Use of a Hydrocarbon Trap to Validate MAX-Bev™ Measurements of Carbonyl Impurities in Beverage Grade Carbon Dioxide

Background

Gas supplier's manufacturer carbon dioxide for various markets, including the beverage industry where carbon dioxide is used in the carbonation of soft drinks. Regardless of the intended use, it is important for the gas supplier to measure the impurities present within the carbon dioxide. In order for carbon dioxide purity to be established and certified to International Society of Beverage Technologists (ISBT) standards, these impurity concentrations need to be measured with precision and accuracy. Some impurities in carbon dioxide, such as acetaldehyde, affect the flavor of the beverage, but others, such as benzene, are critical to measure with high precision and accuracy due to human health risks.

Problem

One set of critical impurities are carbonyl compounds, such as acetaldehyde, which can be difficult to visually observe within the IR spectrum. Low level water present in the carbon dioxide contributes absorption features in carbonyl stretching region of the IR spectrum. These features make it difficult to use normal validation practices to measure the carbonyl impurities. A method of validating the measurement of acetaldehyde in carbon dioxide via FTIR needs to be established to confirm accurate concentrations.

Solution

Max Analytical Technologies has developed the MAX-Bev to measure most impurities within beverage grade carbon dioxide by infrared spectroscopy. This allows for a more streamlined and robust system that requires less maintenance than other technologies. The MAX-Bev has become the industry standard for beverage grade carbon dioxide monitoring following ISBT standards. The MAX-Bev system also utilizes a UV fluorescence analyzer to measure total sulfur content.

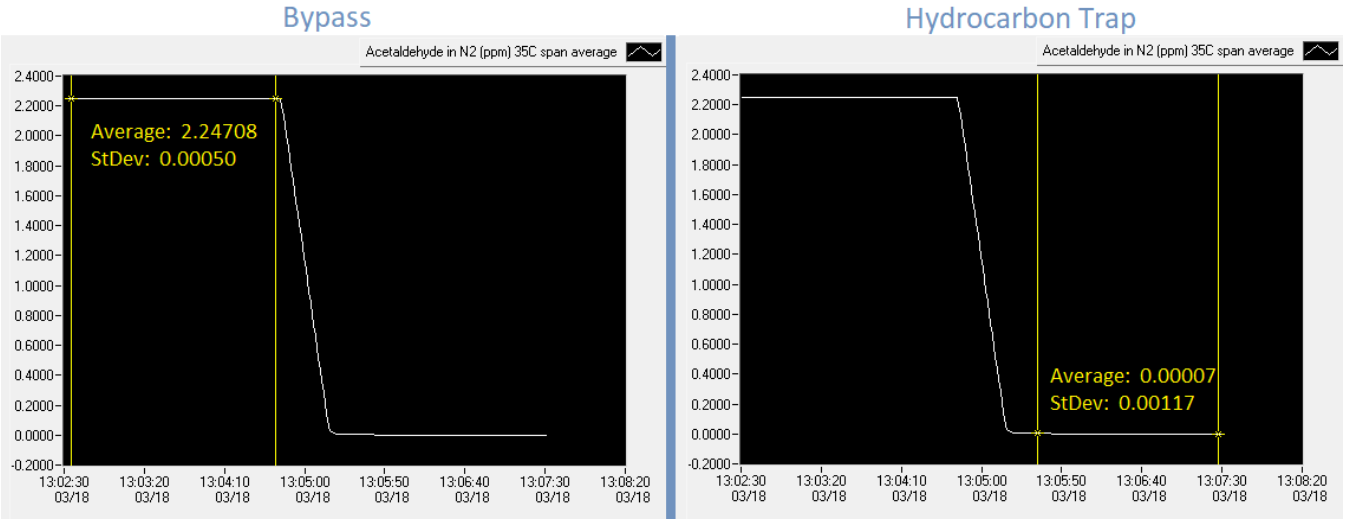
To validate the measurement of low-level acetaldehyde concentrations in carbon dioxide and to demonstrate the technology compliance to ISBT, a hydrocarbon trap with a bypass was utilized in conjunction with the MAX-Bev. During testing, a high purity carbon dioxide cylinder was connected to one sample channel and a 500ppm acetaldehyde cylinder (Appendix I) was connected to the calibration channel. The flow direction was controlled by a Swagelok 3-way ball valve located after the sample multiplexer where the gas mixing occurred. When the valve pointed to the left, the gas mixture flowed through the hydrocarbon trap, then into the FTIR gas analyzer. Conversely when it pointed to the right, the gas mixture flowed through a bypass directly to the FTIR gas analyzer.

The MAX-Bev bypass and hydrocarbon trap were purged thoroughly with nitrogen and once the moisture and carbon dioxide had been removed from the system, a new background spectrum was acquired. The bulk carbon dioxide gas flow was controlled via a mass flow controller (MFC) at 5.0L/min, whereas the calibration gas flow was controlled by a second MFC at 25mL/min. The high purity carbon dioxide and calibration gases were mixed within the sample multiplexer before passing to the hydrocarbon trap or bypass for measurement. This created a 200:1 dilution of acetaldehyde yielding approximately 2.5ppm acetaldehyde in carbon dioxide mixture. Once the mixture had equilibrated, the Swagelok 3-way ball valve was switched between the hydrocarbon trap and the bypass line to obtain the "zero carbonyl" and "sample carbonyl" measurements, respectively. Finally, the acetaldehyde flow was ceased, and the high purity carbon dioxide was measured using the same process to determine the carbonyl concentration in the raw sample gas. This was then compared to a direct reading of the high purity cylinder.

Results

The FTIR was configured to report a data point approximately every seven seconds. The results were reprocessed to average 30 points. Below are the timelines displaying the concentration plots of the acetaldehyde in parts-per-million (ppm). The left timeline has the yellow brackets around the acetaldehyde while in the bypass direction, whereas the right timeline has the yellow brackets around acetaldehyde while in the direction of the hydrocarbon trap. The pressure is approximately 5.0 atm and the temperature is approximately 35°C. Figure 1 displays the results when the acetaldehyde was mixed with the high purity carbon dioxide yielding a 200:1 dilution of the acetaldehyde.

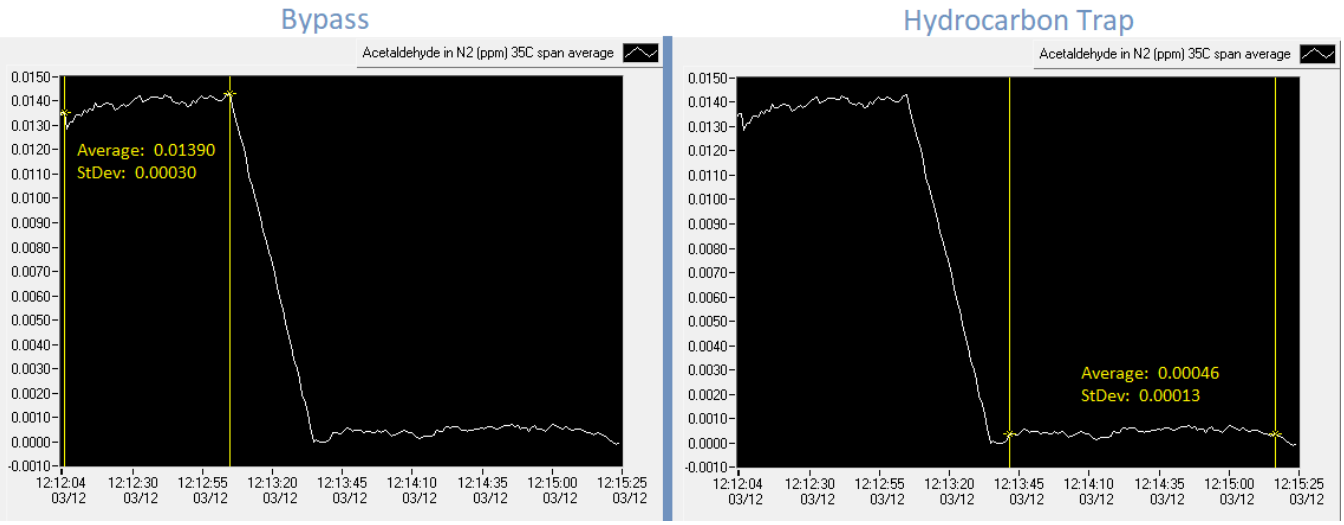
Figure 1: Acetaldehyde concentrations in 200:1 Dilution of Acetaldehyde in High Purity Carbon Dioxide



The 30-point acetaldehyde average through the bypass was 2.25 ppm with a standard deviation of 0.50 ppb. On the other hand, the 30-point acetaldehyde average through the hydrocarbon trap was 0.07 ppb with a standard deviation of 1.2 ppb.

In a final test, only the high purity carbon dioxide was analyzed directly using the same procedure as above. The timelines are displayed below in Figure 2. The 30-point average acetaldehyde results of the carbon dioxide through the bypass was 13.9 ppb with a standard deviation of 0.3 ppb, whereas the 30-point acetaldehyde results of the carbon dioxide through the hydrocarbon trap was 0.46 ppb with a standard deviation of 0.13 ppb.

Figure 2: Acetaldehyde concentrations in High Purity Carbon Dioxide



For the purposes of this experiment, the hydrocarbon trap was positioned between the sample multiplexer and the FTIR, and the MAX-Bev automated validation system was utilized to inject the acetaldehyde. If deployed in an industry setting, the hydrocarbon trap with bypass would be located before the sample port on the rear of the MAX-Bev. A manual injection of acetaldehyde would not be necessary, and any possible carbonyl contamination would be from the raw process gas samples.

Conclusions

1. Under standard conditions, the MAX-Bev measures carbonyl impurities in beverage grade carbon dioxide to below 2 ppb.

2. A hydrocarbon trap can be utilized to remove the carbonyl impurities in beverage grade carbon dioxide to below 1 ppb.

3. If the carbonyl contamination must be validated, the beverage grade carbon dioxide could be measured both directly and after passing through a hydrocarbon trap to measure the impurity by difference.

4. A hydrocarbon trap and bypass line could be added to any sample line entering the back of the MAX-Bev. This trap/bypass system could be added at any time and is not required during initial installation since the valves would be switched manually.

Recommendations

To reduce costs, sampling complexity, and measurement times, it is not recommended to use the hydrocarbon trap and bypass unless carbonyl impurity levels need additional validation. If necessary, hydrocarbon traps and bypass lines could be added to any system or sample line. In this case, a single carbon dioxide line could be utilized but measured twice by splitting the sample between two separate channels of the multiplexer. One channel would have the hydrocarbon trap located just before the sample port, whereas the other would connect directly to the MAX-Bev. In addition, flow through the hydrocarbon trap should only occur during the validation process to extend the life of the hydrocarbon trap. This configuration would allow the sequential measurement of the difference in the carbonyl reading between the hydrocarbon trap and the direct sample.

Appendix I: Acetaldehyde Certificate of Analysis

Airgas
an Air Liquide company

Airgas Specialty Gases
Airgas USA, LLC
6141 Easton Road
Bldg 1
Plumsteadville, PA 18949
Airgas.com

CERTIFICATE OF ANALYSIS

Grade of Product: CERTIFIED STANDARD-SPEC

Customer:	PRISM ANALYTICAL INC		
Part Number:	X02NI99C15A01L7	Reference Number:	160-400815758-1A
Cylinder Number:	CC507485	Cylinder Volume:	144.4 CF
Laboratory:	124 - Plumsteadville - PA	Cylinder Pressure:	2015 PSIG
Analysis Date:	Jan 13, 2017	Valve Outlet:	350
Lot Number:	160-400815758-1A		

Expiration Date: Jan 13, 2020

Product composition verified by direct comparison to calibration standards traceable to N.I.S.T. weights and/or N.I.S.T. Gas Mixture reference materials.

ANALYTICAL RESULTS

Component	Req Conc	Actual Concentration (Mole %)	Analytical Uncertainty
ACETALDEHYDE	500.0 PPM	506.0 PPM	+/- 2%
NITROGEN	Balance		

Approved for Release

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