Attenuated Total Reflection Spectroscopy method for measuring dissolved CO_2 concentration in Beer

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Abstract

Dissolved carbon dioxide is a molecule that vibrates and has a mid infrared absorption band in the electromagnetic spectrum at 4.2 microns. Using Beer-Lambert's Law, precise concentration measurements can be determined using reflective spectroscopy; specifically Attenuated Total Reflection (ATR).

This article will describe inline infrared carbonation monitoring equipment for use on processing lines, fillers, tanks and the Q.A. laboratory.

This article will report results of studies showing flaws in the current Henry's Law method for measuring concentration in beer.

Introduction

The current methods for measuring carbonation in beer use a modified version of Henry's Law, converting pressure and temperature measurements to concentration. This method uses a single constant in Henry's Law equation for density and a single constant for solubility, making the method outdated and inaccurate. It is an indirect method which does not measure the concentration of any individual gas but the composite result of all dissolved gases. In recent years, changes in the beer industry have exacerbated these flaws. Density was introduced as a constant in the Henry's Law equation because temperature pressure instruments do not measure density at all. Historically, this method evolved with the assumption that all beer had comparable density. Light beers, ales and low carbohydrate beers have made this assumption incorrect. In fact, many beers now have a lower specific gravity than water. The use of nitrogen in many beers to give a richer head makes the measurement of pressure inaccurate, both because of the lack of differentiation and because of the differences in the solubility coefficients. Beer with a high alcohol content also has a different density. Additionally, the introduction of high speed bottling lines cause pressure spikes unrelated to carbonation, creating false / apparent CO_2 concentration spikes.

Infrared Analysis using ATR

Most organic compounds have infrared signatures. An infrared signature is defined by characteristic absorption bands on an ideal Planks blackbody curve. Dissolved CO_2 has a characteristic absorption band at 4.27 um. See Figure 1.0.

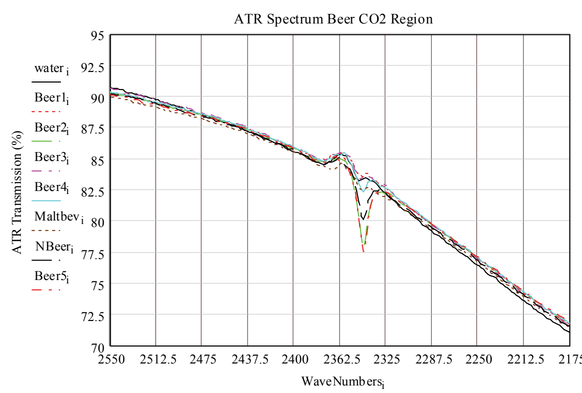

Figure 1.0

Most infrared laboratory measurements are done using a transmittance method. Infrared radiation (heat) is focused through a cell consisting of two infrared transmitting windows such as silicon in a known path length. In the case of liquids, this path length needs to be spaced extremely close (approximately 25 um or .001") because of the strong absorption of water. This technique is impractical for inline measurements because the short path cell would get clogged. A second technique is Attenuated Total Reflection (ATR). Early attempts with inline ATR required the sample be drawn into a "slip stream" to do the measurement (a small amount of beer was taken off line and discarded / reintroduced). This could create sanitary issues. Moreover, the optical bench needed to be thermally stabilized to prevent condensation and temperature drift. Paul Wilks, the founder of General Analysis Corporation and a VitalSensors founder, is noted as the inventor of this method.

Since 2004, VitalSensors Technologies' advancements in hermetic sealing techniques and miniaturization of optics, have made a true inline infrared sensor manufacturable. The VS-3000 is a direct inline measurement unit, with no sidestream, no temperature stabilization hardware and no pumps.

To determine a methods validity, one should look at the fundamental equations on which a method is based. For determining $CO_{2\,c}$ concentration, the temperature-pressure method is based on Henry's Law. In "A Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry" (pp.3), written by Rolf Sanders of the Max-Planck Institute, the relevant equation for volatility (inverse of solubility) is given. Simply put, the solubility of a gas in a liquid is proportional to the density of the liquid divided by the molar mixing ratio (or the ratio of the gas to the liquid based on mass).

$$k_{H,INV}=p_g/x_a=Q_{liq}/(M_{liq} x k_H)$$

Where: $K_{H,INV}$**=volatility**

P_g**=partial pressure gas phase**

X_a**=molar mixing ratio**

Q_{liq}**=Density of liquid**

M_{liq}**=Molar mass of liquid**

k_H**= solubility of gas in liquid**

Equation 1.0

Equation 1.0 raises several issues for the pressure-temperature method. This method implicitly assumes that Specific Gravity is a constant. The Solubility of Carbon Dioxide in the Beer Pressure-Temperature Relationships chart, printed from Zahm and Nagel's website, www.zahmnagel.com, reports that the pressure temperature measurements conversion tables are based on a specific gravity of 1.015 for beer. The table is derived from a methods analysis taken from "Methods of Analysis" American Society of Brewing Chemists 5th Edition-1949. The pressure-temperature method uses a constant for alcohol density in Henry's Law because alcohol concentration is not measured. At one filler line installation, the specific gravity of beer ranged from 1.007 to .998 where the .998 specific gravity was a low carbohydrate beer and the alcohol content ranged from effectively zero to 4 percent. Using the pressure-temperature method for CO_2 produced results with an error almost an order of magnitude above the stated error of the instrument being used.

Zahm and Nagle's beer and water solubility charts can be used to estimate the error with the current method. The data from these charts at 33F and 12PSI give volume to volume measurements of 3.0 for water and 2.84 for beer respectively. Since some of the new low carbohydrate beers have a specific gravity lower than water the problem is exacerbated. Moreover, the solubility of carbon dioxide in alcohol is different then that of water; so beers with either a low or high alcohol content also create a significant error for the temperature-pressure method. The solubility equation states that the solubility of a gas in a liquid is proportional to the density of the liquid divided by the molar mixing ratio or the ratio of the gas to the liquid based on the mass. This means that the alcohol concentration density is proportional to the amount of alcohol in the beer. Ethyl alcohol has a density of .789g/ml versus 1g/ml for water. This should have been taken into account in formulating the Henry's Law method.

Next, the infrared method will be described and then results will be compared. Infrared analysis uses Beer-Lambert's Law. Concentration is directly proportional to the amount of infrared energy absorbed by the sample when the optical path is held constant.

$$A=abc= \log (I_o/I)$$

Where: A= Absorbance

I= radiation Intensity beer CO_2

I_0**= radiation Intensity beer no** CO_2

a= Absorption co-efficient

b= Sample pathlength

c= Concentration of sample

Equation 2.0

The ATR sampling method makes use of the fact that, when a beam of radiation moving within an infrared transparent medium is reflected internally from a surface, a portion of the energy in the beam projects slightly beyond the reflecting surface depending on the index of refraction match between the sample (beer) and the crystal. The intensity of radiation is attenuated additively by the number of reflections. See Figure 2.0.

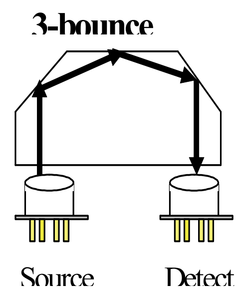

Figure 2.0

In Equation 2.0, two samples are being measured one for I_{0}, the other for I. The sample being measured for I_0 is beer with no CO_2. This can be achieved by forcing CO_2 out of solution. In a closed vessel the temperature of the liquid is raised to its boiling point while a vacuum is pulled. Alternatively, molecules with no infrared absorption, such as nitrogen, can be used to purge CO_2 from the liquid. The sample being measured for I is beer with CO_2 at a known pressure and temperature. For calibration purposes water is used as the sample because Henry's Law coefficients for water are well documented and specific gravity is defined as density relative to water. The index of refraction of beer and water are similar and can be ignored for this measurement technique. Using water will allow the concentration to be "corrected" to historical numbers by using specific gravity and alcohol content numbers.

Comparing pressure temperature to Infrared

VitalSensors collected inline data at a large brewery to compare the pressure-temperature method to infrared analysis.

Vital Sensors TECHNOLOGIES

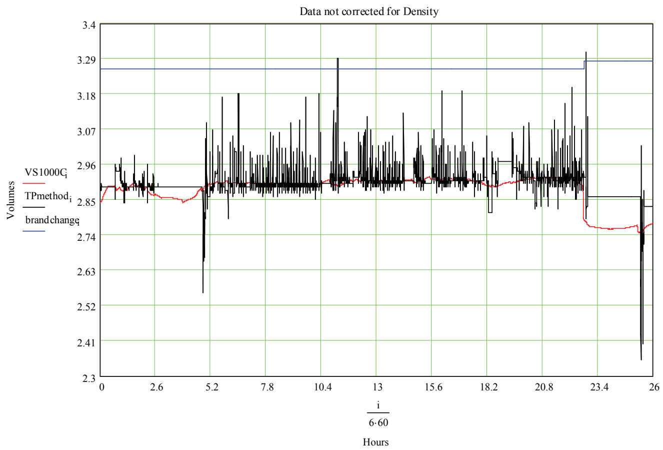

Figure 3.0

In Figure 3.0, the red line is VitalSensors' VS-3000 IR sensor and the black line is an inline pressure-temperature instrument at a Brewery. The blue line represents changes in brand. The spikes on the black line represent "noise" due to pressure surges in the line. The straight black lines represent areas where the pressure-temperature sensor shuts off due to no flow. The infrared measurement shown in red.

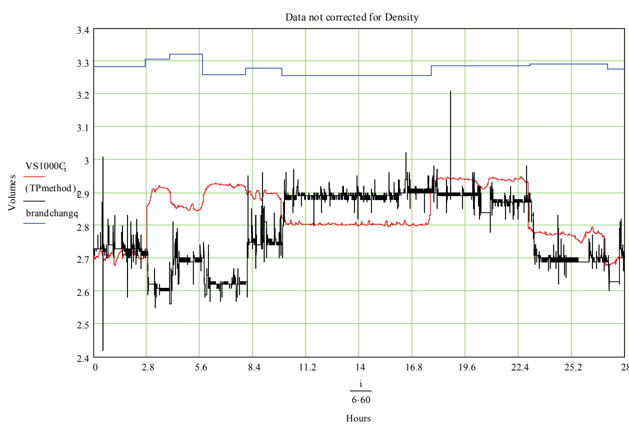

Figure 4.0

Figure 4.0 shows pressure-temperature in black and infrared in red. Notice the sizable differences between the measurements due to changes in brand noted in blue. We also measured specific gravity and alcohol content during this run using a density beer analyzer to prove the prior assumptions that Henry's Law method is outdated and the method using Beer-Lambert's Law would be more correct and require fewer variables. Using MathCAD, a real time correction was done to the pressure temperature measurement using a version of Henry's Law equation with product density and alcohol content density as variables instead of constants. The following graph shows this data as compared to the VitalSensors data.

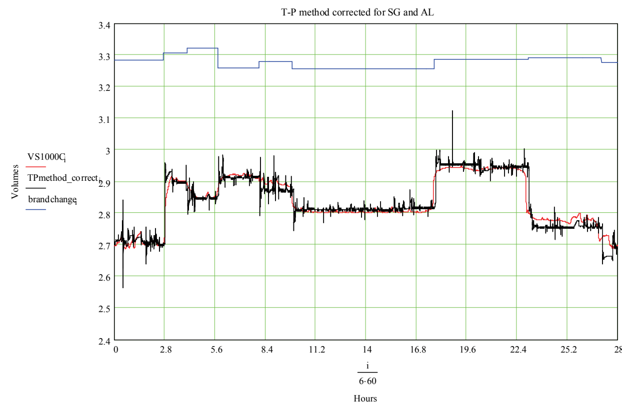

Figure 5.0

Figure 5.0 shows that, once the pressure-temperature method uses density variables for both the density of the beer and the percentage of alcohol, the data becomes identical to the infrared method.

In addition to the need for flow, the in-line pressure-temperature instrument cannot be run during clean in place (CIP) because of the temperatures involved. Figure 6.0 graphs in red the VS-3000 during a clean in place with the inline pressure-temperature instrument shutting off and going to zero. NaOH has a density of 2.1g/ml, double that of water, so both the elevated temperature of the CIP fluid and the difference in solubility of CO_2 allow the VS-3000 to be an effective CIP detector and may be used to measure the CIP flushing out of the system. Even if a pressure -temperature type instrument was able to operate under these conditions, it would not be able to detect the changes in CO2 related to the NaOH, because it does not account for density.

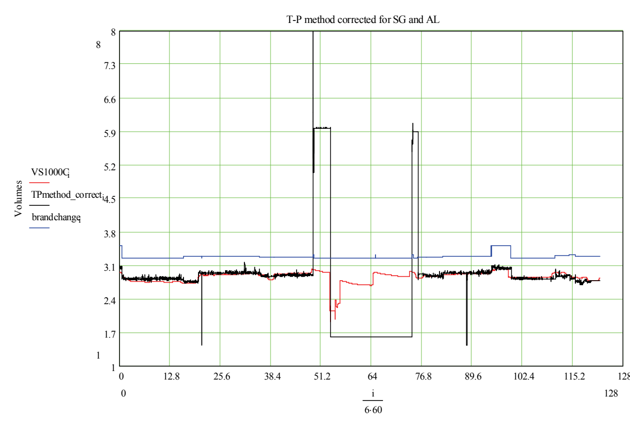

Figure 6.0

An important benefit of the VS-3000 sensor is lower maintenance costs. The instrument has a sapphire optic and is fully solid state (no moving parts). In-line pressure-temperature instruments need to have their diaphragms replaced and some instruments use moving parts to look at the sample stream to help prevent pressure surges in the measurement. IR can be used to measure any parameter with vibrational molecules, including carbohydrates, ethanol, dissolved sugars and organic acids.

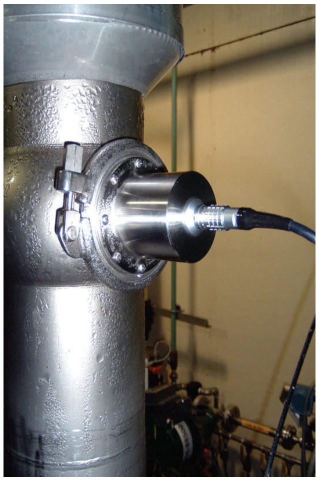

Figure 7.0

Figure 7.0 depicts the VS-3000 installed in a brewery and shows its rugged and compact design. Another benefit of this direct measurement is that it can be implemented on filler lines because the measurement is not affected by ambient temperature. The Varivent fitting allows the VS-3000's optics to be directly in the stream of the product.

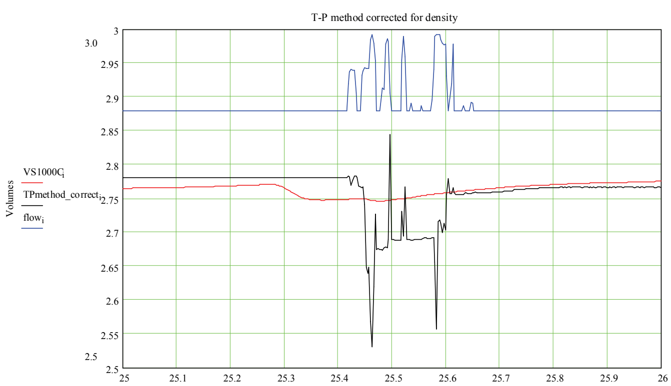

Figure 8.0

Figure 8.0 shows data from a pressure-temperature sensor and the VS-3000 over a period of intermittent flow. The red graph is the VS-3000 and the black is the pressure-temperature, while the blue graph represents flow. The flow induced pressure spikes give a concentration error of 2.4 to 3 volumes or an error of .6 volumes which the VS-3000 sensor does not exhibit.

Conclusions:

Pressure-temperature methods for measuring carbonation inline use an outdated approximation of Henry's Law that employs constants that do not take into account changes in product density. This effectively treats ales, lagers, light beers, high alcohol content beers and low carbohydrate beers as if they had the same specific gravity. An additional error results from using a constant density for ethanol concentration. Vibrational spectroscopy using mid infrared ATR sensors eliminates errors due to density because the sensor is using Beer-Lamberts' Law for concentration. Beer-Lambert's Law relies solely on the absorption of infrared radiation due to the presence of CO_2 molecules in solution. This eliminates a potential error that can be as high as .5 volume/volume, a factor of ten higher then the typical instrument specification.

The VS-3000 sensor offered by VitalSensors Technologies is a solid state device that requires no maintenance, lowering the cost of ownership, and is the only device that measures dissolved ingredients directly without using a slipstream. Other applications for the VS-3000 are measuring dissolved concentrations of CO_2 ethanol, sugars and organic acids in wine, alcopops, soft drinks, juices and other liquids.

References:

The In-Line Determination of Carbon Dioxide in Beer by Infrared Analysis, Paul A Wilks, MBAA Technical Quarterly, Vol. 25, No. 4 pp. 113-116

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Volumes of CO2 Gas Dissolved in Water, Zahm & Nagle Co.

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