

Attenuated Total Reflection Spectroscopy method for measuring dissolved CO₂ 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 temperature and pressure 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uses a single constant in Henry’s Law equation for density and a single constant for solubility, making the method outdated and inaccurate.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 temperature and 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 apparent 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 black-body curve. Dissolved CO₂ has a characteristic absorption band at 4.27 um. See Figure 1.0.

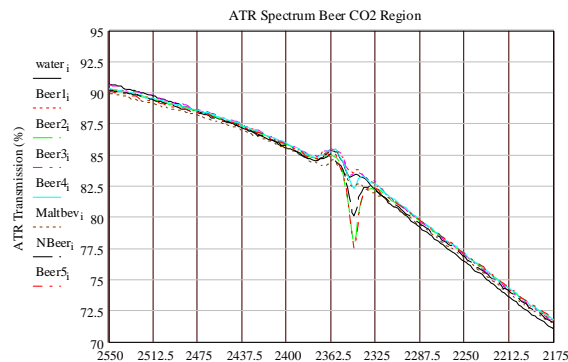


Figure 1.0

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). To date the problem with this technique for inline measurements has been that to get a stable measurement the sample had to be in a “slip stream” i.e., a small amount of beer is taken off line and either discarded or reintroduced to the line, to do the measurement. This may create sanitary issues. 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 technique.

Recently, with advancements in hermetic sealing techniques and miniaturization of optics, it has become practical to design a true inline infrared sensor.

To determine a methods validity, one should look at the fundamental equations on which a method is based on. The temperature pressure method is based on Henry's Law. On page three of the paper "A Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry", 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 current 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 current method uses a constant for alcohol density in Henry's Law because alcohol concentration is not measured. At one installation on one filler line 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 current method 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. If we add to that the fact that the solubility of carbon dioxide in alcohol is different than that of water, beers with either a low or high alcohol content also create a significant error for the current 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

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 new 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.

$$A = abc = \log(I_0/I)$$

Where: **A** = Absorbance

I = radiation Intensity beer CO₂

I₀ = radiation Intensity beer no CO₂

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.

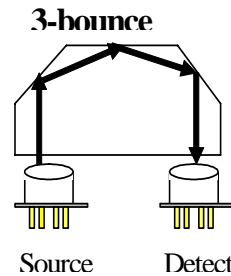


Figure 2.0

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 CO₂. This can be achieved by forcing CO₂ 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 CO₂ from the liquid. The sample being measured for I is beer with CO₂ 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 the same. 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 data at its primary beta site to compare the Pressure-Temperature method to infrared analysis.

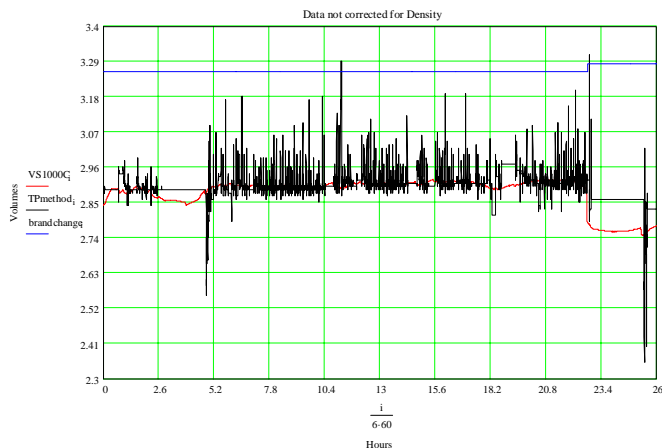


Figure 3.0

In Figure 3.0 the red line is VitalSensors' VS-1000C sensor and the black line is a pressure temperature measurement using the beta site's existing in-line sensor. The blue line represents changes in brand. The noise 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.

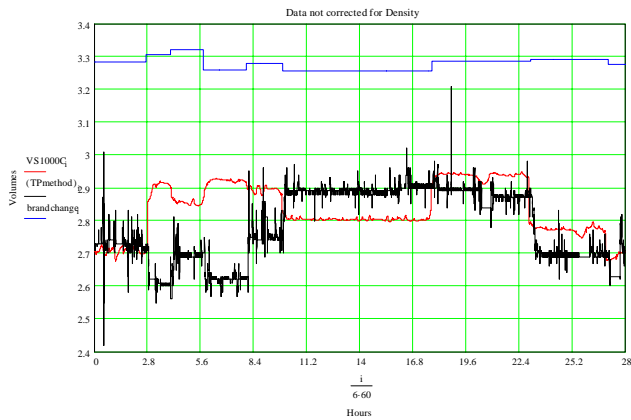


Figure 4.0

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. To prove the prior assumptions that Henry's Law method is outdated and a method using Beer-Lambert's Law would be more correct and require fewer variables, we also measured specific gravity and alcohol content during this run using a density beer analyzer. 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.

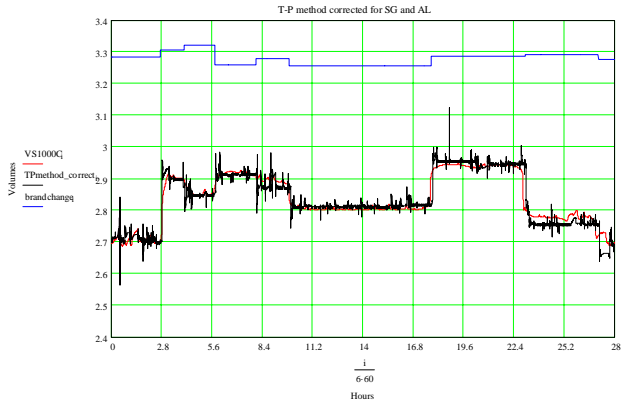


Figure 5.0

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 because of the temperatures involved. Figure 6.0 graphs in red the VS-1000C 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 CO₂ allow the VS-1000C to be an effective CIP detector and may be used to measure the CIP flushing out of the system. Even if a temperature pressure 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 measure density.

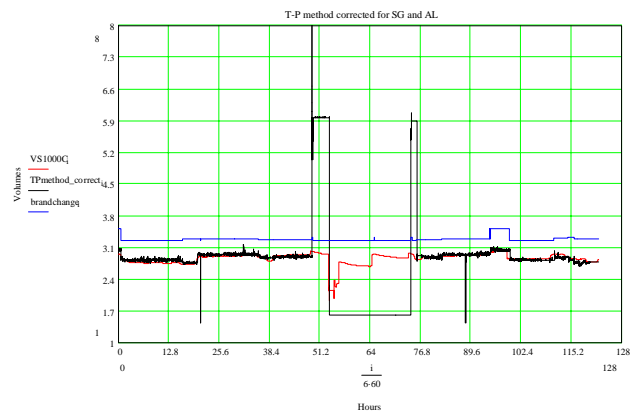


Figure 6.0

An important benefit of the VitalSensors VS-1000C sensor is lower maintenance costs. The instrument uses a stainless steel Varivent flange, has a sapphire optic and is fully solid state (no moving parts). In-line pressure temperature instruments need to have their diaphragms changed and some of the existing instruments use moving parts to look at the sample stream to help prevent pressure surges in the measurement. Infrared can be used to measure any parameter with vibrational molecules, including carbohydrates, alcohol and dissolved sugars.



Figure 7.0

Figure 7.0 depicts the VS-1000C installed at a beta site 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-1000C's optics to be directly in the stream of the product.

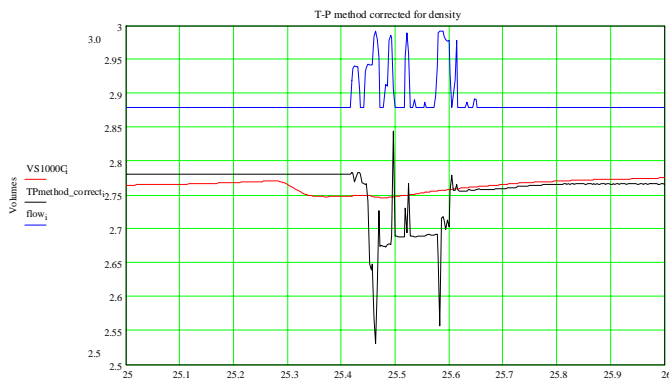


Figure 8.0

Figure 8.0 shows data from a pressure-temperature sensor and the VS-1000C over a period of intermittent flow. The red graph is the VS-1000C 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-1000C sensor does not exhibit.

Conclusions:

The current methods for measuring carbonation online use an outdated approximation of Henry's Law that employs constants that do not take into account changes in product density, effectively treating 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, which relies solely on the absorption of infrared radiation due to the presence of CO₂ molecules in solution. This eliminates a potential error that can be as high as .5 volume/volume, a factor of ten higher than the typical instrument specification.

The VS1000C sensor developed by VitalSensors Technologies is a solid state device that requires no maintenance, lowering the cost of ownership, and is the only device that measures carbonation directly without using a slipstream. Other potential applications for using infrared are measuring the concentration of alcohol, carbohydrates and dissolved sugars.

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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