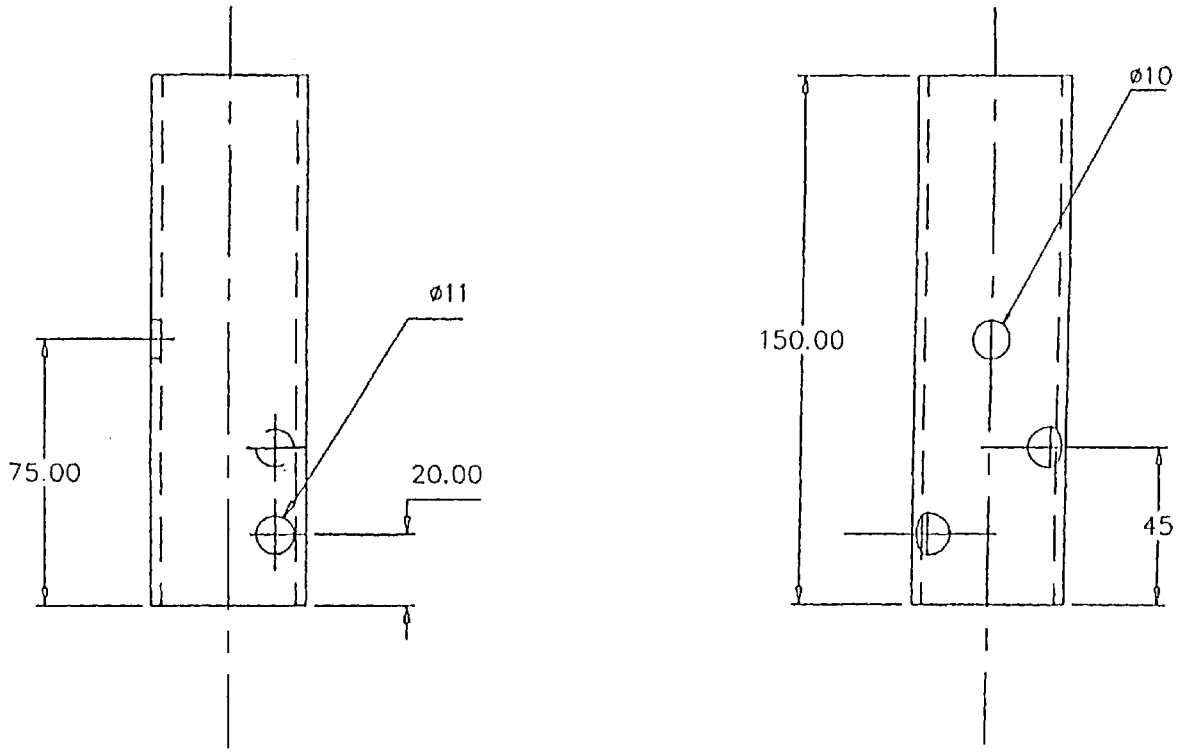


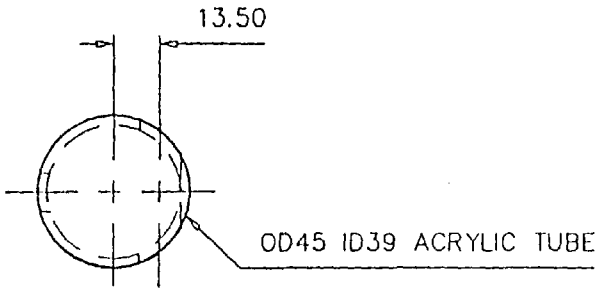
3rd ANGLE	DIMENSIONS IN MM		SCALE	2:1	POLYTECHNIC OF WALES
	TOLERANCES ± 0.5 UOS		DRAWN	C.FIELDEN	
			CHECKED		TITLE: RECYCLE PUMP CONNECTOR
	MATERIAL	ACRYLIC	APPROVED		DRG No. 1.5
	FINISH		DATE	11.03.92	



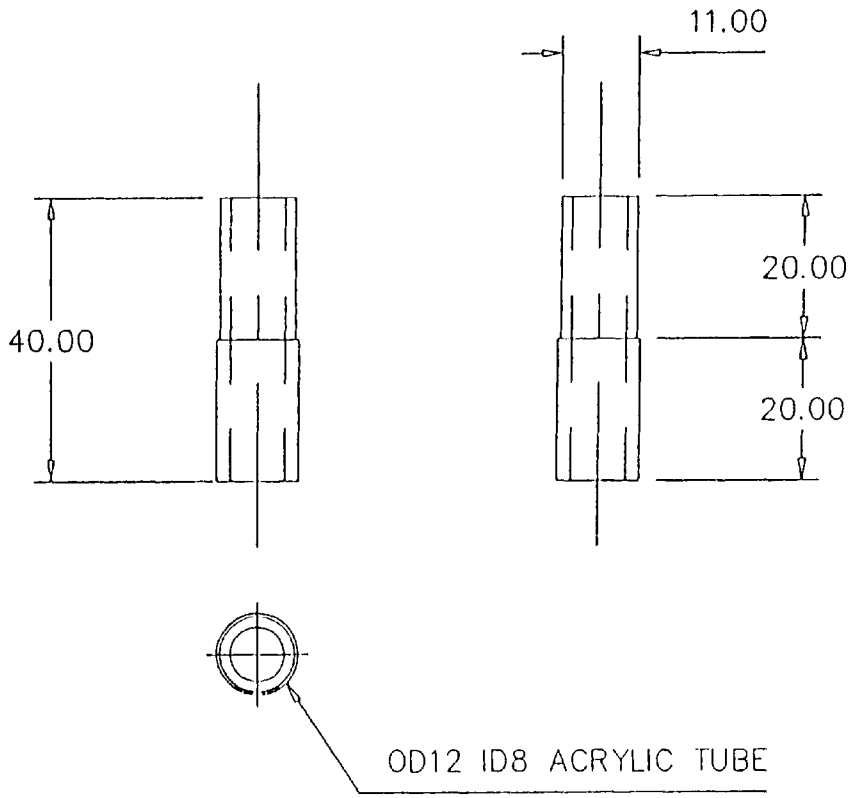


3rd ANGLE	DIMENSIONS IN MM		SCALE	1:2	POLYTECHNIC OF WALES
	TOLERANCES±0.5 UOS		DRAWN	C.FIELDEN	
			CHECKED		TITLE: ACID CHAMBER SUB ASSEMBLY
	MATERIAL	ACRYLIC	APPROVED		DRG No. 2.0
	FINISH		DATE	09.03.92	

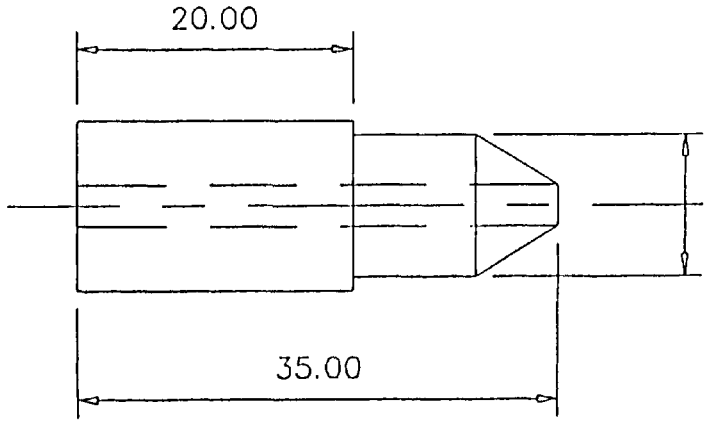


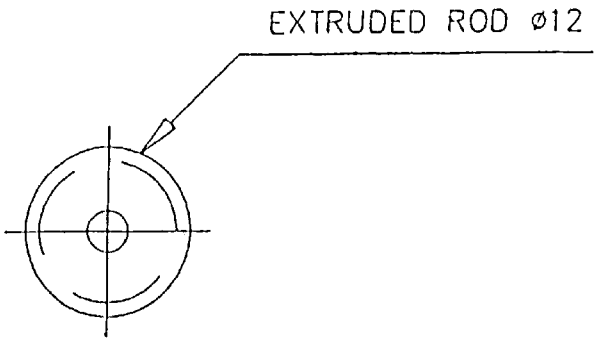


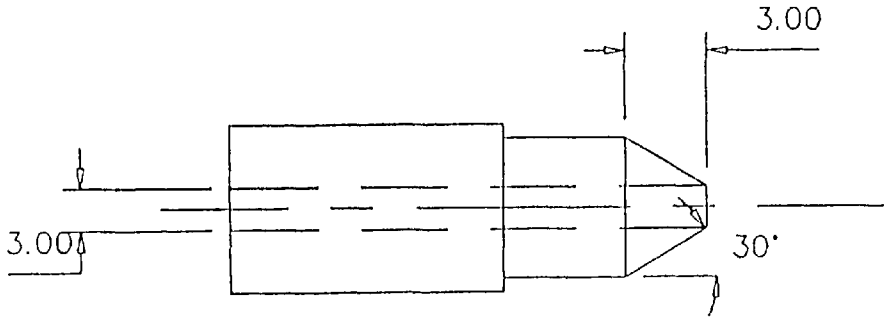
3rd ANGLE	DIMENSIONS IN MM		SCALE	1:2	POLYTECHNIC OF WALES
	TOLERANCES± 0.5 UOS		DRAWN	C.FIELDEN	
			CHECKED		TITLE: ACID CYLINDER WALL
	MATERIAL	ACRYLIC	APPROVED		DRG No. 2.1
	FINISH		DATE	13.03.92	



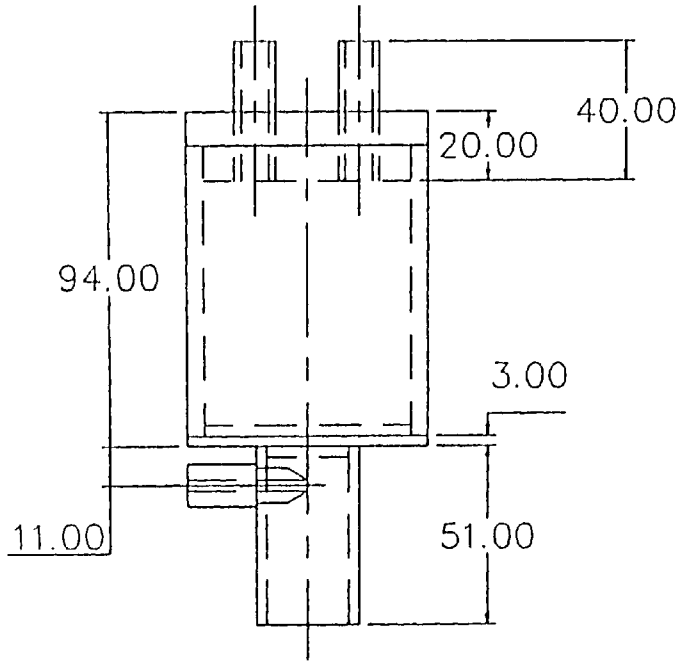
3rd ANGLE	DIMENSIONS IN MM		SCALE	1:1	POLYTECHNIC OF WALES	
	TOLERANCES±0.5 UOS		DRAWN	C.FIELDEN		
			CHECKED		TITLE	DRG No.
	MATERIAL	ACRYLIC	APPROVED		GAS LINE CONNECTOR	2.2
	FINISH		DATE	13.03.92		

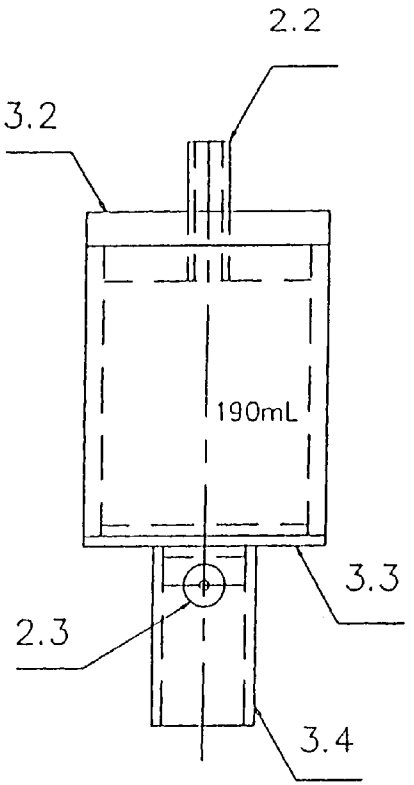


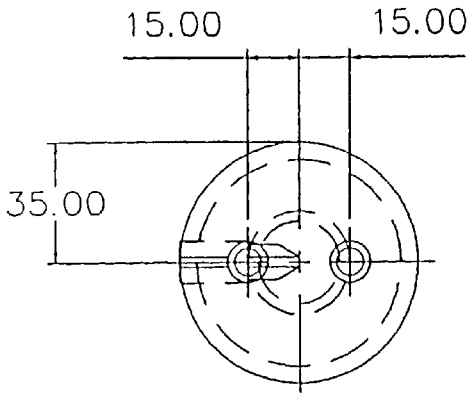




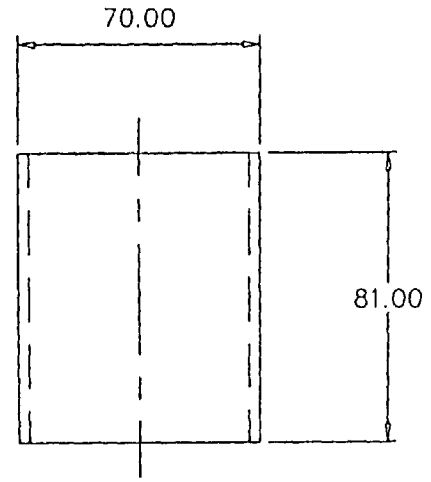
3rd ANGLE	DIMENSIONS IN MM		SCALE	2:1	POLYTECHNIC OF WALES
	TOLERANCES ± 0.5 UOS		DRAWN	C.FIELDEN	
			CHECKED		TITLE: EFFLUENT NOZZLE
	MATERIAL	ACRYLIC	APPROVED		ORG No. 2.3
	FINISH		DATE	13.03.92	

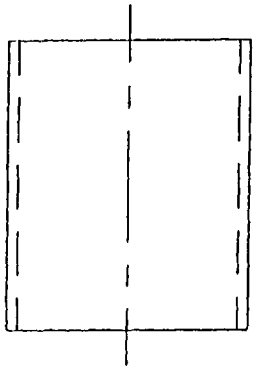


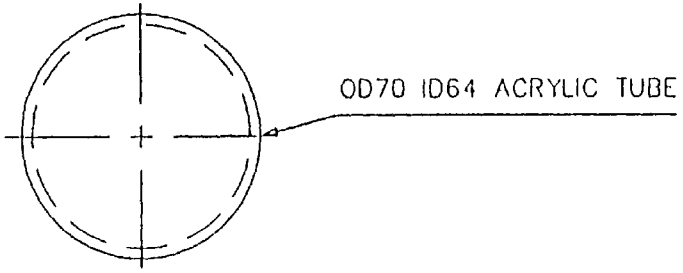




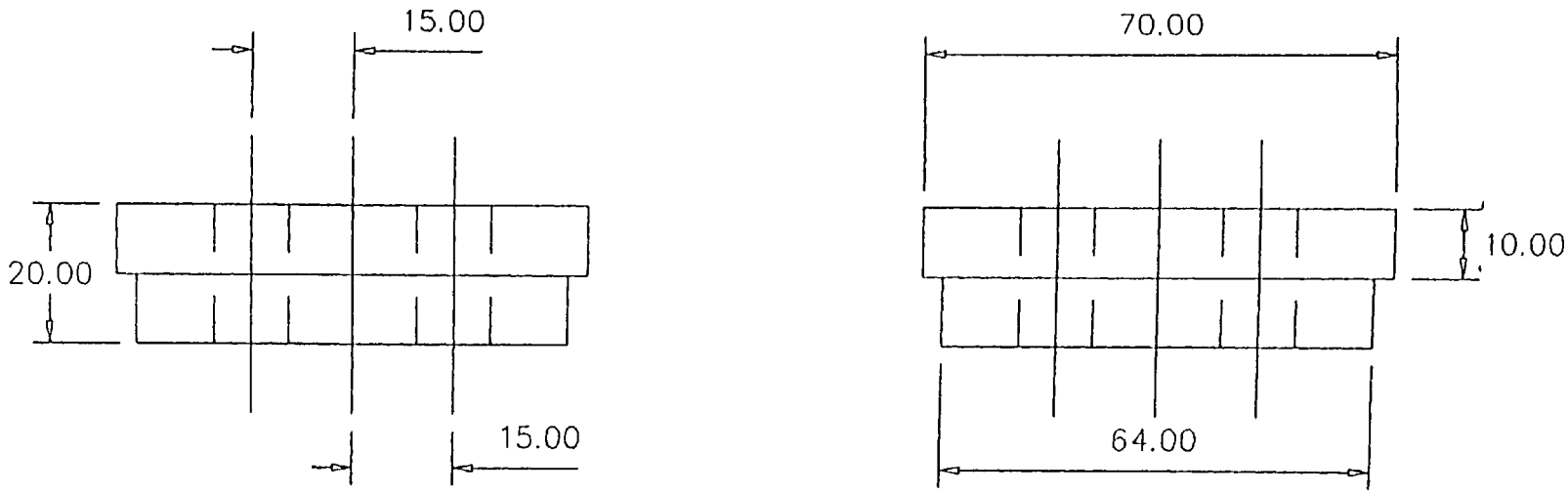
3rd ANGLE	DIMENSIONS IN MM		SCALE	1:2	POLYTECHNIC OF WALES
	TOLERANCES ±0.5 UOS		DRAWN	C.FIELDEN	
			CHECKED		TITLE: VOLUME CHAMBER SUB ASSEMBLY
	MATERIAL	ACRYLIC	APPROVED		DRG No. 3.0
	FINISH		DATE	08.03.92	

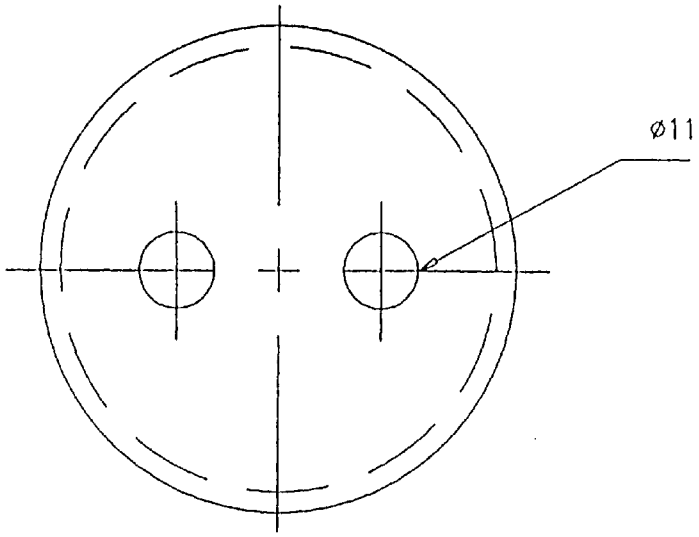




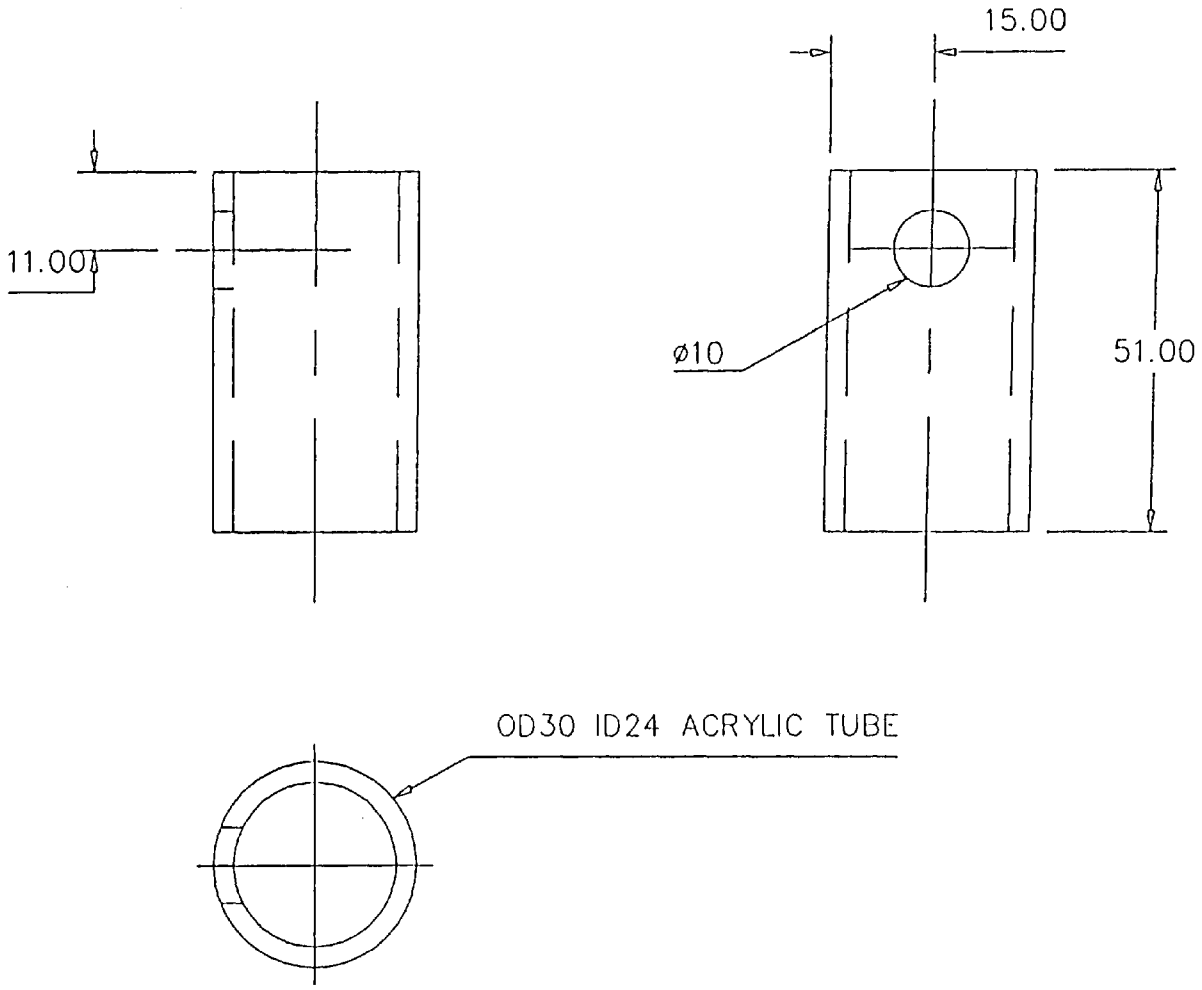


3rd ANGLE	DIMENSIONS IN MM		SCALE	1:2	POLYTECHNIC OF WALES
	TOLERANCES ±0.5 UOS		DRAWN	C.FIELDEN	
			CHECKED		TITLE: VOLUME CYLINDER WALL
	MATERIAL	ACRYLIC	APPROVED		DRG No. 3.1
	FINISH		DATE	13.03.92	



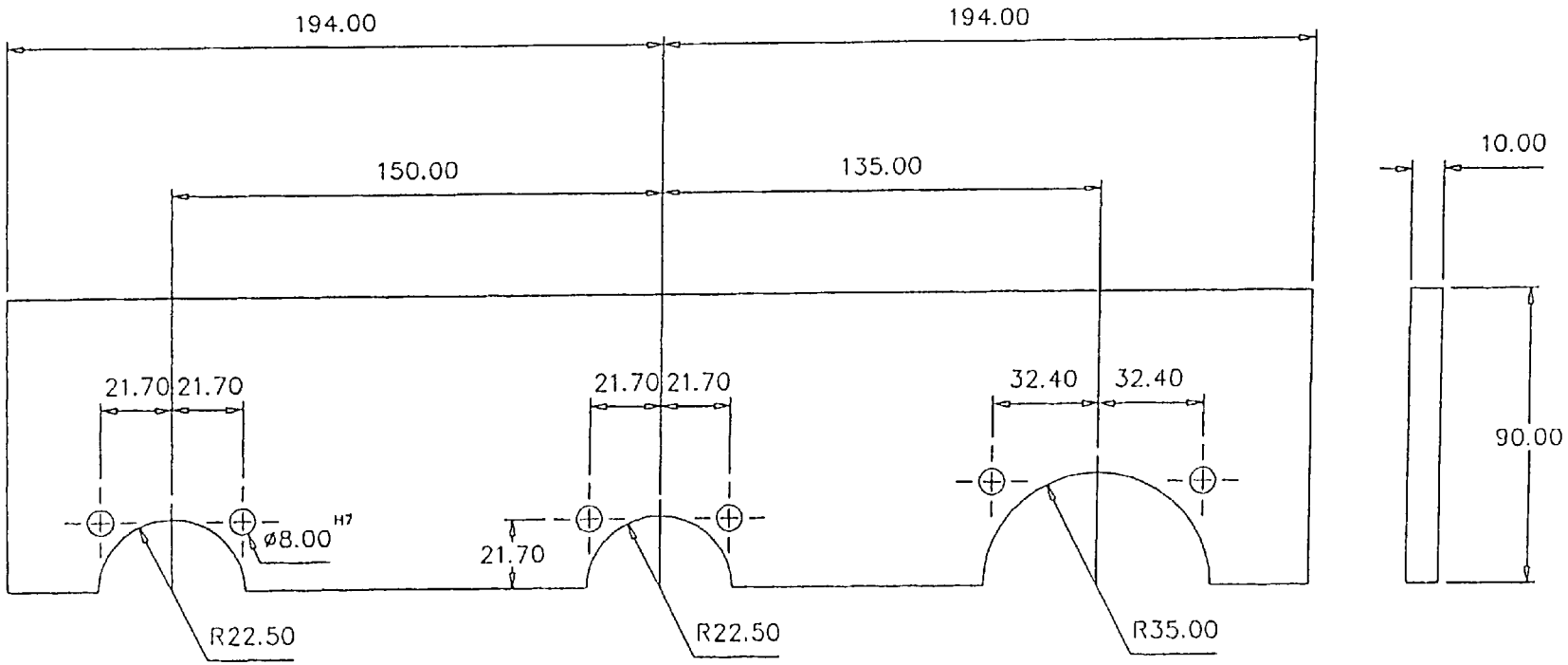


3rd ANGLE	DIMENSIONS IN MM		SCALE	1:1	POLYTECHNIC OF WALES
	TOLERANCES ± 0.5 UOS		DRAWN	C.FIELDEN	
			CHECKED		TITLE: ø70mm UPPER CAP
	MATERIAL	ACRYLIC	APPROVED		DRG No. 3.2
	FINISH		DATE	13.03.92	



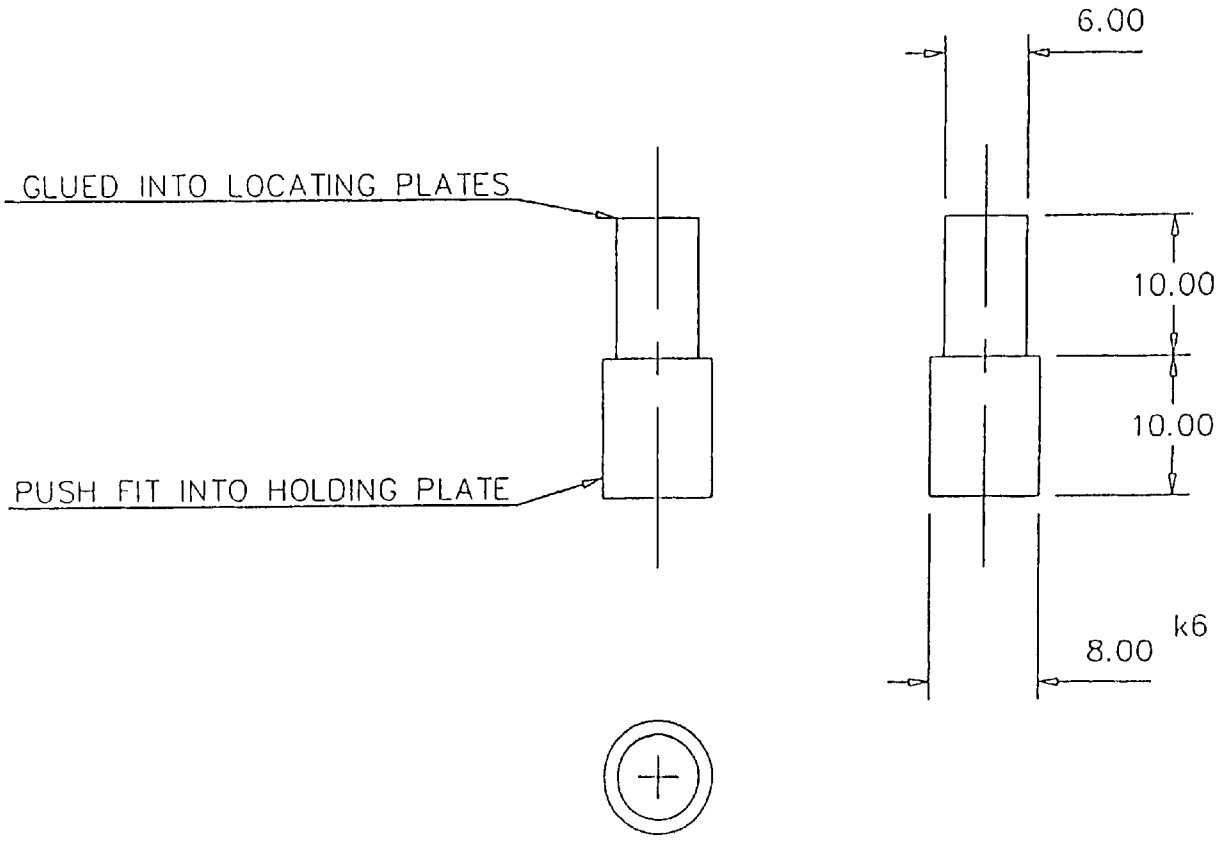
3rd ANGLE	DIMENSIONS IN MM		SCALE	1:1	POLYTECHNIC OF WALES
	TOLERANCES ± 0.5 UOS		DRAWN	C.FIELDEN	
			CHECKED		TITLE: EFFLUENT DISPOSAL PIPE
	MATERIAL	ACRYLIC	APPROVED		DRG No. 3.4
	FINISH		DATE	13.03.92	

H7 +0.15 0



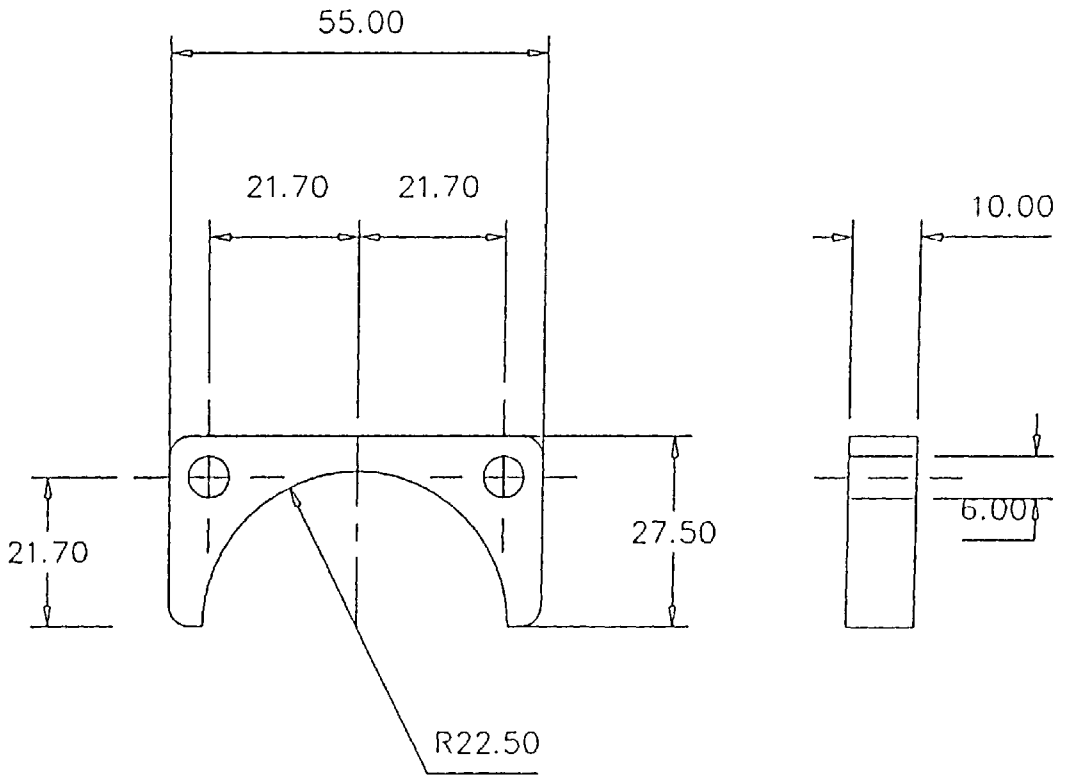
3rd ANGLE	DIMENSIONS IN MM		SCALE	1:2	POLYTECHNIC OF WALES
	TOLERANCES ± 0.5 UOS		DRAWN	C.FIELDEN	
			CHECKED		TITLE: HOLDING PLATE — DRG No. 4.0
	MATERIAL	ACRYLIC	APPROVED		
	FINISH		DATE	25.03.92	

k6 $^{+0.01}_{+0.001}$



3rd ANGLE	DIMENSIONS IN MM		SCALE	2:1	POLYTECHNIC OF WALES	
	TOLERANCES±0.5 UOS		DRAWN	C.FIELDEN		
			CHECKED		TITLE	DRG No.
	MATERIAL	ACRYLIC	APPROVED		CONNECTING PINS	4.1
	FINISH		DATE	25.03.92		

FILLET RADIUS 3mm



3rd ANGLE	DIMENSIONS IN MM		SCALE	1:1
	TOLERANCES ± 0.5 UOS		DRAWN	C.FIELDEN
			CHECKED	
	MATERIAL	ACRYLIC	APPROVED	
	FINISH		DATE	25.03.92

POLYTECHNIC OF WALES

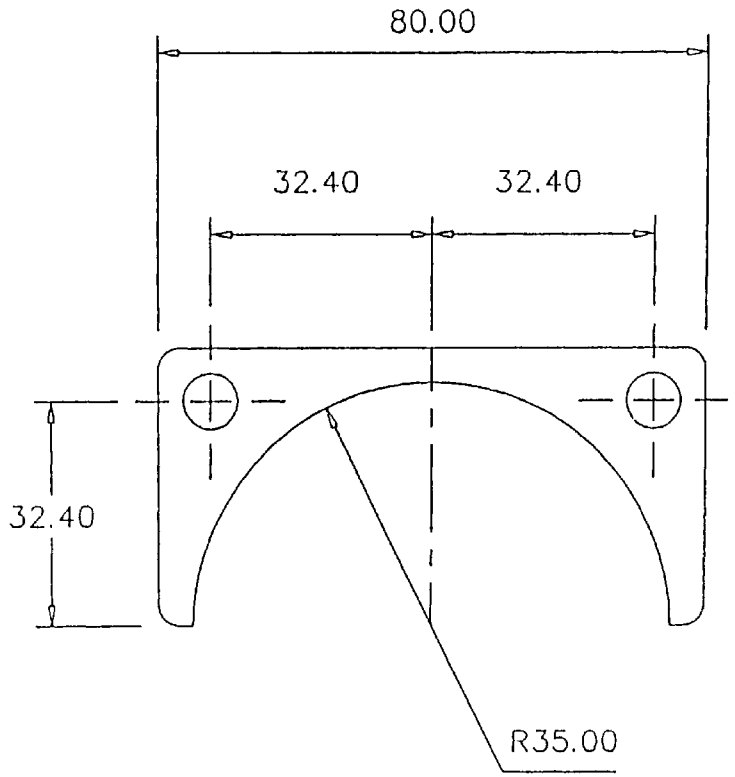
TITLE

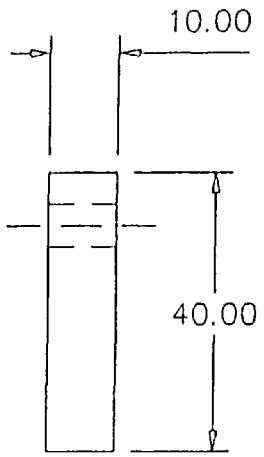
ø45mm LOCATING PLATE

DRG No.

5.0

FILLET RADIUS 3mm





3rd ANGLE	DIMENSIONS IN MM		SCALE	1:1	POLYTECHNIC OF WALES
	TOLERANCES±0.5 UOS		DRAWN	C.FIELDEN	
			CHECKED		TITLE / DRG No.
	MATERIAL	ACRYLIC	APPROVED		ø70mm LOCATING PLATE / 6.0
	FINISH		DATE	25.03.92	