HACH ULTRA

EXCELLENCE IN PROCESS ANALYTICS

Application Note

Beverage No. 07

Calibration of CO_2 analyzers

Every gas measuring instrument requires a method for calibration or verification.

Orbisphere manuals suggest several means for calibrating a CO_2 analyzer. The easiest way is a gas calibration: pure CO_2 gas at a known pressure is injected on the sensor membrane. This is a perfect method if the unknown sample is a gas.

However, if the analyzed sample is a liquid, a slight deviation from the actual value can be noticed: even though the Orbisphere CO_2 sensor measures the CO_2 partial pressure in the liquids, the presence of the liquid can have some effect on the temperature of the sensitive membrane and on the access of CO_2 molecules to the membrane.

In practice, the CO_2 measurements in liquid will indicate 1 or 2 % lower CO_2 level than expected after a gas phase calibration.

One way to prevent this problem is to calibrate in the liquid phase, that's why Orbisphere has developed the CO_2 calibration kits.

Orbisphere CO_2 calibration kits

The aim of this kit is to provide the end user with an accurate and easy to use liquid calibration method.

A known and precise amount of sodium bicarbonate powder is combined in a precise PET bottle, with a ready-made dilute citric acid solution to provide defined, accurate carbon dioxide content in the liquid. During the calibration procedure, this solution can then be circulated through the flow chamber of a thermal conductivity sensor.

The dose of sodium bicarbonate powder is filled into a plastic vial with repeatability better than 0.3 %. Final packages are controlled statistically and the average weight as well as the standard deviation for a batch can be guaranteed. The liquid content is also precisely under control, since the chemicals are supplied ready for use.

The precise PET bottles for the preparation of the test sample have shown variability on their volume under 0.1% during quality checks. This is mainly due to the use of a single mold.

The expansion coefficient with temperature and with pressure has also been measured and taken into account.

The combination of the previous elements will provide a traceable test sample with a unique accuracy of +/- 0.5%.

This is an acceptable condition in order to calibrate or verify our analyzer with a specified accuracy of 1%.

Most CO_2 analyzers, including Orbisphere, measure the partial pressure of the CO_2.

Since the solubility of CO_2 is different in pure water and in sodium citrate solution, some corrective factor should be applied to the theoretical calculation.

Hach Ultra, have measured the solubility of CO_2 in the final calibration solution at different temperatures and computed correction tables for various analyzer settings (patent pending).

The calibration tables will be delivered in the starter kit and will tell the user which number to enter in their instrument during calibration or which value they should read on their display during a verification, depending on analyzer settings.

Example:

orbisphere www.hachultra.com

CO2 Calibration Table (V/V)

Select column according to instrument unit setting			
Tem. (°C)	V/V in Water	V/V in Beer	V/V in Cola
6	3.353	3.149	3.266
8	3.332	3.151	3.275
10	3.310	3.150	3.284
12	3.289	3.145	3.292
14	3.268	3.137	3.300
16	3.248	3.126	3.307
18	3.227	3.112	3.313
20	3.207	3.096	3.318
22	3.187	3.076	3.321
24	3.167	3.054	3.323
26	3.147	3.029	3.323
28	3.127	3.002	3.320
30	3.108	2.973	3.315
32	3.088	2.942	3.308
34	3.069	2.908	3.298
36	3.050	2.873	3.286
38	3.031	2.836	3.271
40	3.012	2.798	3.252

At 25°C (77°F) in sodium citrate liquid, the CO_2 concentration computed from known chemical quantities, and volumes will be 3.038 V/V or 5.861 g/kg (equilibrium pressure : p_{CO2} = 4.208 bar)

For an analyzer configured to measure CO_2 in beer, the concentration corresponding to this pressure at same temperature will be 3.042 V/V.

For the instrument set for CO_2 in water, the value will be 3.157 V/V and 3.323 V/V for Cola units.

How to use the calibration kit:

A “Starter kit” containing all the items required for preparing 10 samples (including the calibration bottle), and a “Refill kit” containing 10 spare samples (no bottle) are available with 2 carbonation levels.

Preparation steps:

- The dilute citric acid is poured in the calibration bottle.
- Its temperature measured roughly (the effect of the temperature is not highly critical and a 2°C error in temperature will not generate more than a 0.5% error on the CO_2 concentration). The table has temperature increments of 2°C and a coarse linear interpolation between these values will further reduce the error.
- The adaptor piece is screwed on the calibration bottle, and the bicarbonate test tube is gently inserted through the adapter making sure the tube floats on the liquid.
- The bottle is then be tightly closed. At this time, the bottle can be tilted bottom up and vigorously shaken. The goal is to make sure no bicarbonate powder is left in the tube.
- The bottle can then be left sitting on a table for 3 minutes or more (intermittent shaking would speed up the process). Once all the powder is dissolved, the bottle can be shaken for 2 or 3 strokes just before use.
- The calibration sample has to be used the same day it was prepared, preferably within one hour. A CO_2 loss of about 1% per day has been typically observed.

The analyzer settings should be clearly identified in order to use the suitable column of the conversion table.

As with any other sample, the piercing process is critical for a reliable measurement.

Before piercing, we have to make sure the forcing gas pressure is higher than the sample pressure (depends on the temperature: about 5 bar forcing pressure at 25°C). Also make sure the flow chamber exit is closed.

During the piercing step, make sure there are no leaks around the needle and no degassing in the bottle. In case there is a burst of bubble in the bottle at that time, do not attempt to calibrate the analyzer. Prepare another calibration sample instead.

Systems components

Model	Description
32313	CO_2 calibration: starter kit, high level. Calibration bottle + adapter + reagents from model 32314.
32314	Refill kit. High level. Reagents to prepare a reference solution to calibrate CO_2 analyzers. High carbonation 3 to 8 g/kg
32315	CO_2 calibration: starter kit, low level. Calibration bottle + adapter + reagents from model 32316.
32316	Refill kit. Low level. Reagents to prepare a reference solution to calibrate CO_2 analyzers. Low carbonation 0 to 3 g/kg.