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Advances in Gas Control Technology in the Brewery

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The use of nitrogen as a process gas, foam enhancer and flavour modifier has come to the fore over the last 10 years, with dissolved gas specifications becoming more stringent. Increasingly, marketing and consumer requirements for a targetted product identity or image have to be met, not only for taste but, perhaps equally as importantly for the consumer, presentation. This has resulted in dissolved gases playing a major role in the characteristics of a beer.

Furthermore, the gas content of the product on leaving the brewery (and at dispense) is more tightly controlled to avoid wastage due either to fobbing or to flat beer.

This review concentrates on practical methods for gas control in the brewery and how gas content can be measured.

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Gas in Brewing

Nitrogen has been in use in the brewery for over 50 years[1]. In the 1940's, Guinness used air to top-pressure their cask stout which resulted in some nitrogen dissolution, giving improvements in beer presentation. Subsequently in the 1950's and 60's pure nitrogen was used as a top-pressure gas.

Since this initial discovery the use of nitrogen in dispense has gained pace, through the early days of mixed gas dispense in the 1950's and 60's to its current use with lagers, ales and stouts, both for dispense in-trade and in small package for the take-home market. Nitrogen was also used in the brewery as a process gas and not only in the nitrogenation of stouts but for deoxygenation of dilution liquor from the mid-1960's onwards. The advantages of nitrogen over carbon dioxide as a process gas are discussed.

The highest profile development accompanying the use of nitrogen in small pack in recent years has been the so-called widget, which has been the subject of a Review in this series. The market share of widget products, which now embraces bottled as well as canned beer, has grown at a remarkable rate.

In 1994 widget beers accounted for 13% of the U.K. take home market[2], and with canned beer sales rising at 6-10% per year[3], the widgeted beer volume looks set to increase further. One particular brand saw a five-fold increase in sales after a widget was introduced[2].

Gas Properties

In the context of brewing, nitrogen is considered to be chemically inert, in contrast to oxygen and carbon dioxide. Oxygen is very reactive in beer[4], and many products of oxidation have serious implications for product quality. As a result it is now common place for breweries to specify a dissolved oxygen concentration of less than 50 ppb in their products.

Carbon dioxide is acidic (Figure 1), this gives beer its characteristic mouth tingle and bite. The three gases differ quite markedly in their solubility; at

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

Figure 1

Henry's Law

$$P_A = C_A \times H_A$$

C_A = concentration in moles of gas A, in the total moles of the solution
H_A = Henry's Law constant for gas A (temperature dependent)
P_A = partial pressure of gas A

Figure 2

atmospheric pressure and 0°C, carbon dioxide is 115 and 50 times more soluble than nitrogen and oxygen respectively. The Henry's constant for a particular gas increases with increasing temperature, which means that the solubility of all gases decreases with increasing temperature (Figure 2), though that of carbon dioxide does decrease more rapidly than the other two[5]. The solubility of a range of gases in water/alcohol mixtures is discussed in some depth by Cargill[6].

The insolubility of nitrogen lends itself to a number of processing applications[1,7]. Not only can it be used at high pressures without risk of over gassing, (in contrast to carbon dioxide), but also to deaerate dilution liquor for high-gravity brewing. Racking and packaging can be carried out under a nitrogen atmosphere to prevent ingress of air or, more specifically, oxygen, and to the same end can be used to blanket liquids in tanks with little dissolving into the liquid as would be the case were carbon dioxide used. In addition, nitrogen will not react with caustic used in in-place cleaning, in contrast to carbon dioxide.

Nitrogen is used to replace some carbon dioxide in beer to achieve a creamier, more stable foam head and in some cases specifically to make the flavour smoother and softer.

One of the most significant advantages of nitrogen over carbon dioxide is the unit volume cost, the former being less than half the price of the latter. Nitrogen is often considered to be safer than carbon dioxide; an increase of 0.2% in CO_2 and 2% in N_2 concentration over that in air represent the respective human tolerance.

Nitrogen also disperses more easily than carbon dioxide as it is lighter than air, whereas carbon dioxide collects at floor level.

In spite of these factors it is imperative that precautions are taken, as asphyxiation by nitrogen (oxygen depletion) comes without warning, whilst in the case of carbon dioxide breathing becomes laboured before loss of consciousness.

Gas Control

Historically, the simplest technique for ensuring saturation is to bubble the required gas through the base of a vessel whilst maintaining a top-pressure.

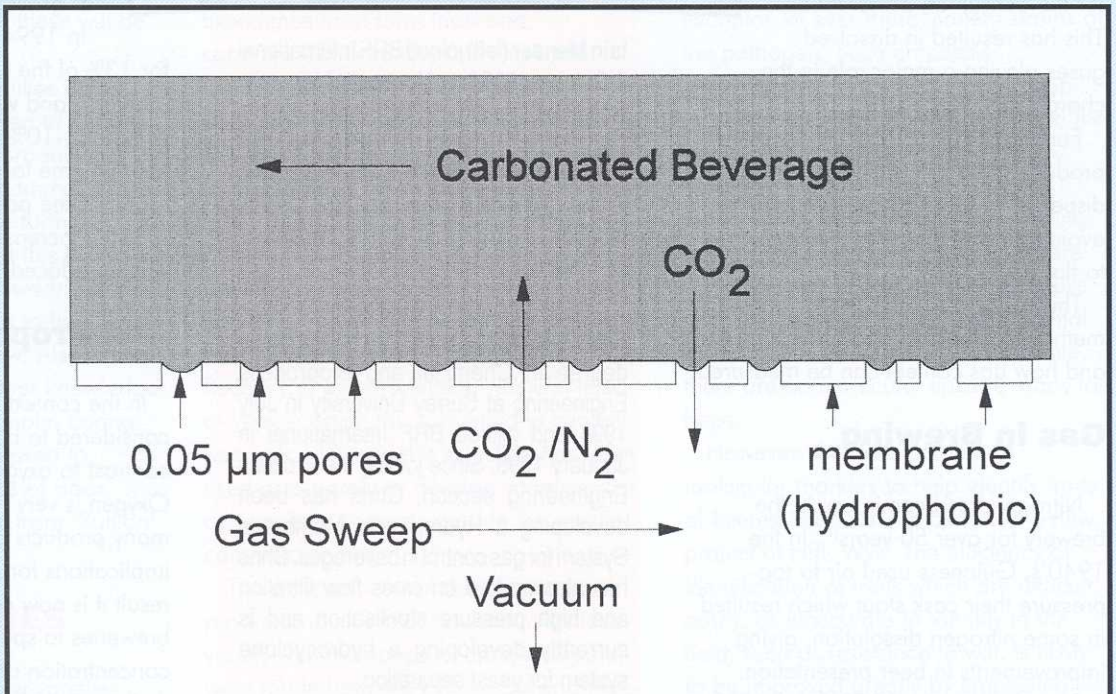

Figure 3: Hydrophobic membrane gas control system

However this has proven unsuitable for modern QA/QC requirements because of excessive foaming, gas usage and variable dissolved gas levels. The improved techniques currently available can be classified as either dispersive or non-dispersive.

Dispersive systems involve some form of gas injection, incorporating various methods to ensure complete dissolution and can be divided into single pass and recirculation systems. Non-dispersive systems involve the use of hydrophobic membranes to allow the direct contact of a gas and liquid without the formation of free gas in the beer[8].

Decarbonation is universally achieved in tank by a combination of release of top-pressure and purging from the base with nitrogen, thus stripping out excess carbon dioxide, sometimes known as gas washing[9].

	HEADMASTER	HOECHST
Structure	Hollow Fibre Molecular	Hollow Fibre Microporous
Surface area (m2)	2.8	1.4
Max. Pressure (bar)	6.9	4.1
Max. Op. Temp. (0C)	30	40
Fibre Material	Polysulphone	Polypropylene

Table 1:Comparison of Headmater and Hoechst membrane systems

This process also results in the dissolution of some nitrogen causing QA and QC problems with varying dissolved nitrogen levels and the risk of particle formation. However, it is now possible to decarbonate very simply with the development of membrane systems utilising a vacuum and/or nitrogen sweep on the gas side, i.e. without contacting the beer with nitrogen. Liquor deaeration techniques are numerous, boiling being the simplest, but packed columns, with nitrogen stripping, the most widespread[10].

However, membrane systems are becoming increasingly prevalent due to their efficiency, efficacy and compactness.

Non-dispersive systems: Hydrophobic membranes Theory

The basic principle of operation involves the provision of a hydrophobic barrier, in the form of a hollow fibre, between a gas and a liquid allowing gas to diffuse into or out of the liquid without the need for intimate mixing (Figure 3). Each membrane is constructed from a bundle of such fibres, with gas on the inside of the fibres and liquid on the outside. Each fibre has a high surface porosity, thus the membranes act as very high surface area contactors between gases and liquids. Using this membrane technology it is possible to exchange gases into or out of a liquid by adjusting the gas pressures or composition on one side of the membrane.

The overall gas transfer rate is dependent on gas phase resistance, membrane resistance and liquid phase resistance. The gas phase resistances are negligible due to high rates of gas diffusion. Membrane resistance is dependent upon the membrane material, but is generally low. Overall rate of mass transfer is essentially liquid phase controlled, with diffusion of the gas, into or out of the bulk liquid, being the rate limiting step. The rate at which gases transfer into or out of solution is determined by the partial pressure difference between the liquid and gas phases. Therefore, for gas addition duties the partial pressure of a gas will be higher in the gas phase giving a positive driving force. For gas removal duties the partial pressure in the gas phase must be lower.

Membranes

Two membranes are currently available: (a) from Permea Inc./ Headmaster Ltd. incorporating Pulsar™ modules, and (b) from Hoechst Celanese/Realm, both of which operate via the mechanism described above, but which have significant mechanistic differences. In the case of the Pulsar™ modules, the effective barrier between gas and liquid is provided physically by a semi-permeable skin of polysulphone and by the hydrophobicity of the Hoechst fibres. A comparison of the two membranes is given in Table 1.

The Hoechst membrane fibres have a microporous structure providing discrete sites for gas and liquid to contact directly. This means that the membrane resistance to mass transfer is negligible and liquid phase diffusion becomes the rate limiting step. Trials completed by BRFI with the Hoechst Celanese membrane show that it is typically capable of achieving dissolved nitrogen concentrations of 50 ppm and dissolved carbon dioxide concentrations of 9 g/l. Using a mixed gas ratio of 50:50 (% by vol.) it is possible to increase the dissolved nitrogen concentrations by 40 ppm and dissolved carbon dioxide concentrations by 1 g/l simultaneously. By increasing the ratio of nitrogen in the mixture to 90:10 (% by vol.) it is possible to increase dissolved nitrogen concentrations to 55 ppm and simultaneously reduce carbon dioxide concentrations by 1.5 g/l. Using a vacuum it is possible to reduce dissolved carbon dioxide concentrations by up to 4 g/l depending on the initial concentration. Finally, dissolved oxygen concentrations in water have been reduced to 40 ppb with a combination of vacuum and nitrogen sweep on the gas side of the membrane.

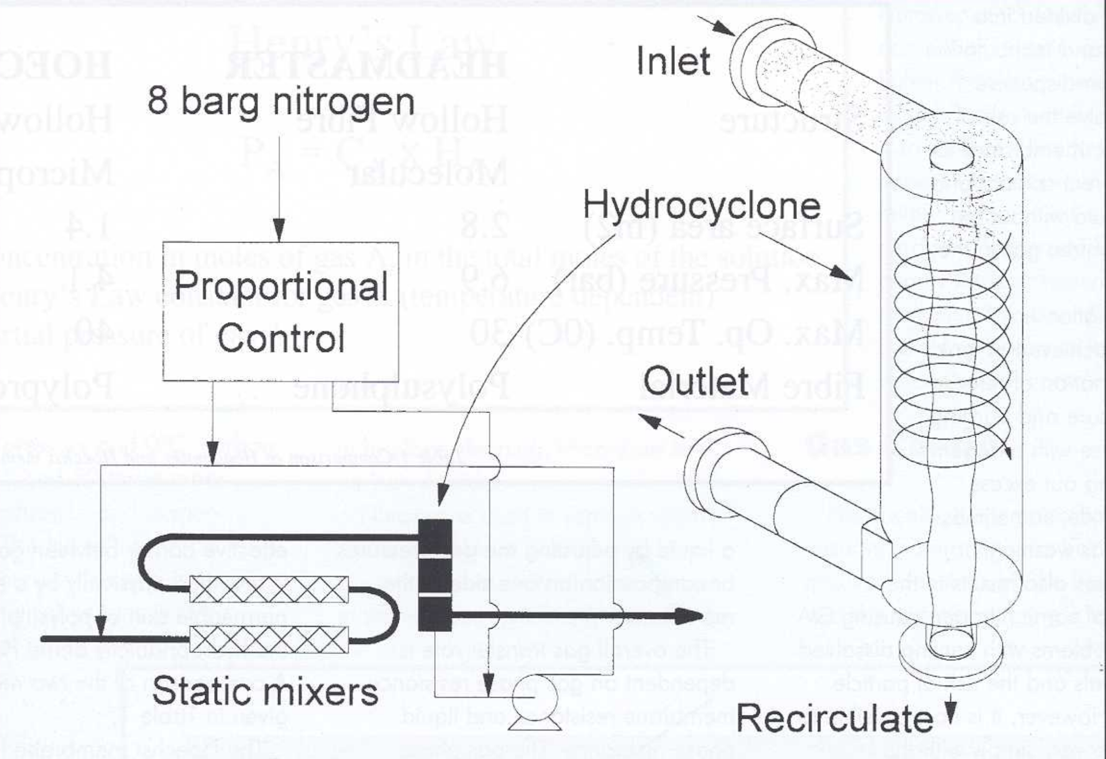

Figure 4: Tuchenhagen gas injection system

The Pulsar™ modules have an asymmetric graded structure that is permeable to gases at a molecular level[11]. This means that the membrane resistance to mass transfer is a factor and the overall mass transfer rate will be a combination of liquid phase resistance and membrane resistance. However membrane resistance is small compared to the liquid phase resistance although the outer skin has a selectivity for permeation of different gases with carbon dioxide passing faster than nitrogen. We have no performance data from the Headmaster system but it has been successfully tested in several commercial breweries.

Dispersive systems: Direct injection Theory

Dispersive systems employ a very simple concept relying on injecting gas into a liquid stream, ensuring that the gas bubbles injected are as small as possible thereby increasing the surface area for mass transfer.

The simplest dispersive system is "in tank", as mentioned earlier. However more sophisticated methods are now available which can be split into single pass and recirculation systems. Single pass systems combine injection with a combination of three commonly used alternatives: (i) turbulence promoters, i.e. static mixers\accelerators, (ii) high pressure, and (iii) long pipe runs/holding tubes, all of which aid dissolution. The only recirculation system available utilizes a hydrocyclone post-injection to separate undissolved gas from the liquid stream, recirculating the fob/liquid removed by the hydrocyclone to ensure the correct dissolved gas levels are obtained.

Systems

Alpha Laval have developed a single pass system in conjunction with Carlberg-Tetley specifically to nitrogenate beer. It was designed to be placed post-pasteuriser, utilising the high pressures generated from this process and incorporates mixers/accelerators along with high pressure to ensure dissolution. In-line nitrogen detection before and after injection, integrated with beer-stream flow measurement and nitrogen mass-flow control, complete the control loop[12].

APV have developed a single pass system initially for carbonation, but it can be modified for nitrogenation. The system involves spraying the beer stream into an infusion chamber (containing an atmosphere of the gas), in order to increase greatly the surface area for mass transfer. The infusion chamber is split into four sections and beer is sprayed into each section in reduced quantities, until the fully gassed product is discharged from the base of the chamber. Gas bubbles that have not dissolved are finally broken up by means of a blender downstream . Gas content is adjusted by measuring gas content after the infusion chamber and controlling the gas feed valve accordingly[13].

Canongate Technology have developed a single pass system designed to be located post-pasteuriser incorporating both nitrogen and carbon dioxide injection. The gas addition is via a Whitteman injector, which is positioned some distance from the pasteuriser to allow time for gas dissolution, and is mass flow controlled[14].

The Fullpack system was developed by the GEA group of which Tuchenhagen are a member and has been superceded by the Tuchenhagen system described below. It is a single pass system involving high pressure and a trim chiller to encourage mixing prior to a constant pressure vessel. Nitrogen addition is adjusted to beer flowrate which is controlled by the level in a constant pressure vessel[15].

Tuchenhagen have developed a recirculation system incorporating a hydrocyclone to separate undissolved gas from the clear beer stream, feeding it back into the system prior to the hydrocyclone (Figure 4). The control system will not allow gas to be injected above the saturation level for the temperature and pressure of the system, ensuring that the outlet beer stream contains the required level of dissolved gas[16].

Applications

The most important gas transfer duties for the brewing industry are carbonation, nitrogenation, decarbonation and deaeration. Individual brewers have their own priorities, but with the current interest in cream ales, nitrogenation is of specific interest for ale producers. Some nitrogenated premium lagers are also beginning to appear on the market. The principal industrial use of membrane systems is process water deaeration, with the main users being the electronics industry which has a requirement for deaerated ultrapure water. Of greater relevance to the brewing industry is the fact that the soft drinks industry currently uses this technique to carbonate dilution liquor[17]. Membrane systems have the potential for use on all of the above duties and are currently used in commercial breweries for nitrogenation and liquor deaeration[18]. Direct injection systems are widely used in commercial breweries for nitrogenation and carbonation along with carbonation of dilution liquor in the soft drinks industry.

Advantages/ disadvantages

The major advantage of a membrane system is that it covers all gas transfer requirements including decarbonation and even simultaneous nitrogenation and decarbonation. They are non-foaming, efficient, compact, controllable, accurate and easily tailored to suit individual needs. The one possible disadvantage is that of membrane life, which can only be predicted at present but which will be a function of both the frequency of use and aggression of cleaning solutions. It is worth noting that membranes have been used continuously for a number of years to deaerate water with no process problems.

The main advantages of dispersive systems are their current widespread availability and acceptance, their disadvantage being the risk of formation of haze resulting from the production of insoluble particulates as a result of foaming and micro-bubbles during nitrogenation. The other comparative disadvantage is their limitation to gas addition duties only.

Dalton's Law

$$P_T = P_X + P_Y + P_Z \ldots$$

P_T = total pressure

$P_{X,Y}$ *etc* = partial pressures for individual gases X, Y *etc*

Figure 5

Gas Measurement

An integral part of gas control in the brewery is the ability to determine the gas content of the liquid medium. The techniques to achieve this can be divided into two main categories: those measuring in- or on-line and those off-line. The former methods involve a device that is inserted into the main body of liquid or a by-pass, be it in a beer line or bright beer tank. The latter category requires a sample being taken from the process vessel or small package for analysis by a separate instrument.

We have restricted the review to in- and on-line gas detectors, in particular those that can be, and often are, used with the gas control systems discussed earlier. Buckee has briefly reviewed the broader field of classical and current methods of determining dissolved nitrogen concentration[19].

Permeable Membrane Detectors On/In-line

An example of an in-line dissolved carbon dioxide analyzer is the Canongate Embra Carbocheck[20]. The fundamental features of the probe include an evacuated chamber into which the dissolved gases diffuse across a gas-permeable silicone rubber membrane. The theory behind this meter is that a dissolved gas will diffuse into the chamber until a pressure is reached that is equal to the partial pressure of that gas in solution. The pressure is then determined by a pressure transducer and the temperature of the beer recorded by a resistance thermometer upstream of the analyzer. A microprocessor then calculates the concentration of carbon dioxide in solution. The natural selectivity of the silicone rubber diaphragm for the permeability of carbon dioxide coupled with the much lower levels of oxygen and nitrogen in traditional beers, means that the meter is effectively a carbon dioxide selective probe.

However, it would be inappropriate to measure the carbon dioxide in a highly nitrogenated beer using this probe. This is because a higher pressure would be recorded in the chamber due to the combined partial pressures of nitrogen and carbon dioxide, to give a misleadingly high concentration (Figure 5).

The carbon dioxide can diffuse in both directions through the membrane allowing the chamber and liquid to be in a dynamic equilibrium at all times. The chamber can be evacuated to prevent build up of unwanted gases in the cavity which would lead to erroneous readings. The precision of the instrument has been shown to be ± 0.08 vol. in production trials with a number of different beers, when tested in comparison to a Corning 965 instrument. The instrument can also alert an operator to a sudden ingress of air (oxygen) into the system. The probe has been used as a process management facility in a direct injection carbonation unit (Figure 6).

Orbisphere Laboratories have developed two types of in-line gas analyzer probe[21,22]. One is the carbon dioxide and/or nitrogen detector that relies on similar permeable membrane principles to those described above. The probe construction is shown in Figure 7. The receiving volume is flushed with a purge gas for a set time, after which the sample gas diffuses through the membrane due to a partial pressure gradient from the sample liquid to the receiving volume. The thermal conductivity of the gases in the chamber are then detected by a sensor which outputs a signal that is used together with the diffusion rate and a temperature correction to give the final gas concentration. The purge and detection cycle gives an updated display approximately every 20 seconds. The accuracy is ± 2 and 4% for the carbon dioxide and nitrogen probes respectively, across their full working temperature range of 0-50°C.

The second Orbisphere Laboratories probe uses a different method for the detection of dissolved oxygen for in-line and small package applications[22]. The probe comprises two noble metal electrodes that are immersed in an electrolyte solution.

The dissolved gases once again diffuse through a gas-permeable membrane where the oxygen is selectively reduced, producing an electrical current that is proportional to the oxygen concentration. Depending on the instrument used for a particular application 1 ppb to 400 ppm can be detected at up to 70°C.

Oxygen concentration can also be determined by polarography using a Mettler Toledo Ingold probe[23]. The probe is essentially an electrochemical cell, with an anode and a cathode in electrolyte, separated from the sample by a permeable membrane. The probe is contacted with the sample, either in process (vessel or line) or from small package. Oxygen diffuses through the membrane and is reduced at the cathode by a voltage specific to oxygen. A portable analyzer is also available which uses the same principle.

This chemical process produces a small electrical signal that is amplified and adjusted according to a calibration to give the dissolved oxygen concentration. The probe responds in approximately 1 minute (at 25°C) and is stable to better than 2% of the displayed value per week.

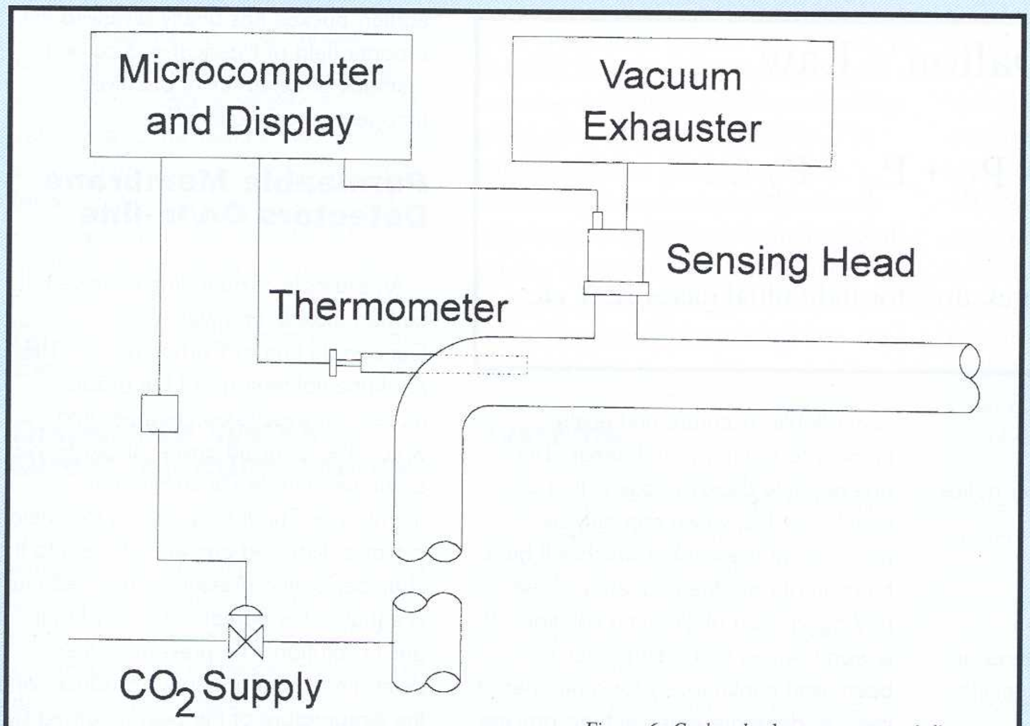

Figure 6: Carbo check process control diagram

Mass

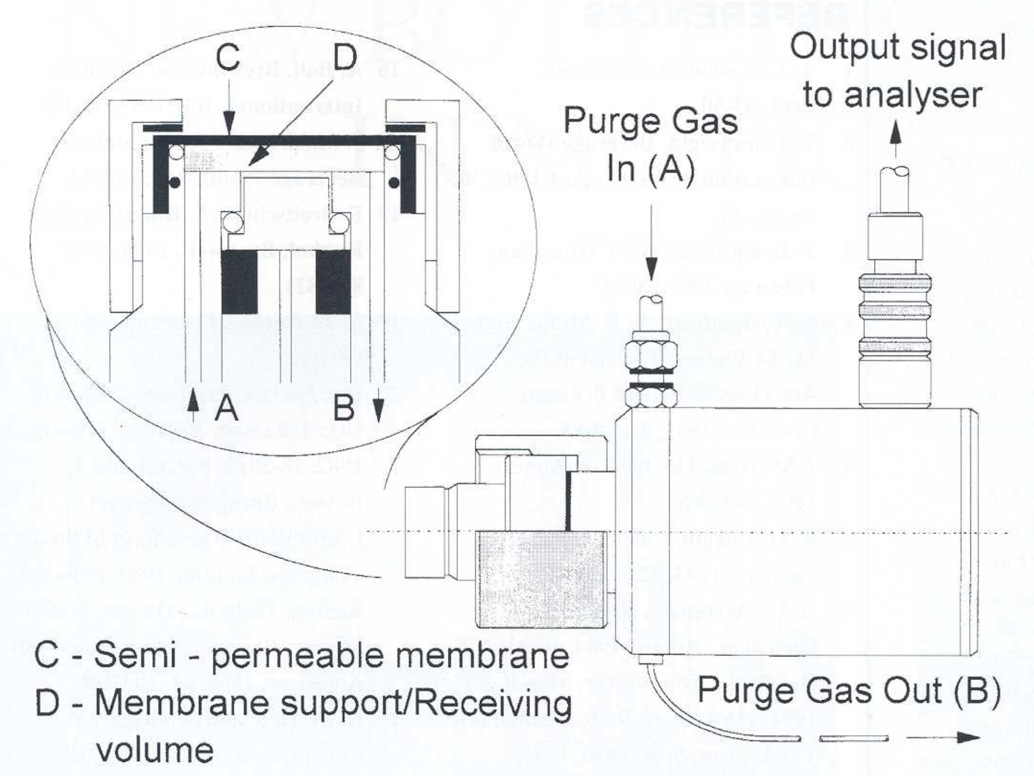

Figure 7: Diagram of an Orbisphere Laboratories N_2/CO_2 probe

ppm, but an operating precision of ± 1 ppm is quoted.

Wisk and Siebert have developed a gas chromatography method for analysis of oxygen and nitrogen concentration for small pack beer[26]. The gas in the headspace and bulk beer were equilibrated (by horizontal agitation) and the small pack pressure measured with a pressure transducer. The headspace volume was determined and the gases analyzed by gas chromatography. These were all the data required to determine the oxygen and nitrogen content of the small package. While the analysis only takes 5 minutes per sample, the equilibration after agitation (and subsequent foam collapse) can require up to several hours. Chromatograph response signals for multiple injections from the same package gave good statistical reproducibility for oxygen and nitrogen.

Knight has reported on the development of a process chromatographic technique for the determination of nitrogen, oxygen and carbon dioxide (and ethanol) content of beer[27]. A bypass is taken from the beer line, from which a sample loop is diverted. A small sample volume is passed onto a combination of three columns (with helium) by a sophisticated valve control system giving enhanced flexibility and sensitivity in determining nitrogen and oxygen in one operating mode, and carbon dioxide and ethanol in another.

An analysis cycle takes 3 minutes for

Spectrometry

A hybrid of the on/in-line Carbocheck has recently been developed using the same principle of diffusion of gases through a permeable silicone rubber membrane. The sensor head used in the carbon dioxide probe is modified and connected to a quadropole mass spectrometer, that separates the gases according to their respective masses[24]. The combined partial pressures of dissolved gases are determined by the sensor head pressure transducer and the ratio of these gases is established by the mass spectrometer. These data (including the relative permeability rates) allow the microprocessor to determine the actual concentrations. Repeatability was shown to be excellent, the mass spectrometer drifting by less than 4% per month.

Gas Chromatography

The essence of gas chromatography is passing a sample mixture down a long, small bore tube (column) that is filled with a stationary phase. The sample mixture is carried in a flow of carrier gas, typically helium, and is separated according to each constituent's ability to pass through the stationary phase. A detector is positioned at the end of the column which can determine the relative proportions of the sample components.

Cope et al. have developed an on-line nitrogen measurement system that samples from a process line or storage tank, strips the beer of gas and analyzes it by gas chromatography[25]. The beer is sampled from the bulk liquid, from which a specified volume is fed into a stripping cell to remove the gas from the beer. This gas is passed into a gas chromatograph with a carrier gas flow of helium. This analysis cycle takes 6 minutes. The concentration of dissolved nitrogen is determined by the chromatograph, with reproducibility of ± 0.48 ppm over the range of 4-16 the separation of nitrogen and oxygen though there is adequate separation for this to be reduced to approximately 1 minute.

A more recent reference to on-line measurement of dissolved oxygen and nitrogen combines traditional gas chromatography separation and analysis methods with a novel sample preparation system[28]. Bright beer is diverted from a beer stream or keg into a mass transfer cell which consists of a small bore silicone rubber tube wound round a stainless steel support tube.

The beer is run over this silicone tube and back into the main beer stream. A small proportion of the dissolved gas diffuses into the rubber tube and is taken up by a flow of carrier gas which then enters a gas chromatograph. Carbon dioxide is removed pre-analysis, then nitrogen and oxygen are separated and the proportions of each determined by a thermal conductivity detector. Dissolved nitrogen can be measured to an accuracy of ± 1 ppm.

Conclusions

In recent years the need for tighter control of dissolved gases in brewing has demanded increasingly more sophisticated techniques, for example the development of hydrophobic membranes and hydrocyclone technology. More accurate detection instrumentation has also been developed to determine oxygen levels in order to help safeguard against its deleterious effects. At present, there are only a few intruments available for the determination of dissolved nitrogen compared to those for carbon dioxide.

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