Instruments for Measurement of Dissolved CO_2 and O_2 in Beverages

CboxQC | CboxQC At-line
CarboQC | CarboQC At-line
OxyQC | OxyQC Wide Range
PFD filling device (Plus)

Product portfolio

CarboQC
CarboQC At-line

OxyQC
OxyQC Wide Range

CboxQC
CboxQC At-line

CarboQC ME
plus Option O_2

Product portfolio

CboxQC and **CboxQC At-line** are **combined CO_2 and O_2 meters** to determine **the true amount of dissolved CO_2** and **O_2** in beverages for use

- **in the lab** in combination with the **PFD filling device**
- and **at-line.**

Product portfolio

CarboQC and **CarboQC At-line** are **CO_2 meters** to determine **the true amount of dissolved CO_2** in beverages for use

- **in the lab** in combination with the **PFD filling device**
- and **at-line.**

Product portfolio

CarboQC ME (plus Option O_2) is a **CO_2** and **O_2 measuring module** to determine **the true amount of dissolved CO_2** and **O_2** in beverages

– **designed** to be used with Anton Paar's **Generation M** instruments

Product portfolio

OxyQC and OxyQC Wide Range are **O_2 meters** to determine **the true amount of dissolved O_2** in beverages for use

- **in the lab** in combination with the **PFD filling device**
- as well as **at-line**

Note: the instruments are designed to be used for both lab and at-line applications and are equipped with a rubber protection.

Product portfolio

Whether directly
at the production line,
in the **lab** or **as part of an analyzing system,**

*…the **best** instrument for **every** application…*

Why is dissolved CO_2 measured?

The **CO_2 content**

- strongly **influences** the **fresh taste** of beverages

and

- is a **considerable cost factor**

CO_2 measurement ensures

- **consistent taste**
- **cost-efficient dosing** due to production control

Where is dissolved CO_2 measured?

CO_2 is measured in…

- Soft drinks
- Beer, mixed beer, cider
- Mineral water
- Wine and sparkling wine

Why is dissolved O_2 measured?

The **O_2 content**

- strongly **reduces** the **shelf life** of beverages

and

- can **cause corrosion of cans**

O_2 measurement ensures

- **product safety**
- consistent **beverage quality**

Where is dissolved O_2 measured?

O_2 is measured in…

- Beer, mixed beer, cider
- Wine and sparkling wine
- Juices
- Some soft drinks

growing demand due to trend towards natural flavorings, addition of vitamins and avoiding of preservatives

Basics of CO_2 measurement

Fundamental gas laws in beverage **CO_2** measurement

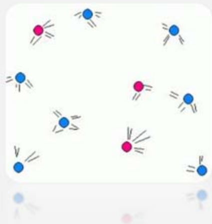
Henry's law

William Henry [1775 – 1836]

Dalton's law

John Dalton [1766 – 1844]

'Real gas law'



CO_2 measurement

$$c_{CO_2} = \xi_{CO_2} * p_{CO_2}$$

$$p_{tot} = p_{CO_2} + p_{Air} + p_{H_2O}$$

$$m = \frac{(p*M*V)}{(R*T*Z)}$$

c ... CO_2 concentration
p ... CO_2 partial pressure
ξ ... absorption coefficient

m ... CO_2 mass
M ... molar mass
Z ... compressibility factor

V ... volume
R ... gas constant
T ... temperature

Basics of CO_2 measurement

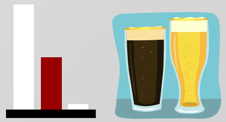
Henry's law

$$c_{CO_2} = \xi_{CO_2} * p_{CO_2}$$

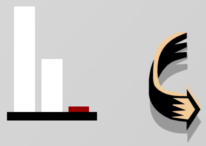
c_{CO_2}	… Concentration of CO_2 in a liquid
ξ_{CO_2}	… Absorption coefficient/solubility
p_{CO_2}	…Partial pressure of CO_2

Absorption coefficient ξ is influenced by:

Temperature



Beverage composition
(sugar, alcohol, flavors, …)



Other influences
(CO_2 pressure, dissolved air …)

***The CO_2 solubility** in beverages is up to **20% lower** than it is in **pure water**!*

Basics of CO_2 measurement

Measurement units

Gram per liter	[g/L]	Grams of CO_2 per liter of liquid
Volumes	[vol.]	Volumes of CO_2 at 0 °C and 1.01326 bar (std. atmosphere) dissolved per liquid volume
1 vol. = 1.976 g/L		Conversion

Anton Paar's CO_2 measuring principle

Anton Paar

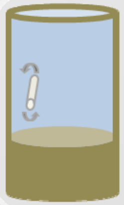
What makes the Multiple Volume Expansion method that outstanding?

Anton Paar's CO_2 meter **selectively** determines the **concentration of dissolved CO_2** in beverages **not influenced** by other residual gases such as **air** or **nitrogen**.

Anton Paar's CO_2 measuring principle

Anton Paar

How does the Multiple Volume Expansion Method work?

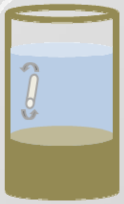


The **measuring chamber** is **completely filled** with sample and **closed by valves.**

The **volume** of the measuring chamber is **expanded.**

Pressure and **temperature equilibrium** is **generated.**

Equilibrium pressure and **temperature** are **measured.**



The measuring chamber **volume** is **further expanded, equilibrium** is **generated** and **pressure** and **temperature** are **measured again**.

The **two pressures/temperatures** are used for **CO_2 determination** and **dissolved air compensation.**

Anton Paar's CO_2 measuring principle

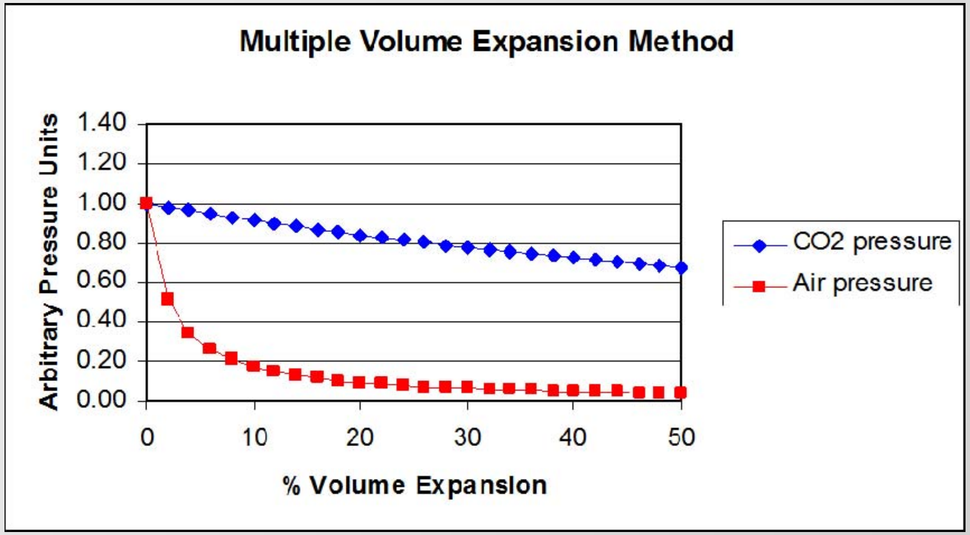
Why does the selective measurement work?

The Multiple Volume Expansion method makes use of the fact that the **solubility of air** in beverages **is much lower** than that of **CO_2**!

How does this work? …see the next slides!

Anton Paar's CO_2 measuring principle

Why is there no influence of other residual gases in the CO_2 result?



- The **CO_2** pressure **decreases gently** due to the **large solubility of CO_2** in beverages
- The **air** pressure **decreases excessively** due to the very **low solubility of air** in beverages

Anton Paar's CO_2 measuring principle

Anton Paar

MVE method – selective measurement

Additional output of Anton Paar's CO_2 meter:

- Air Index (sum of dissolved N_2 + O_2)
- O_2 Index (dissolved O_2) → if beverage is filled under O_2
- N_2 Index (dissolved N_2) → if beverage is filled under N_2
- Package pressure

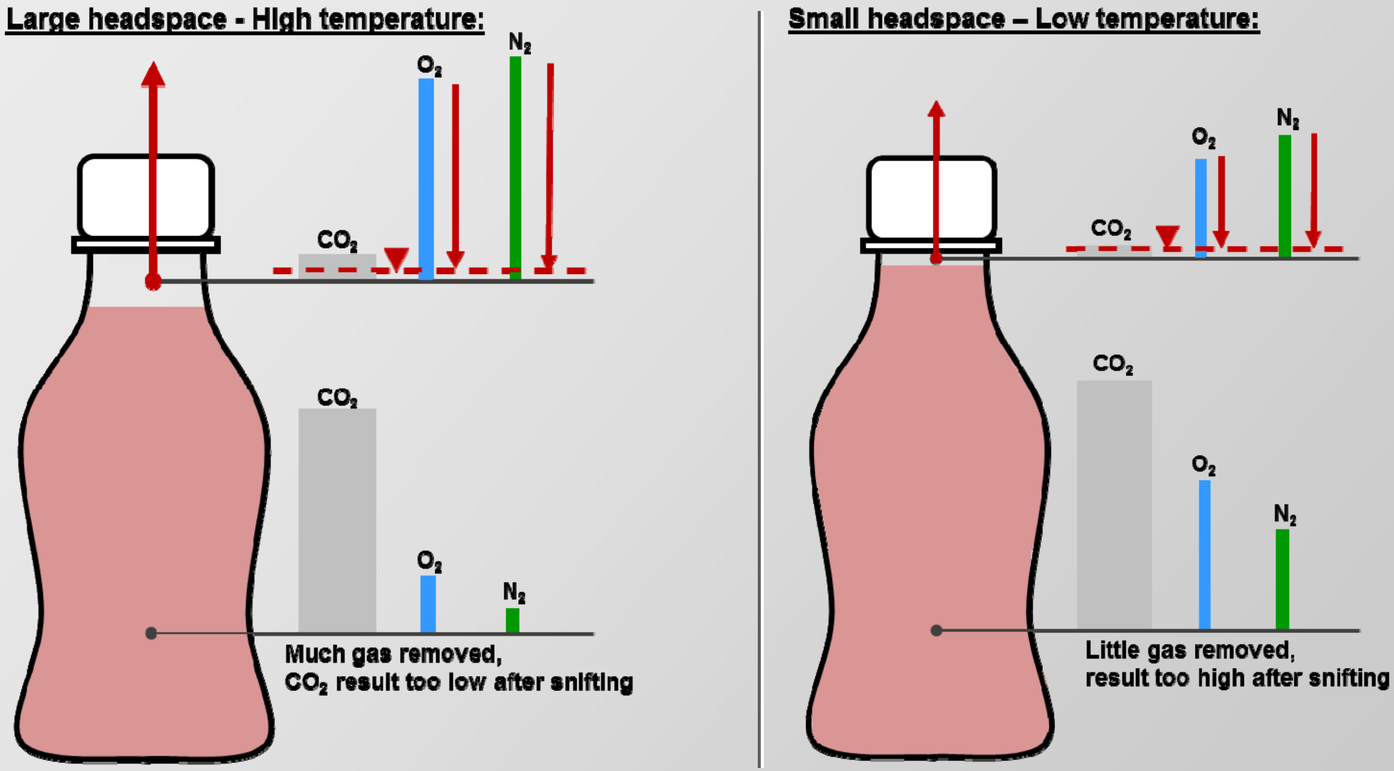
Results just for orientation !

Influences of CO_2 measurement

Why do CO_2 results differ depending on the measuring method used?

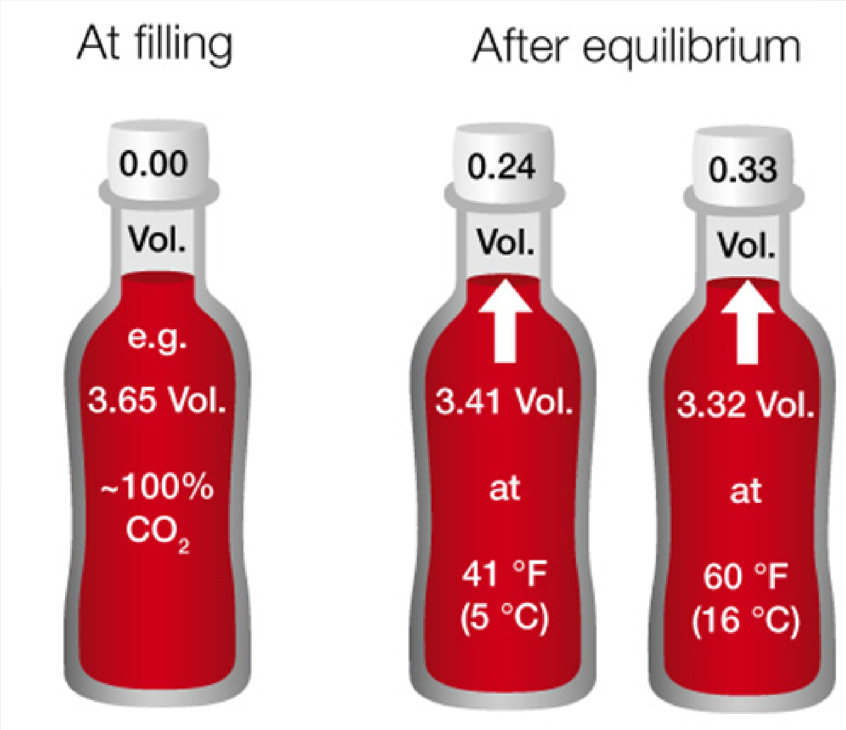
- **Influence of altitude**
  No altitude correction vs. integrated absolute pressure sensor of Anton Paar's CO_2 meters for accurate correction
- **Influence of snifting**
  Traditional p/T methods require snifting by releasing the overpressure in the headspace to the ambience in order to correct the influence of other gases; CO_2 also gets released
- **Influence of methods and tables**
  Traditional p/T methods require tables which compensate the effect of snifting
- **Influence of dissolved air in the sample**
  No pressure differentiation vs. partial pressures of air and CO_2 within the MVE method; the MVE method measures CO_2 independent of other dissolved gases

Measurement influence: snifting with p/T methods



- Snifting effect depends on:
  - extent of pressure
  - equilibrium
  - headspace percentage
  - duration of snifting
  - temperature
  - CO_2 content, etc.
- Thus variable amounts of CO_2, O_2, and N_2 are removed from the package prior to the equilibration and p/T measurement

Measurement influence: gas distribution in a package



Headspace:
Cans: 3 – 5 %
Bottles: 5 – 12%

Non-equilibrium state at bottle/can filling requires vigorous shaking of bottles/cans after filling!

Measurement influence: temperature dependency

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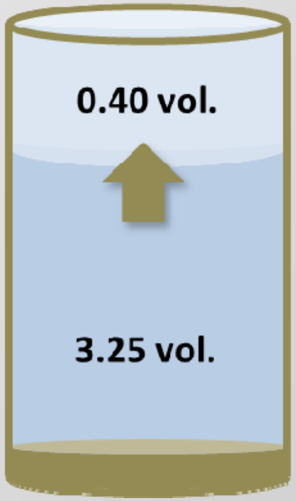
Bottle with e.g. 10% headspace

Equilibrium state:
at 5 °C (41 °F)

Equilibrium state:
at 25 °C (77 °F)



Measurement in a small range of package temperatures is necessary! Temperature-compensated measure-ment is possible.

Basics of O_2 measurement

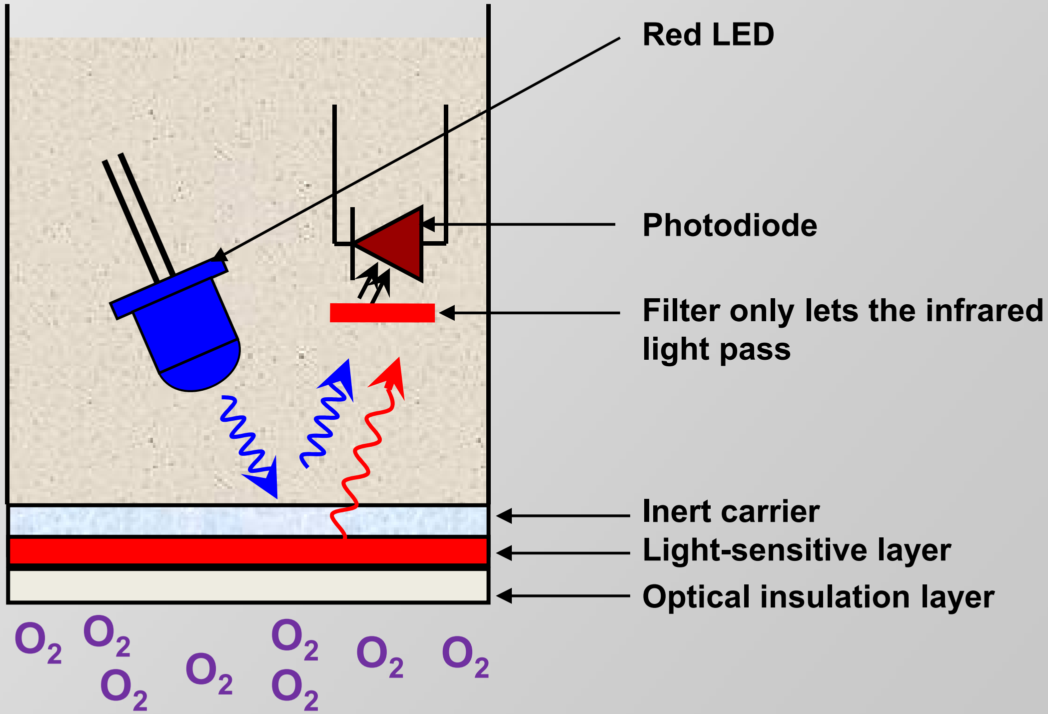
Optochemical O_2 measurement

The new series of oxygen meter with CboxQC, OxyQC and OxyQC Wide Range use an **optochemical sensor** for **fast** and **highly accurate** determination of dissolved oxygen.

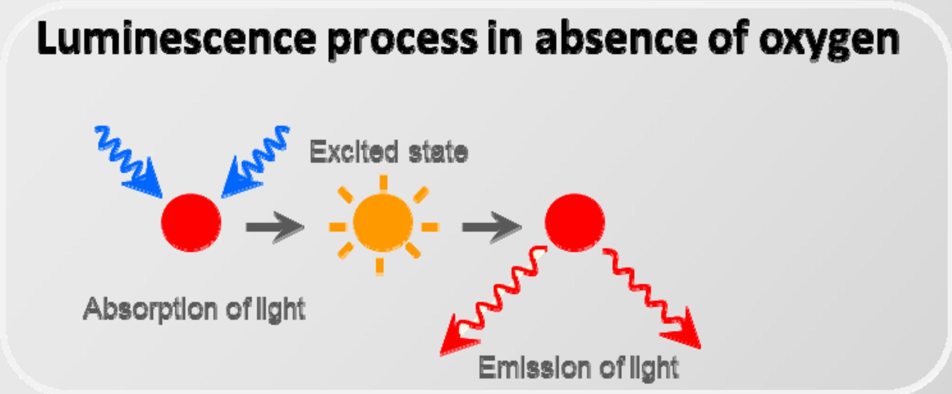
Oxygen is measured based on the **effect of dynamic luminescence quenching** and is **measured while liquids are flowing through the cell** – it's **not** a **stationary** measurement.

Physical principle of O_2 measurement

- **Optochemical O_2 sensor**
- Inside the sensor, a light-emitting diode illuminates the light-sensitive layer.

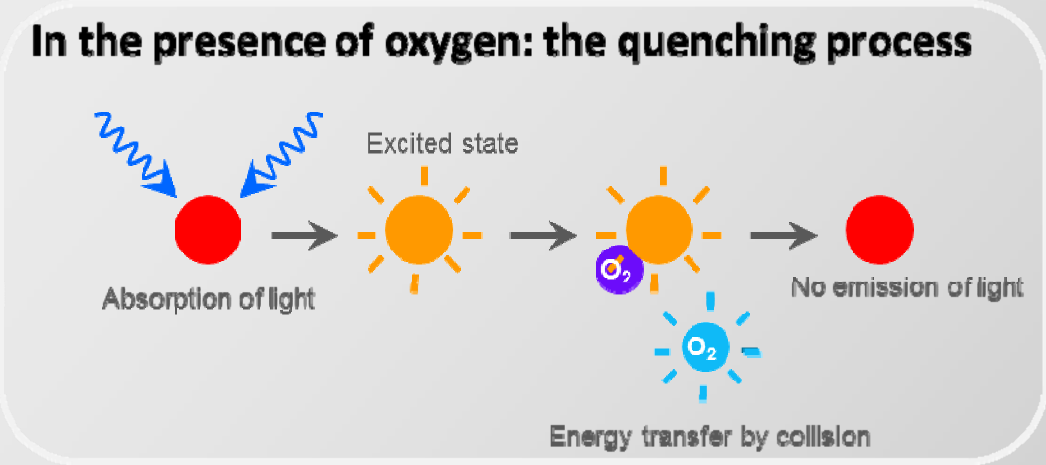


O_2 measuring principle



- Dye molecule absorbs light
- Transfer of electrons to higher energy level
- Return to the original energy level, emission of light (luminescence)

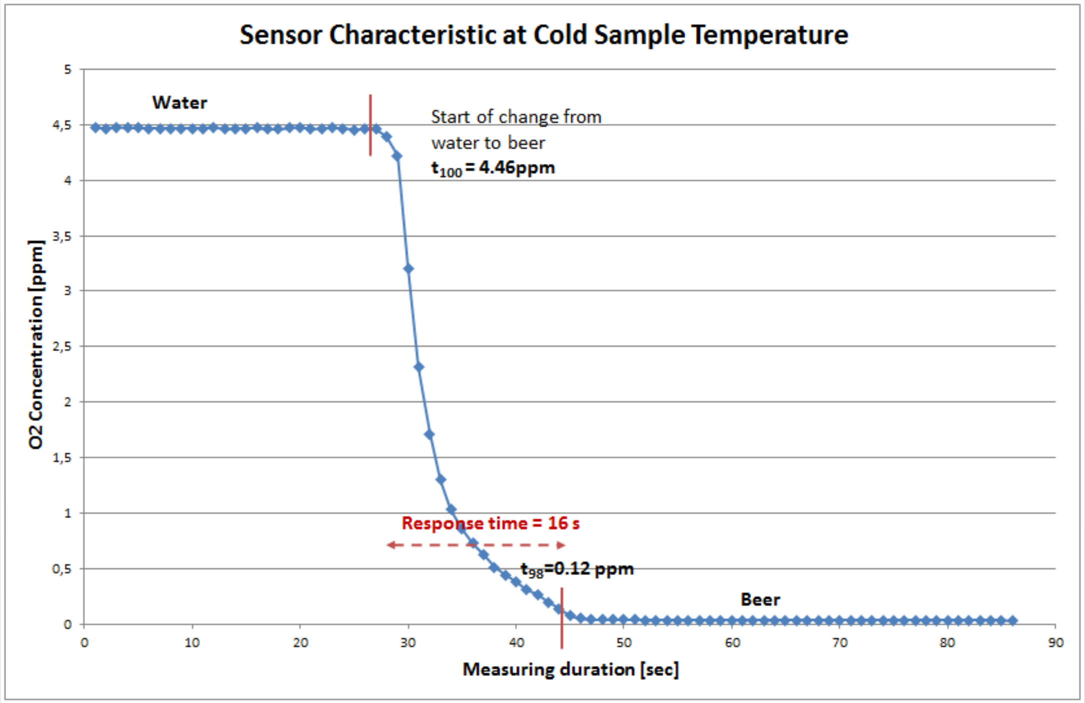
O_2 measuring principle



- Dye molecule absorbs light ➔ Transfer to a higher energy level
- Collision with oxygen: deactivation of the dye molecule
- Return to the original energy level, no emission of light

Fast response time and ideal temperature behavior

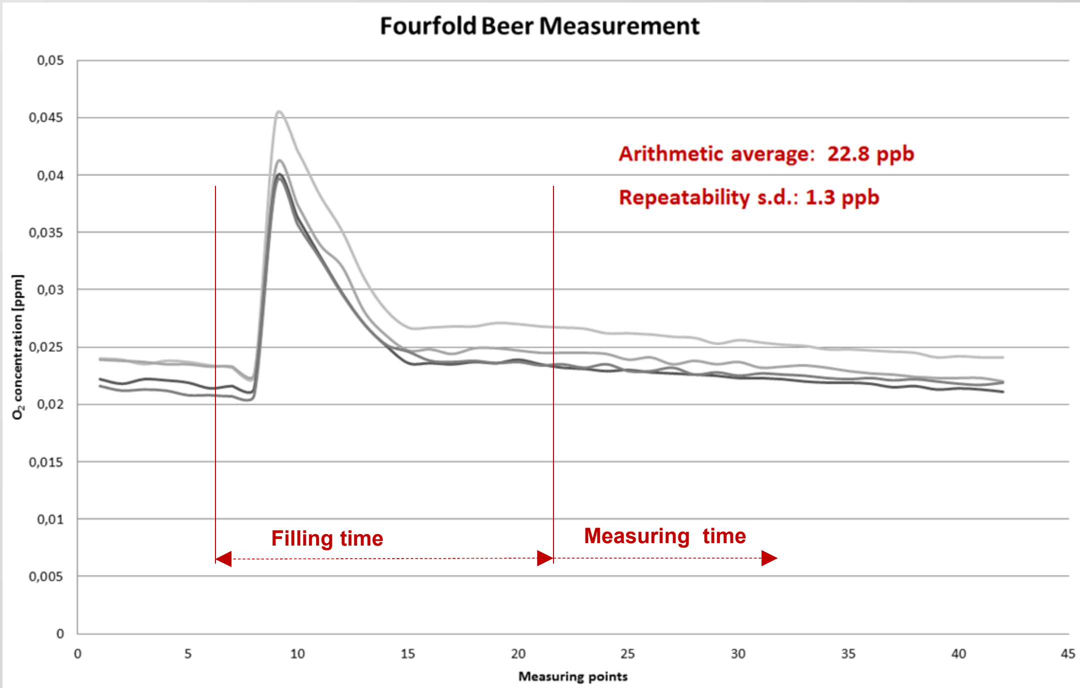
- The sensor characteristic shows a **response time** of **less than 20 s** when changing from **water to beer** at **4 °C to 7 °C**
- Excellent measurement **stability**
- Even with **cold samples**



High repeatability of the O_2 sensor

Measurement conditions:

- 0.5 L beer
- 6 °C to 11 °C
- Rinsing volume before start: **240 mL**
- Rinsing volume between each measurement: **50 mL**



Basics of O_2 measurement

Measurement units

- [mg/L] Milligrams of O_2 per liter of liquid
- [ppm] Parts per million
- [ppb] Parts per billion
- [% Air-sat.] Percent saturation in Air
- [% O2-sat.] Precent saturation in Oxygen

1 mg/L = 1 ppm = 1000 ppb

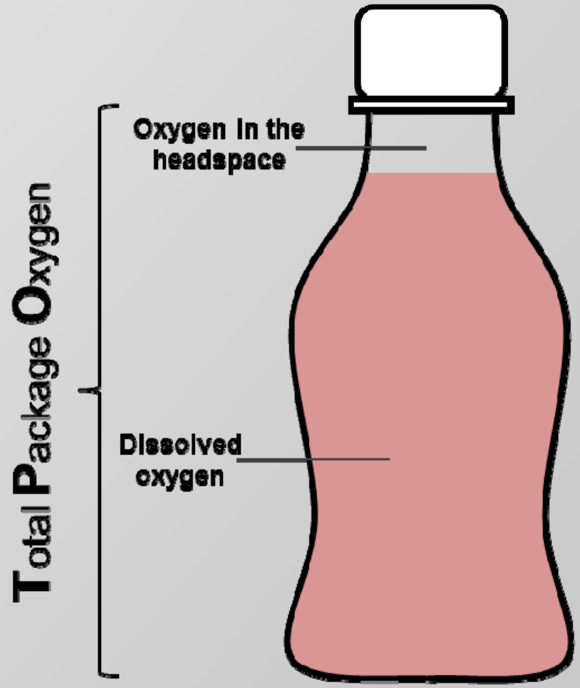
Basics of TPO measurement

What is TPO?

- Total Package Oxygen is the sum of dissolved and headspace oxygen

Why determine TPO?

- Dissolved and headspace oxygen in beverages reacts with certain beverage components.
- Oxidation products may cause changes in aroma and taste, color changes, loss of nutritional value.



Basics of TPO measurement

- **Measure dissolved oxygen, calculate TPO!**
  - Reliable information on Total Package Oxygen in beverage packages can be obtained by measuring dissolved oxygen and calculating TPO under the following conditions:
    - equilibrium established.
    - correct determination of dissolved oxygen.
    - correct temperature measurement.
    - correct brimful volume and actual volume information.
    - correct empty weight and total weight information.

Basics of TPO measurement

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- **The affordable way: measure dissolved oxygen, calculate TPO!**

CboxQC (At-line) | OxyQC | OxyQC Wide Range:
AP-SoftPrint (from V1.5) provides calculation via volume and weight information.

O2	temp.	Brim volume	Liquid volume	TPO	TPO/L	Air Content	Total Air
ppm	C	ml	ml	mg	mg/L	ml	mg
2,665	24	110	100	1,1	11,2	4,1	4,4
5,641	26,6	3000	2700	71,5	26,5	263,1	284,9
5,641	26,6	130	120	2,6	21,3	9,4	10
5,641	26,6	500	450	11,9	26,5	43,8	47,5
1,76	20	500	450	3,5	7,7	12,4	13,6

AP-SoftPrint

Option O_2, CboxQC in combination with Generation M series:
Master instrument provides calculation.
(available from SW-release 2.40)

DMA Generation M software