APPLICATION NOTE

HOW TO MEASURE DISSOLVED OXYGEN IN THE BREWERY

In Wort

Techniques have now been developed to ensure total gas dissolution. They are based on proprietary designs with extremely high internal pressures and turbulence. Oxygen is best used in these new devices to avoid excessive gas volumes. The practice in a modern brewery is to very tightly control dissolved oxygen (±0.5 ppm) and to use only just enough. This ensures consistent fermentations and minimum beer loss in excess yeast.

Because of particulates and the need for feedback control, it is preferable to use an in-line oxygen analyzer for measurements in wort.

Bright Beer

Typical dissolved oxygen values vary widely between breweries, but values should be less than 0.05 ppm.

Whether measuring in bright beer or wort, it is imperative that all gases are in solution before oxygen is measured by the analyzer. Soluble gases such as oxygen are displaced by bubbles, which artificially reduce the dissolved concentration value.

Portable Measurements

When sampling beer, always fully open the sample valve and regulate the beer flow using the flow control on the outlet side of the instrument. In this way the sensor will always be at the beer pressure, and although it does not matter if the beer leaving the instrument is degassing, this will ensure that beer on its way to the sensor is clear and bubble-free.

Flow rate through the instrument is not critical, but it should be low enough that there is no degassing at the oxygen sensor.

Be aware that the first measurement of the day will have a slower response, since the sensor must rid itself of any air accumulated in the instrument. It must also adjust to the beer temperature.

To track down the source of oxygen contamination, the portable 3100 Dissolved Oxygen Analyzer can be used for spot checks but also has the facility to be left on the sample point for several hours as a portable data logger. At the end of the day these results can be downloaded to a computer and viewed graphically to see if any oxygen pick-up has occurred.

When particular points in the process are identified as frequent sources of oxygen ingress, then in-line analyzers can be installed downstream from that point to provide permanent monitoring.

Hach 3100 Portable Dissolved Oxygen Analyzer — components

Industry standard oxygen levels throughout the brewery	
In wort	8 – 17+ ppm
Fermentation	< 10 ppb
Filtration	5 – 50 ppb
Bright beer after filtration	10 – 50 ppb
Beer at the filler	10 – 30 ppb
Package dissolved O_2 (bottle)	20 –50 ppb
Package dissolved O_2 (can)	30 – 60 ppb
Total package dissolved O_2	40 – 150 ppb

In-line Analysis

Finished beer is a very expensive product; if it is damaged by oxidation, these effects cannot be reversed. Because of this, it is recommended to continually monitor the process in order to give an immediate warning should oxygen pick-up occur.

Oxygen sensors can be installed in most parts of the beer line, including near bends and valves, but must be placed as far away as possible from pumps, CO_2 injection or wort aeration sites.

Install sensors into horizontal or ascending piping, never in descending product lines.

Always install the sensor so that it lies horizontally. It is particularly important never to put any sensor, for oxygen or otherwise, vertically into the top of a pipeline since an air pocket could be trapped here and effective CIP would be impossible.

All Hach systems are designed to withstand hot (99°C) or chemical cleaning-in-place without damage or performance loss.

Hach instrumentation allows selectable thermal cut-offs. By setting this value to a low temperature, just above that of the beer, the sensor will automatically switch off if the line is empty or is being cleaned. Use of this feature will greatly extend the routine maintenance cycle.

Package Analysis

Target dissolved oxygen values vary, but ideal concentration should be less than 0.5 ppm. Many breweries now achieve in-package dissolved oxygen levels of less than 0.025 ppm.

Samples are obtained from kegs by applying a gas top pressure of CO_2 or N_2 to the keg to drive the beer out.

Samples are obtained from bottles or cans with a package piercer, by pressurizing the head space to push the beer past the oxygen sensor. (Systems are also available to measure total liquid and headspace O_2, CO_2, and N_2 in a single package.)

Important points:

a) The applied CO_2 or N_2 pressure must be higher than the pressure of the total dissolved gases in the beer, to prevent bubble formation.

b) Always measure packages immediately after filling and before pasteurization, because the heating process allows dissolved oxygen to react rapidly with the beer. As much as 60% of the oxygen can be consumed during pasteurization.

c) Always shake packages vigorously before piercing to equilibrate the head space and dissolved gases. TPO concentrations are based on shaken package measurements.

Note: If measuring glass bottles, always make sure that a protective screen or other device is put in place before top gas pressure is applied, in case the bottle is flawed.

Oxygen in the Package vs. Shelf Life

Oxygen trapped in the package contributes to flavor degradation in beer. The greater the amount of oxygen, the greater the flavor degradation. The oxygen content of a package can be measured to determine if the origin of the oxygen is from the headspace, or from the filling operation.

Beer consumes the oxygen in the package over time. In most beer, the majority of the oxygen is consumed over the period of one week, but the flavor doesn't change for two to three months. Below is a graph of the oxygen concentration of a package over time. In the graph below, note that there are no units. This is because the oxygen consumption of packaged beer can vary greatly, depending upon the storage temperature, type of beer and beer yeast content.

Sometimes the half-life can be a day and sometimes it is just a few minutes. Understanding how quickly your beer reacts with oxygen will help you develop measurement protocols to allow for the most accurate measurements.

Oxygen in the Package—Finding the Source

Oxygen is introduced into the package in two places: during filling or in the headspace through incomplete fobbing. Filler oxygen can come from air already in the beer or from air trapped in the bottle or filler tubes during filling. Headspace oxygen comes from air trapped in the headspace after the closure is applied. Because the partial pressures of gases in the headspace and the liquid are not at equilibrium immediately after packaging, all packages should be shaken before measuring dissolved O_2 (or N_2 and CO_2).

Typically, the largest concentration of oxygen is found dissolved in the beer. The following steps can be used to determine whether the filler or the jetter is the major contributor of oxygen. All measurements should be taken on unpasteurized beer.

1. Pull six packages off of a moving filler that is free from starts and stops.

2. Measure three of the packages after shaking them for five minutes.

3. Measure three of the packages that have not been shaken.

4. Compare the dissolved O_2 concentration of the average measurement from each group.

If the value goes up after shaking, the major source is in the headspace. If the value goes down, as is typical, the major contribution is from the liquid. From this it can be determined if the jetter or the filler is the source of greatest oxygen content.

Oxygen exposure after packaging — Crown closures and O_2 ingress into bottles

After packaging, beer sold in bottles is still susceptible to increased oxygen exposure from the oxygen ingress through crown closures. Crowns provide a semi-permeable barrier between the beer in a bottle and the air outside the bottle. The normal oxygen content in the bottle is significantly lower than the oxygen content of the air outside the bottle. Through passive diffusion, both oxygen and nitrogen leak into the package. With the exception of newer oxygen scavenging and barrier crown closures, little can be done to eliminate the closure leakage.

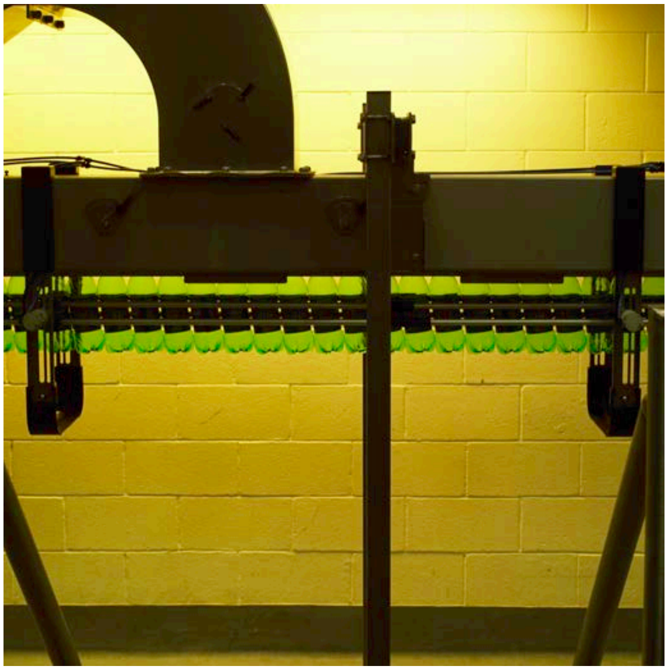
The oxygen then reacts with the beer in the bottle and effects the flavor of the beer. This leakage or ingress tries to equilibrate the partial pressures of the gases both inside and outside the bottle. Because the oxygen in the bottle is constantly reacting with the beer, the oxygen content of the bottle remains very low.

Typical crown closures “leak” 1 to 2 ppb of oxygen into the package per day. Over a three month period, the cumulative amount can be as much as 180 ppb of oxygen ingress. In many instances, this ingress is greater than the total oxygen exposure of the beer before bottling. Considering the great strides that have been made over the last few years to reduce the total oxygen content of the beer during packaging, many breweries now have a total oxygen package content of less than 40 ppb.

The Hach 6110 or the 3100 with a package piercer, can quickly measure the dissolved gases in the package. This can help you better understand the total oxygen exposure of your beer during the packaging process.

Gas Phase Analysis

The Hach system allows you to measure both the dissolved oxygen concentrations of beer or carbon dioxide used for tank purging. These analyzers offer a dual phase capability, which allows the user to switch back and forth between liquid and gas phase measurements.



Since gases are compressible, the sampling technique is different from the procedure for liquids. To measure volume %O_2 you must ensure the gas is at atmospheric pressure by using the following method:

- Control the flow through the instrument before the analyzer where the sample originates.

- Open the flow on the analyzer to minimize back pressure through the instrument.

- Use a gas sample flow of 100 ml/min or less.

At the Carbonator

When injecting CO_2 to beer, the CO_2 added must contain virtually no oxygen since large concentrations of CO2 are being added under high pressure, which could rapidly lead to a build-up of dissolved oxygen.

Adding carbon dioxide at high pressure

Amount of added CO_2	Concentration of O_2 impurity in CO_2		
	0.001%	0.005%	0.02%
0.5 V/V	7 ppb	35 ppb	142 ppb
1.0 V/V	14 ppb	71 ppb	284 ppb
2.0 V/V	28 ppb	142 ppb	567 ppb
	Dissolved oxygen added to the beer		

Useful Units and Conversions

Oxygen
At 20°C dry air contains 20.94% O_2 = 209,400 ppm by volume.
100% humid air contains 20.45% O_2 = 204,500 ppm by volume.
In solution, 1 mg/kg O_2 is often called 1 ppm (by weight).

All the following solubility statements assume a pressure of 1 atmosphere.
When water is saturated with air it will contain:
    9.10 ppm O_2 at 20°C (68°F): 14.64 ppm O_2 at 0°C (32°F).
Therefore, considering oxygen measurements at 20°C:
    204,500 ppm by volume is equivalent to 9.10 ppm by weight.
When water is saturated with pure oxygen it will contain:
    43.45 ppm O_2 at 20°C (68°F): 69.90 ppm O_2 at 0°C (32°F).

Carbon Dioxide
Dry air contains approximately 0.03% CO_2.
1 volume CO_2 per volume of beer = 1.98 grams / kg at 20°C.
Carbon Dioxide is far more soluble in water than oxygen.
When water is saturated with CO_2 at 1 atm pressure it will contain:
    1.72 g/kg CO_2 at 20°C (68°F): 3.37 g/kg CO_2 at 0°C (32°F).

Nitrogen
Dry air contains approximately 78% N_2.
In solution, 1 mg/kg N_2 is often called 1 ppm.
Nitrogen is less soluble in water than oxygen.
When water is saturated with air it will contain:
    15.3 ppm N_2 at 20°C (68°F): 23.2 ppm N_2 at 0°C (32°F).
When water is saturated with nitrogen it will contain:
    19.7 ppm N_2 at 20°C (68°F): 29.8 ppm $N_{....}$ at 0°C (32°F).

Pressure
1 atm absolute = 1013.25 mbar = 1.013 bar = 760 torr = 0 atm gauge.
All pressures for solubility data above are in absolute units.

Packages
In a typical small package, the same weight of oxygen will be found in 15 mL of headspace as in 440 ml of beer. Thus, shaking is required to ensure equilibration before analyzing.

Always shake very vigorously, as this will cause the formation of very small bubbles, which equilibrate much faster than large bubbles.

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