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La Quinta, California

The Evolution of CO₂ Measurement

What does it bring breweries and
what is the next step?

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Week 25 -2015

The Science of Beer

Content:

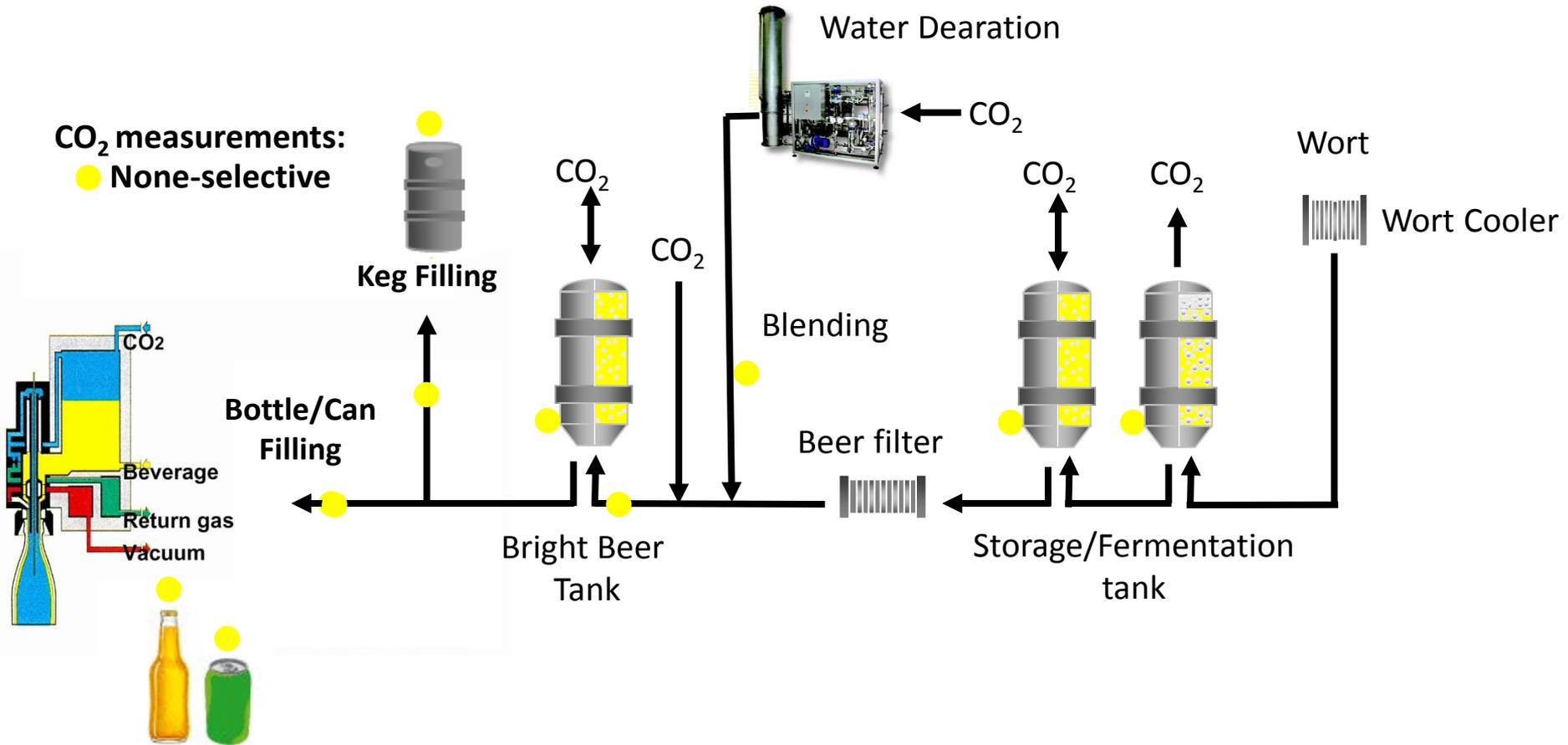
- Applications
- Setting the standard
- CO₂ measurement, General
- Influence factors
- CO₂ measurement of packages
- New technologies
- Calibration/Verification
- Good practice

How does a brewery determine the optimum gas content for a new product development?



By Tasting (Tasting Panels)!

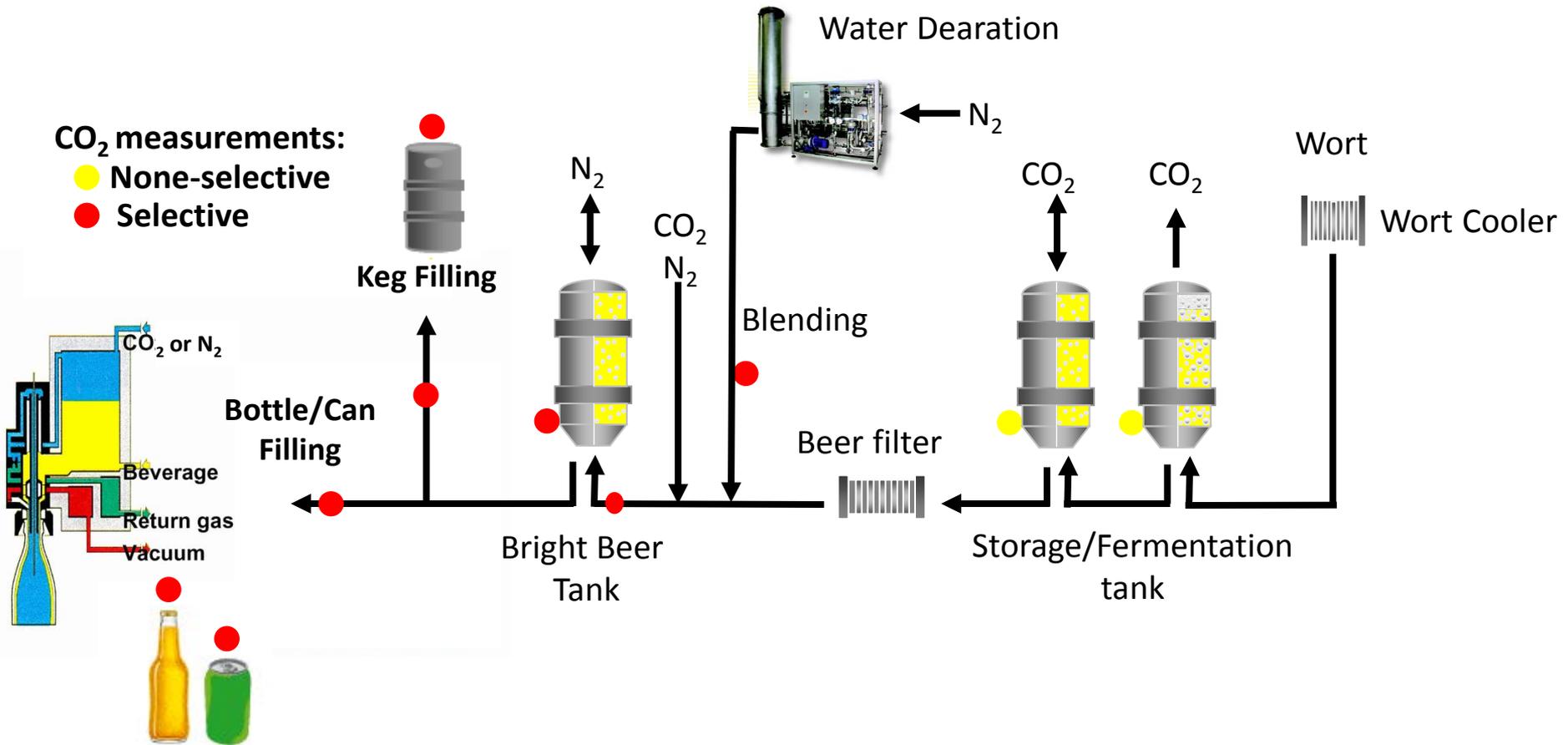
CO₂ MEASUREMENT, Typical Applications with CO₂



Medium used to transport beer, flush production lines and used as counter pressure on tanks is important in the choice of the CO₂ measurement.

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CO₂ MEASUREMENT, Typical Applications with N₂



Medium used to transport beer, flush production lines and used as counter pressure on tanks is important in the choice of the CO₂ measurement.

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CO₂ MEASUREMENT

Which standard CO₂ Measuring Methodology is followed?

**ASBC Method of Analysis
or
Analytica-EBC?**

Evolution of CO₂ MEASUREMENT

Evolution of CO₂ MEASUREMENT results in a wide range of CO₂ Measuring Methods

CO ₂ measurement methods	ASBC Methods	EBC Methods
- Manometric (mechanical)		
- P&T	beer-13	9.28.3
- Multi-volume expansion	beer-13	9.28.5/6
- Membrane		
- Manometric (optical)		
- Adsorption		
- None invasive		
- Chemical/titrimetric		
- Blom & Lund		9.28.1
- Titration (Corning)		
- Special CO ₂ detectors		
- Thermal conductivity		9.28.4
- Attenuated Total Refraction ATR		

CO₂ MEASUREMENT

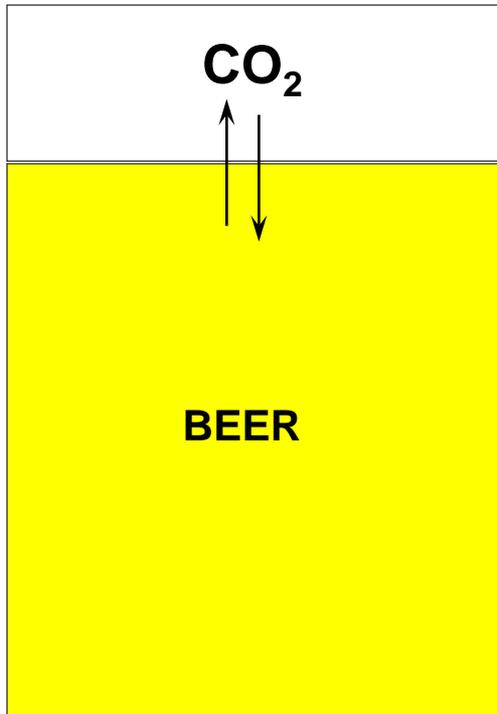
Estimated 90 % of CO₂ MEASUREMENT currently used in brewing industry:

Henry's Law

"The volume of gas dissolved in a liquid is proportional to the pressure of the gas above the liquid "

CO₂ MEASUREMENT

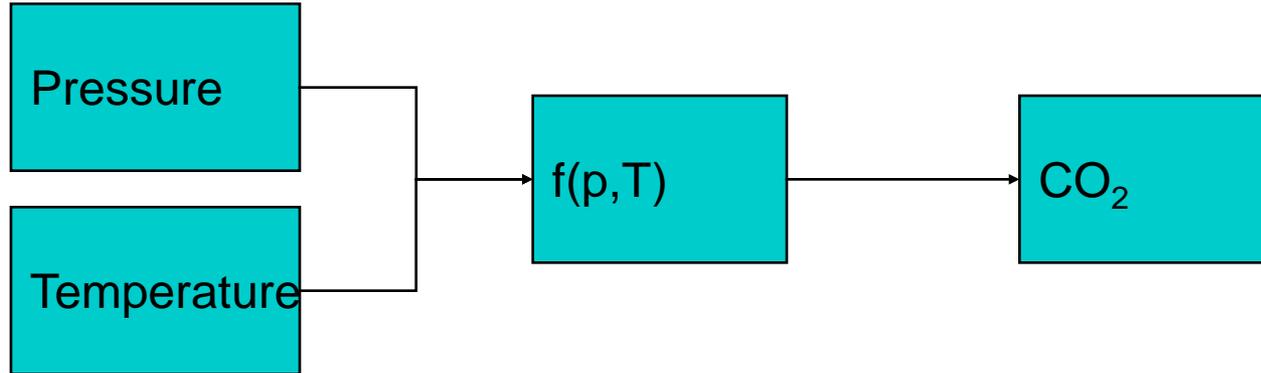
CO₂ MEASUREMENT BASED ON HENRY'S LAW



Henry: $CO_2 = P * f(t)$

CO₂ MEASUREMENT

FUNCTIONAL DIAGRAM HENRISCH LAW



CO₂ MEASUREMENT

CALCULATION OF CO₂ EQUILIBRIUM CONCENTRATION according to **ASBC**

$$\begin{aligned} \text{CO}_2 [\text{Vol}] = & 3.45778 - 7872.43 \cdot P \cdot 10^{-5} + 1513.53 \cdot T \cdot 10^{-4} + 7779.99 \cdot P^2 \cdot 10^{-7} + \\ & 3963.09 \cdot T^2 \cdot 10^{-7} - 1677.07 \cdot P \cdot T \cdot 10^{-6} - 2791.5 \cdot P^3 \cdot 10^{-9} + \\ & 4679.44 \cdot P^2 \cdot T \cdot 10^{-9} - 1424.25 \cdot P \cdot T^2 \cdot 10^{-8} + 116.914 \cdot P^2 \cdot T^2 \cdot 10^{-9} \end{aligned}$$

- CO₂ = CO₂ equilibrium concentration in Volume
- P = equilibrium pressure (partial) in psig
- T = temperature of the liquid in °F.

Note:

- Calculation based on beer with Specific Gravity (sp gr) of 1.01 kg/l
 - Conversion from % by weight to volume: CO₂ [Vol] = 5.0607 x CO₂ [% by wt] x sp gr
-

CO₂ MEASUREMENT

CALCULATION OF CO₂ EQUILIBRIUM CONCENTRATION according to **EBC**

$$CO_2 [\% m / m] = A \times (p [\text{barg}] + p_{atm} [\text{bara}]) \times e^{\left(C + \frac{D}{T [^\circ\text{C}] + 273,15} \right)}$$

- CO₂ = CO₂ equilibrium concentration
- A = conversion factor/compensation factor
- p = equilibrium pressure (partial) in barg
- p_{atm} = atmospheric pressure in bara
- C = solubility-dependent factor (-10.74*)
- D = product- dependent factor (2617.25*)
- T = temperature of the liquid in °C.

* Calculation based on beer with an OG of 12 °Plato and apparent attenuation of 80 %

Conversion from % m/m to Volume: CO₂ [Vol] = 5.061 x CO₂ [% m/m] x S (specific gravity)

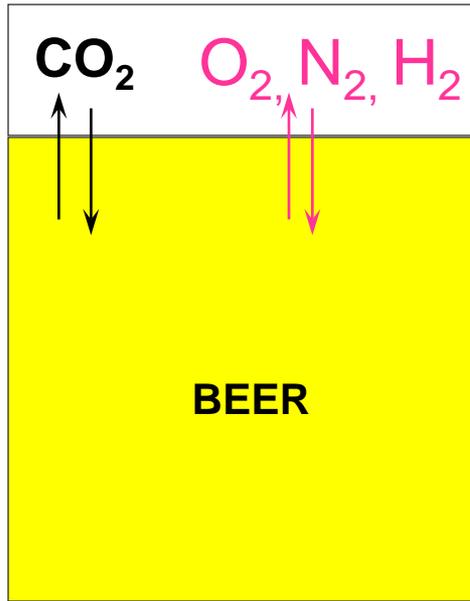
CO₂ MEASUREMENT

ERROR SOURCES MANOMETRIC CO₂ MEASUREMENTS

- Foreign gasses in the beverage
- Changes in the atmospheric pressure
Note: Solved in most of the digital CO₂ meters by using a absolute pressure measurement
- Composition of the beverage

CO₂ MEASUREMENT, effect Foreign Gasses

CO₂ MEASUREMENT based on HENRY's and DALTON's LAW



Henry: $CO_2 = P * f(t)$

Dalton: $P = [P_{CO_2} + P_{O_2} + P_{H_2} + P_{N_2}]$

CO₂ MEASUREMENT, effect Foreign Gasses

SELECTIVE CO₂ MEASUREMENT OF PACKAGED BEER;

calculation of CO₂ equilibrium concentration compensated for headspace air:

By ASBC CO₂ chart:

Calculate correction for partial pressure of air in headspace to be subtracted from the measured gauge pressure

$$P_{corrected} [psig] = \left(P [psig] + 14.7 - \frac{v_{air}}{v_{head\ space}} \times 14.7 \right)$$

By EBC:

$$CO_2 [Vol] = A \times \left(p [barg] + p_{atm} [bara] - p_{atm} \times \frac{v_{air}}{v_{head\ space}} [bar] \right) \times e^{\left(C + \frac{D}{T [^{\circ}C] + 273,15} \right)}$$

CO₂ MEASUREMENT, Failures due to Foreign Gasses

Supposition 1: Effect of air

O₂ and N₂ dissolved are proportional to atmospheric conditions

O ₂ content ppm w/w	simulated CO ₂ content [Vol]				
	0°C	5°C	10°C	15°C	20°C
0.10	0.02	0.02	0.02	0.02	0.02
1.00	0.21	0.20	0.19	0.18	0.16

Supposition 2: Effect of Nitrogen (N₂ or CO₂/N₂ mix-gas injection)

N ₂ content ppm w/w	simulated CO ₂ content [Vol]				
	0°C	5°C	10°C	15°C	20°C
1	0.06	0.05	0.05	0.05	0.04
10	0.55	0.53	0.49	0.45	0.42

CO₂ MEASUREMENT, Failure due to Composition of Beverage

- CO₂ solubility in beer 12 °Plato is approximately 0,96 x CO₂ solubility in water
- CO₂ solubility in soft drink with 10 g/l sugar (=10 °Brix) is approximately 0,90 x CO₂ solubility in water
- As the extract content gets smaller the CO₂ solubility in beer approaches the solubility in water
- Rule of thumb: approximately 1% CO₂ solubility per 3 °Plato or 1 °Brix

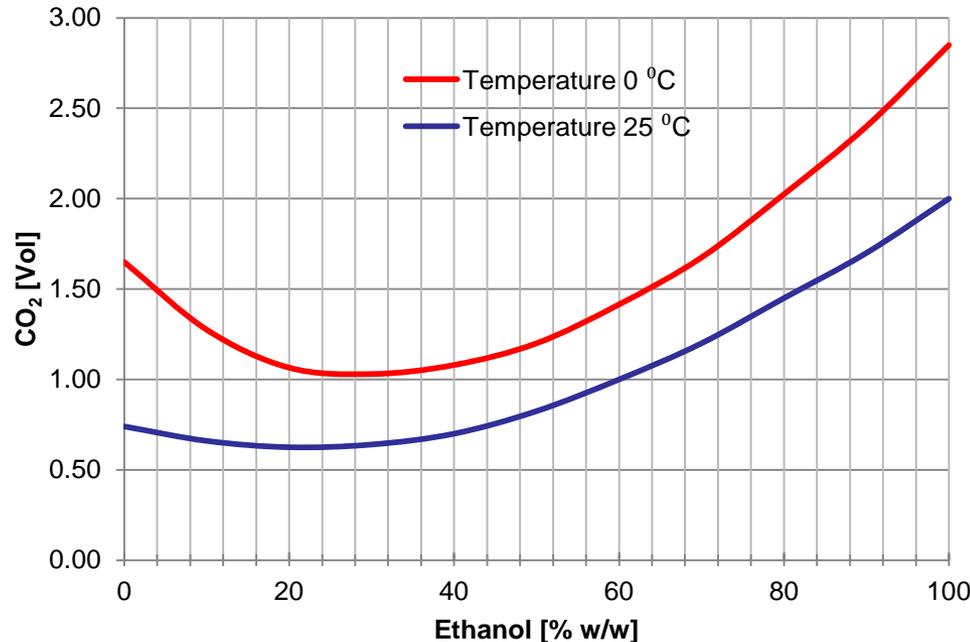
Note: In practice the difference in CO₂ solubility will not be taken into account

CO₂ MEASUREMENT, Influence of Ethanol Content

Information in literature different opinions are found :

- Paukner: in a range of 4-6 % Ethanol the CO₂ solubility is comparable with water
- Haffmans:

CO₂ solubility in water/ethanol solution at atm. pressure



Note: In practice the difference in CO₂ solubility will not be taken into account

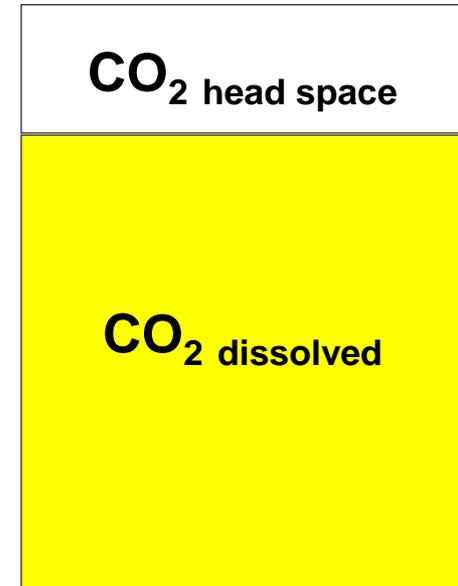
Methods of CO₂ MEASUREMENT, Effects of Failures

CO ₂ measurement methods	ASBC Methods	EBC Methods	Selective	Gas/liquid	Remark
- Manometric (mechanical)					
- P&T	beer-13	9.28.3	X	gas	
- Multi-volume expansion	Beer-13	9.28.5/6	√	gas	Anton Paar
- Membrane			√	gas	Gas selective membrane, only in-line
- Manometric (optical)					
- Adsorption			√	gas	only in-line
- None invasive			√/X	gas	only bottles (glass & PET), can measure CO ₂ pressure and total pressure
- Chemical/titrimetric					
- Blom & Lund		9.28.1	√	liquid	
- Titration (Corning)			√	liquid	
- Special CO₂ detectors					
- Thermal Conductivity		9.28.4	√	gas	Orbisphere
- Attenuated Total Reflection ATR			√	liquid	only in-line

CO₂ MEASUREMENT of PACKAGES

CO₂ MEASUREMENT of PACKAGES, Temp. Effects

- CO₂ Measurement of Packaged beer (bottle, can and/or keg)
- $CO_{2\text{ total}} = CO_{2\text{ head space}} + CO_{2\text{ dissolved}}$
- $CO_{2\text{ total}} = \text{constant and independent of temp.}$
- When temp. increases:
 $CO_{2\text{ head space}} (\uparrow) + CO_{2\text{ dissolved}} (\downarrow)$
- Example: packaged bottle
 $V_{\text{liquid}} = 300 \text{ ml}$
 $V_{\text{head space}} = 15 \text{ ml}$
 $CO_{2\text{ dissolved}} \text{ at } 10\text{ }^{\circ}\text{C} = 2.65 \text{ Vol}$
 $CO_{2\text{ dissolved}} \text{ at } 20\text{ }^{\circ}\text{C} = 2.61 \text{ Vol}$



CO₂ MEASUREMENT of PACKAGES, Temp. Effects (cont.)

Possible solutions:

- Always measure the CO₂ concentration of packages on a standardized temp. for example 25 °C (according to ASBC method).
- Use an instrument that is able to measure the CO₂ concentration temperature independently: A “new” CO₂ quantity “CO₂ temp standard CO₂ TS” or “normalization temp.” was introduced.

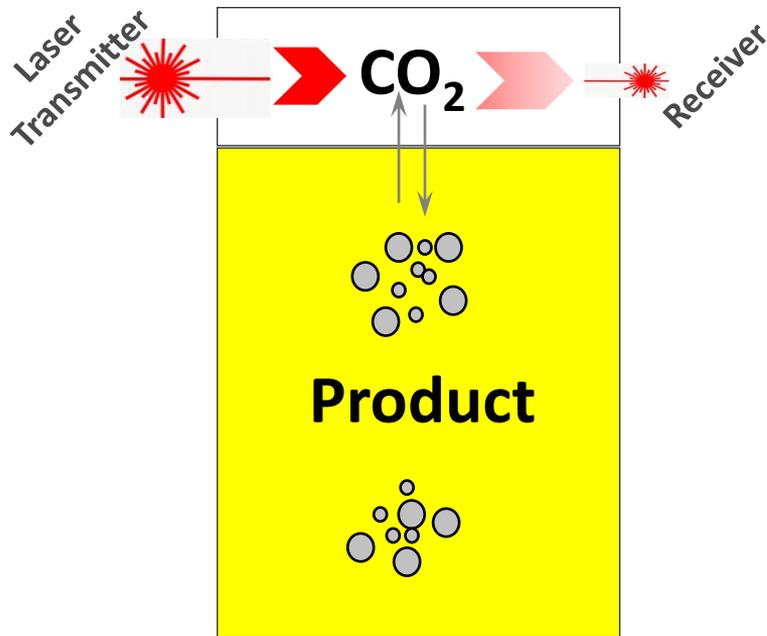


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CO₂ MEASUREMENT of PACKAGES, Non-Invasive

Next step in selective CO₂ MEASUREMENT of Packaged beer (bottles only)

NON-INVASIVE CO₂ Measurement



- Package remains unopened.
- Equilibrium pressure, Total pressure and temp. are measured without contacting the bottle.



Non-Invasive CO₂ Measurement, Video (real time)



5-10 seconds for results !

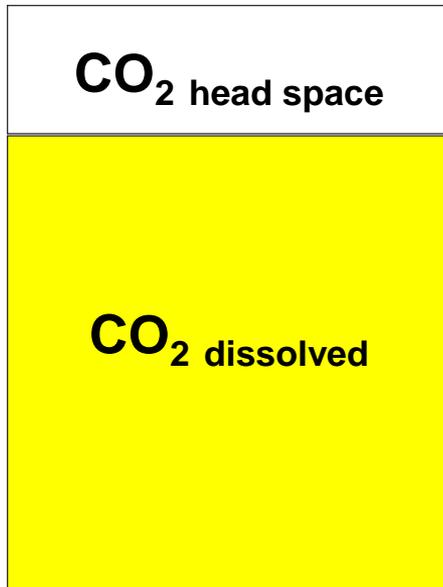
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CO₂ MEASUREMENT of PACKAGES, Next Step???

Next step in CO₂ Measurement of Packaged beer (bottle, can):

Analogue to TPO:

Measurement of TPCO = CO₂ total = CO₂ head space + CO₂ dissolved ???



- No attemporation: CO₂ total makes the CO₂ measurement of packages temp. independent.
- No equilibration of package, when measured separately (as performed in the Haffmans Automator)



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CO₂ MEASUREMENT, ATR-Method (in-line)

New in-line CO₂ measurement technology is ATR.

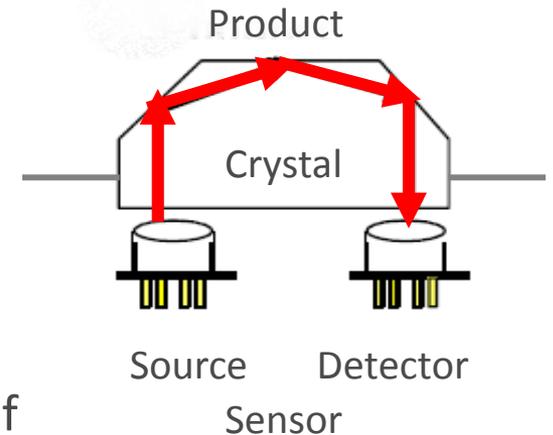
ATR Uses of infrared light (IR) and its Attenuated Total Reflectance (ATR).

Infrared beams are directed under an angle onto the optically crystal, made sapphire, that is installed at the probe's process connection and is in contact with the product.

The infrared light enters the liquid surface and through Absorption, it will attenuate and the reflected spectrum of this beam is measured.

ATR CO₂ measurement is:

- Selective
- Fast (short measurement interval) and
- Beverage composition has no influence



CO₂ MEASUREMENT CALIBRATION

CO₂ MEASUREMENTS, Calibration

Manometric (mechanical):

- Calibration of pressure and temperature (indirect).

Manometric (optical):

Adsorption:

Calibration (indirect)

- CO₂ Differences with lab result to be corrected.

None-invasive:

Calibration (indirect) of

- total pressure and partial CO₂ pressure by using a certified gas (CO₂ or CO₂/N₂ mixture) at different pressures.

Special detectors:

Thermal Conductivity:

Calibration (indirect) with

- Certified gas (one point or two point calibration)

ATR

- 7 fixed products stored (Beer, beverage, beverage diet, wine, mineral water, strong beer, MID) and one to create a customer specific product.
 - Field calibration adjusting and aligning to trends in a repeated manner against lab result (use of offset or gain adjustment).
-



CO₂ MEASUREMENTS, Verification

Trace CO₂:

- An installation that produces water with a known CO₂ quantity based on pressure and temperature conditions.



High precision Calibration Kit

An accurate determined quantity of sodium Bicarbonate is combined with a ready-made diluted Citric acid solution to provide an accurate carbon dioxide concentration only to be used to calibrate/verify the thermal conductivity sensor.

CO₂ MEASUREMENT, Good Practice

1. Use one CO₂ calculation, without compensating for CO₂ solubility, or density for all beers and beverage types at all stages of the production.
This avoids operators involved in CO₂ measurement needing to adjust CO₂ formula's for each product which can lead to mistakes.
2. At beverage development, determine preferred CO₂ content through taste panels.
This CO₂ content is calculated based on the CO₂ calculation above.
3. Reproducibility of CO₂ measurement is relevant for proper CO₂ control, true CO₂ level not relevant;
4. Use selective CO₂ measurement when foreign gas contents do not allow proper quality control.

What do all these CO₂ methods bring brewing industry

New CO₂ meter/measuring method have different advantages;
Reduction of sample preparation/faster results
Choice needs to be fine tunes with product/application
Need for standardization

Issues:

Comparability of CO₂ measurement/methods
Calibration of special detectors (ATR and Thermal Conductivity) against master



THANK YOU FOR YOUR ATTENTION!



Frank Verkoelen