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IMPROVED METHOD FOR CO_2 MEASUREMENTS

Thermal conductivity sensor for selective determination

CO_2 (carbon dioxide) is a critical ingredient in beer, soft drinks and other beverages. The traditional method of determining carbonation by measuring the total pressure overestimates the amount of CO_2 in the drink due to the presence of other gases, resulting in consumers experiencing a flat drink. An improved method of measuring CO_2 uses thermal conductivity technology to measure the "true" amount of CO_2 in beverages independent of other gases. Hach Ultra has developed and patented a TC (thermal conductivity) sensor with no moving parts or drift.

The European Brewery Convention tested the determination of CO_2 in package beer by thermal conductivity and included the approved method in Analytica-EBC. A traceable and trustworthy liquid phase validation and calibration standard was also developed in order to ensure improved confidence in CO_2 results. The measurement of CO_2 using a thermal conductivity sensor is a more accurate method for measuring carbonation to ensure final product quality and product consistency.

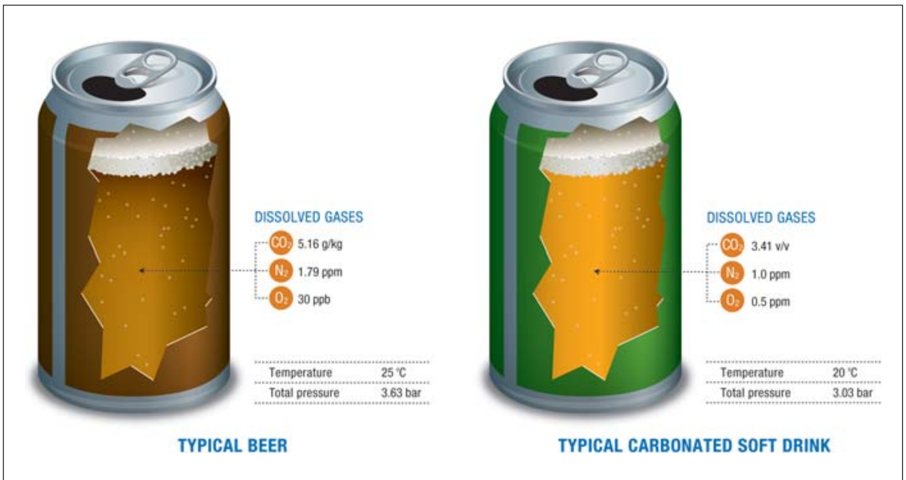

Figure 1: Dissolved gases found in a typical can of beer and carbonated soft drink.

CO_2 yields the head to beer, bite to soft drinks, fizz to sparkling mineral water and the cork pop and bubbles to champagne and sparkling wine.

In beer, CO2 not only contributes to perceived fullness or body and enhances foaming potential; it also acts as a flavour enhancer. In soft drinks, CO2 makes the drink more refreshing through its stimulation of the mouth's mucous membranes adding a sensation that the soft drink is colder than it actually is. CO2 also brings out the aroma since the bubbles drag with them the aromatic components.

The consequences of inaccurate CO2 measurements are high as consumers might find the beverage too unpredictable to purchase again. The traditional method for determining CO2 in beverages is subject to influences from other gases, such as oxygen and nitrogen which are found in air. As the amount of oxygen changes throughout the process due to many reasons, its effect on carbonation is undetected by the traditional method. The result is an overestimation of the amount of CO2 dissolved in the beverage.

An improved method for accurately measuring CO_2 in beer, soft drinks and other carbonated beverages is required in order to eliminate errors associated with the influence of other gases. Ideally, the system should also have a low total cost of ownership, low maintenance requirements with an easy to perform validation system.

CO_2 measurement points in the beverage industry include fermentation, CO_2 recovery, CO_2 addition, tank venting, storage tanks, at the filler and in final packages. The specifications for CO_2 and other dissolved gases vary from industry to industry and product to product. Figure 1 shows typical gas concentrations in beer and carbonated soft drinks.

Methods to determine CO_2

The most common measurement technique for determining CO_2 concentration in beverages is to measure the total pressure and temperature of a sample. This method, known as the P/T method, involves measuring the total pressure and temperature and then calculating the CO_2 concentration in the liquid.

This method to determine the amount of CO_2 is risky because it assumes that the only gas which ist present in the beverage is CO_2, which is not the case. Air, in varying amounts, is always present.

Figure 2: High precision CO_2 calibration kit.

The total pressure is actually due to the sum of all the partial pressures, as shown below.

$$p_{total} \neq p_{CO_2}$$

$$p_{total} = p_{CO_2} + p_{O_2} + p_{N_2} + p_{H_2O}$$

The amount of air changes depending on several factors, including source water temperature, incomplete de-aeration and air contamination during production, filtering, and filling. Air doesn't taste or feel like CO_2. Most CO_2 tables take into consideration the amount of water vapor, shown here as PH_2O. However, these tables do not consider the amount of air, partial pressure of N_2 and O_2. Therefore the partial pressure of air contributes to the error in total pressure measurements. Below is an example of how this error might not be visible using the P/T method in a typical soft drink production plant:

Packages with low CO_2 and high air (high dissolved O_2 and N_2) look identical to packages with target CO_2 and low air when using a P/T method; therefore the P/T method is not the best for ensuring CO_2 quality and final product consistency since the amount of air in the process changes from day to day.

Interference from air can be virtually eliminated using a volume expansion method. This method, known as the MVE method, involves a system to fill a measurement chamber to measure the total pressure and temperature. The chamber is expanded and the total pressure and temperature are measured again. The amount of CO_2 is then calculated. This method, however, uses a complex and delicate system that introduces the risk of mechanical failure and leaks, thereby increasing the total cost of ownership. Additionally, the CO_2 result is still a calculation and is based on total pressure measurements.

An improved method to determine the actual CO_2 in a beverage is to use thermal conductivity. This method, known as TC, is ideal because specific gases can be measured with no influence from any other gases. Each gas has a different thermal conductivity.

Thermal Conductivity:

Heat (in calories) transferred for one second in this gas, between two 1 cm² surfaces placed 1 cm apart, when the temperature difference between these two surfaces is 1°C.

The TC sensor's measuring technique is a combination of a gas diffusion membrane and a gas thermal conductivity detector. The small volume enclosed between the diffusion membrane and the thermal conductivity detector is periodically flushed with a purge gas. After each purge, the gas to be measured diffuses from the sample through the membrane, changing the thermal conductivity of the gas surrounding the detector. It is the rate of change of the thermal conductivity that allows the specific concentration of the gas to be calculated.

Benefits of using TC technology

In order to be able to measure the actual amount of CO_2 in beverages independent of other gases Hach Ultra has developed and patented a TC sensor with no moving parts or drift. Both these features contribute to increased uptime by minimizing the need for maintenance. One of the biggest

Table 1: P/T method vs. TC method for CO_2 measurement

3.03 bar, 20°C	CO_2 (using P/T)	CO_2 (using TC)	Dissolved O_2	Dissolved N_2
Package # 1	3.5 V/V	3.41 V/V	0.5 ppm	1.0 ppm
Package # 2	3.5 V/V	3.17 V/V	3.0 ppm	6.0 ppm

benefits of using TC technology is the ability to calibrate the sensor in the liquid phase. This directly reflects actual working conditions to improve accuracy. Hach Ultra has designed a traceable and trustworthy liquid phase validation and calibration standard with defined CO_2 content of +/– 0.5 % CO_2.

The calibration solution is prepared in a precision calibration bottle. A known and precise amount of sodium bicarbonate powder is combined with a ready-made dilute citric acid solution to provide defined, accurate carbon dioxide content in the liquid. In less than 3 minutes the solution is ready for use, saving time and simplifying the calibration process. Preparation of the reference solution requires no handling of aggressive chemicals ensuring the whole process is safe for laboratory personnel and operators. Regular validation ensures confidence in product quality.

Figure 5: Portable CO_2 analyser using TC sensor.

Another benefit of the TC technology is its testing by the EBC (European Brewing Convention) showing better repeatability and reproducibility over P/T methods.

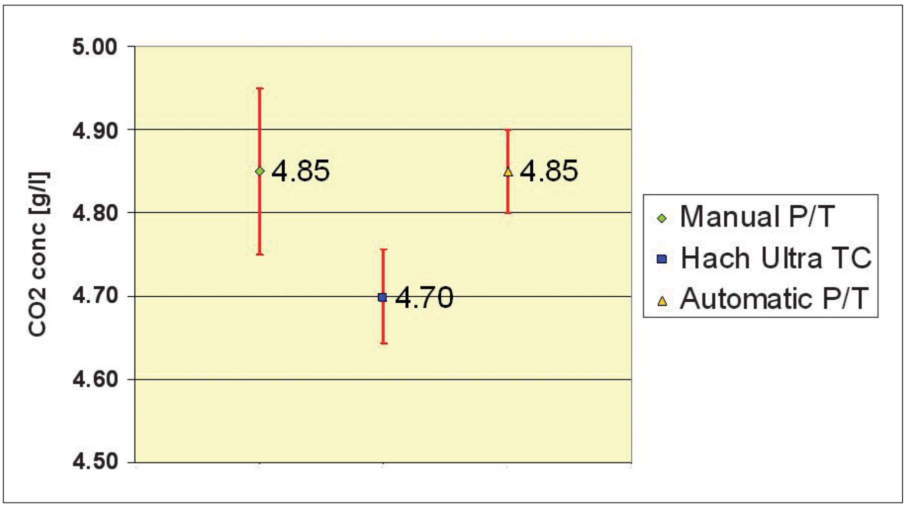

Figure 3: Repeatability r95 of CO_2 analysers.

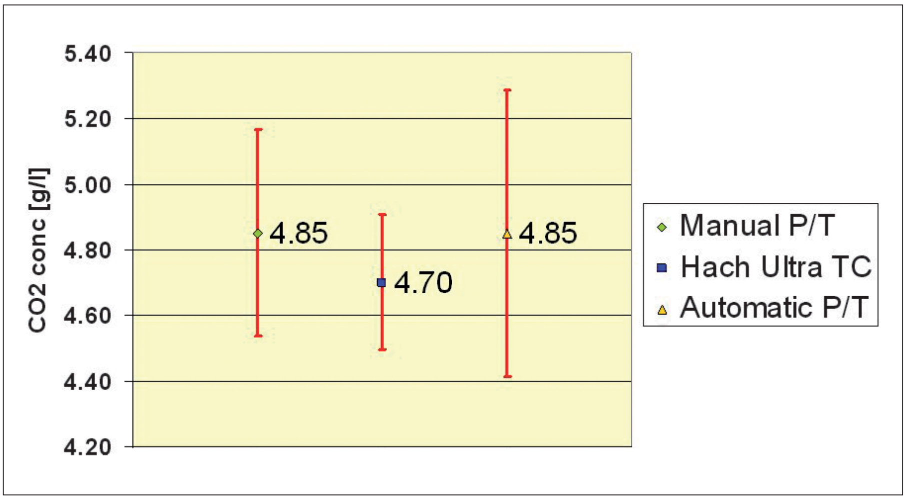

Figure 4: Reproducibility R95 of CO_2 analysers.

In 2004, the determination of CO_2 in package beer by thermal conductivity was collaboratively tested by the Analysis Committee of the EBC according to ISO Standard 5725 in order to determine its suitability for publication in Analytica-EBC. The Hach Ultra Orbisphere Portable CO_2 Analyser was tested in order to determine its repeatability (r_{95}) and reproducibility (R_{95}) values.

Twenty-three laboratories participated in the test. The organisation of the collaborative trial and the statistical treatment of the data were performed according to the International Standard ISO 5725-2. In the trial the method was tested with three beers having a range of CO_2 values between 4,8 and 7,0 g/l. Two bottles of each beer sample were sent in duplicate to each laboratory.

Repeatability (r_{95}) was found to be independent on the mean value and was 0,08 g/l over the range 4,7 to 6,9 g/l. Reproducibility (R_{95}) was found to be dependent on the mean and was 0,54 mg/l over the range of CO_2 tested. The conclusion of the test recommended the inclusion of the Hach Ultra Orbisphere Portable CO_2 Analyser using the thermal conductivity method in Analytica-EBC.

The manufacturer offers TC sensors for measuring true CO_2 in process, laboratory and portable applications. Some of the applications include bright beer tank CO_2 measurements using a portable analyser, CSD (carbonated soft drink) quality control using a process Brix/CO_2 system and low level CO_2 content in wine using a non-destructive lab-based CO_2 analyzer. The TC CO_2 sensors offer a number of benefits:

- Measurement of CO_2 is unaffected by other gases, improving accuracy and confirming customer product quality of measurements in still wines, low carbonated and very fizzy drinks

- Optimum total cost of ownership, with low maintenance, no moving parts in the measurement cycle, small sample volume requirements and less product waste, fast response time and a robust design for long life

- Calibration is traceable using the High Precision Calibration Kit, confirming accuracy of results and offering simple and rapid validation between calibrations
- One sensor type covers the broadest range of CO_2 measurement, in-lab, at-line, or in-line providing a comprehensive, cost effective package for CO_2 measurement throughout the production process

Figure 6: Process CO_2/Brix analyser for soft drinks using TC sensor.

- Process analysers can be calibrated/validated by comparing results using the same sensor technology to a calibrated/validated portable instrument using the High Precision Calibration Kit

Conclusion

Measuring the total pressure and temperature of a carbonated beverage is a quick method for determining CO_2 content; however the error in using this method is that it results in an overestimation of CO_2 due to the influence of air. The amount of air changes depending on several factors, including source water temperature, incomplete de-aeration and air contamination during production, filtering, and filling.

An improved method for measuring CO_2 in beer, soft drinks and other carbonated beverages is required in order to confirm final product quality. Thermal conductivity is a measurement method that is unaffected by other gases, improving accuracy of CO_2 results and ensuring final product quality and product consistency.

Hach Ultra offers TC sensors with no moving parts or drift for measuring the actual CO_2 in process, laboratory and portable applications. The EBC approved method uses a patented TC sensor than can be calibrated in the liquid phase, which directly reflects actual working conditions to improve accuracy. Hach Ultra provides a more accurate method for measuring carbonation with a complete solution to ensure final product quality and consistency. □

Figure 7: Process multi-channel CO_2 analyser using TC sensor .

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Product Manager for CO_2 analysers started with Hach Ultra in 2004 after seven years of Project Management experience in an international packaging company.

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Beverage Market Manager. He started with Hach Ultra in 1998 as a Regional Sales Manager in the USA. In 2000 he was promoted to Key Account Manager for Soft Drinks and Bottled Water in the Americas. Since 2005 he has been the Beverage Market Manager and currently works at Hach Ultra's global headquarters in Geneva, Switzerland.