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Novel optochemical method for the non destructive determination of oxygen in encapsulated beer bottles

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Introduction

The applicability of optochemical oxygen sensors has been demonstrated for a wide range of different applications. One of these applications is the non-destructive monitoring over time of the oxygen content inside transparent glass bottles for the brewery industry. Oxygen in alcoholic beverages is responsible for a variety of processes, which cause the ageing of the products and consequently the shortening of their shelf lifetimes. The oxygen concentration in the headspace of the filled beer bottles results from the remaining oxygen in the headspace after the high pressure water jet injection during the filling process, from the equilibrium between the inward oxygen diffusion through the crown caps and on the oxygen consumption due to the oxidization of beer or of the oxygen scavengers eventually inserted in the crown caps. In this paper we describe a non-destructive optochemical method for monitoring the oxygen content in the head space of filled beer bottles. It allows investigations on the oxygen diffusion through different types of crown caps and on the oxygen consumption due to scavengers and beer itself.

Principle

The measurement system consists of an oxygen sensitive membrane and of an optoelectronic read-out module. The sensitive membrane is obtained by dissolving and immobilizing an oxygen sensitive dye in a suitable polymer matrix and is inserted in the inner volume of the bottle (Figure 1). The read-out module is responsible for excitation and detection of the luminescence lifetime of the sensitive membrane, by means of a phase measurement technique. The phase shift which results in the difference between excitation and luminescence depends on the oxygen concentration around the sensitive membrane in the bottle.

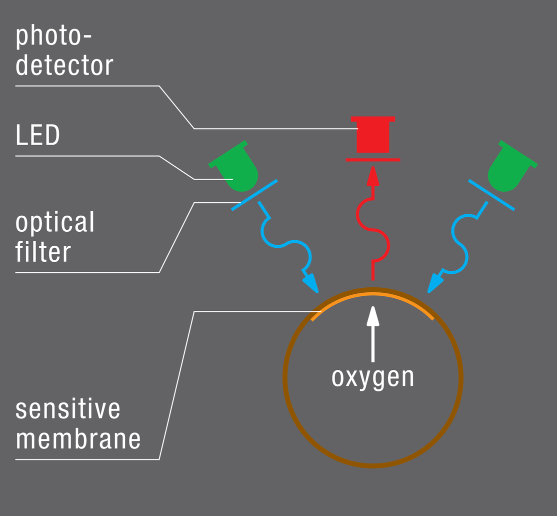

Figure 1: Principle set-up of the optochemical oxygen measurement system with the oxygen sensitive membrane inside the device to test and the optoelectronic excitation (light emitting diodes and optical filters) and detection (photodiode and optical filter).

Oxygen diffusion through crown caps

Experimental

For the determination of the oxygen diffusion through crown cap closed glass beer bottles with oxygen scavenger in the first set-up empty beer bottles were closed with the crown caps and afterwards the head of the bottles were cut so that the resulting headspace was app. 20 ml. On the cut area of the beer bottle the measurement device with the oxygen sensitive element was glued with Araldite 2012 epoxy adhesive (see Figure 2 and Figure 3).

Before the oxygen measurements the space inside the bottle was swilled with high purity N_2 until a oxygen value of 1–3 ppm was reached. Then the gas pipelines were mechanically closed by cold soldering. In three of the six bottles the oxygen scavenger was activated before, in one the oxygen scavenger was not activated. Furthermore two bottle heads were filled with an overpressure of CO_2 and activated scavenger.

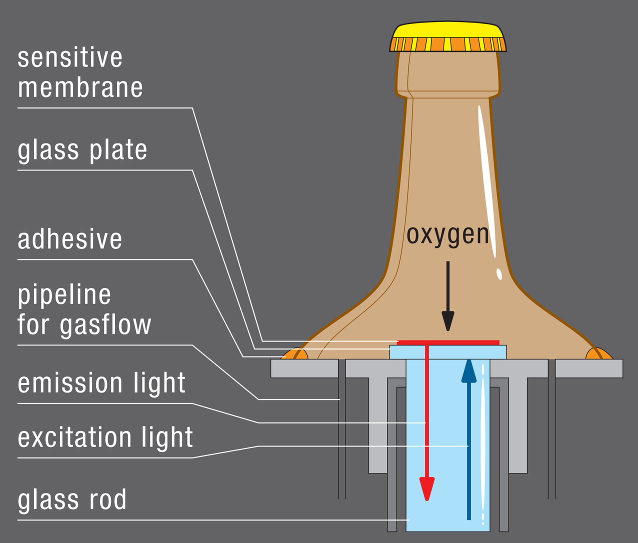

Figure 2: Measurement set-up for the determination of the oxygen diffusion through crown caps. The cut head-space of the bottle is glued on a metal plane. Stainless steel pipelines provide a gas flow to evacuate the head-space with nitrogen. The measurement unit is placed at the bottom of the metal plate.

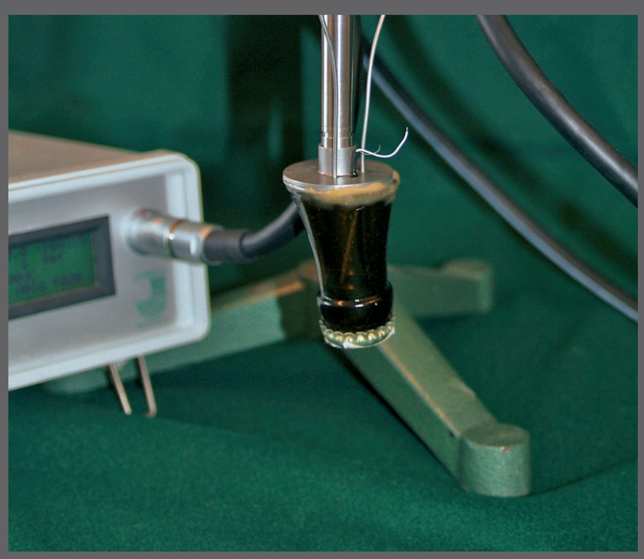

Figure 3: Picture of the measurement set-up to determine the oxygen diffusion through crown caps.

Results

The results of the measurements (see Table 1) show significant differences between the samples. The oxygen diffusion of app. 570 µg / (½ l * ½ year) for the bottle without activated scavenger stands in good correlation with 500 µg / (½ l * ½ year) determined with a Mocon Oxtran measurement system [1]. Unfortunately this device cannot be applied for wet measurements and with overpressure, and so for the other samples no reference values could be determined.

The results of the measurement with CO_2 overpressure show a lower diffusion of 65–85 µg per ½ l and a half year. The reason for this lies in the higher initial pressures in the bottle heads.

Nr.	Start-pO_2 (Pa)	End-pO_2 (Pa)	Meas. Time (days)	O_2-Diffusion (Pa/day)	Atmosphere	O_2-Diffusion [µg/(½* ½y)]
1	1.20	15.2	3	4.7	N_2, Wet	220.1
2	0.80	16.9	3	5.4	N_2, Wet	252.9
3	6.74	67.2	5	12.1	N_2, Dry	566.6
4	2.80	15.5	3	4.2	N_2, Wet	196.7
5	0.10	30.1	21	1.4	CO_2, Wet	65.6
6	0.10	27.8	21	1.8	CO_2, Wet	84.3

Table 1: Results of the oxygen diffusion tests with activated scavenger (6475P) in N_2 (Nr. 1, 2, 4), without activated oxygen scavenger in N_2 (Nr. 3) and activated scavenger in an overpressure of CO_2 (Nr. 5, 6) in the bottle head.

Oxygen measurments in factory filled

Experimental

For the second test series the oxygen sensitive element was directly incorporated in the bottle neck of the glass bottles (Figure 5). After calibration the bottles were filled with beer and encapsulated with crown caps with different oxygen scavengers and barriers in a beer ampoule filling system. The oxygen measurements were performed initially after enclosure of the bottles and after 3, 6, 10 and 13 days with the instrumentation shown in Figure 4. Furthermore some crown caps were sealed with Araldite 2012 adhesive to prevent any oxygen diffusion. Between the measurements the bottles were stored in 95 % oxygen atmosphere at ambient temperature (25 ± 1 °C).

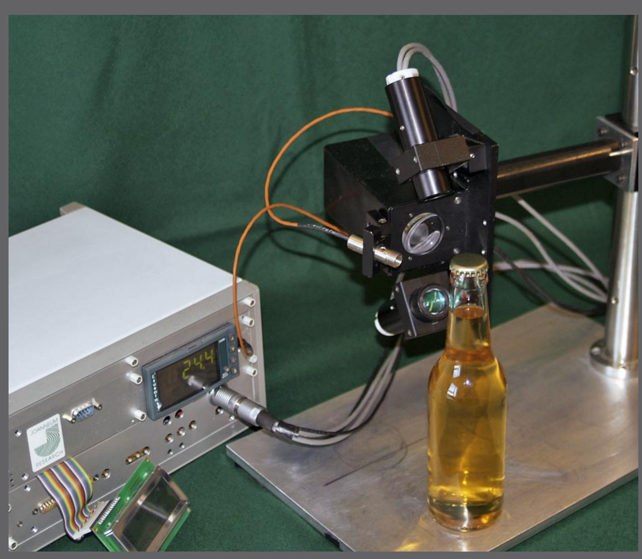

Figure 4: Measurement set-up for the determination of oxygen in encapsulated beer bottles.

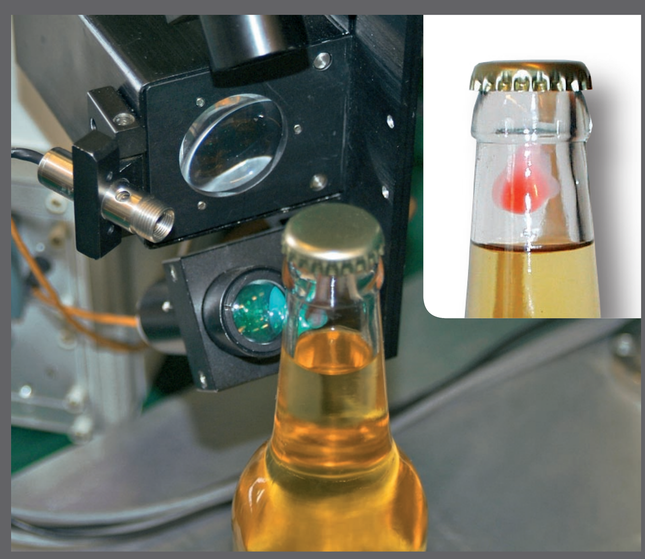

Figure 5: Bottleneck of a beer ampoule with the directly incorporated oxygen sensitive element on the inner side.

Results

The results of the measurements over time (Figure 6) show a significant difference between the different sample types. The best results concerning oxygen diffusion were obtained with the oxygen barrier Oxylen SC-25 and the scavenger 6475P. They show a significant lower oxygen amount after 13 days in the bottle than the bottles without scavenger. Furthermore the sealed bottles without scavenger show now change in the oxygen amount inside the bottle after day 3. This means that the oxygen consumption due to beer was not observed during this measurement period (10 days). On the other hand the bottles with 45 mg/l ascorbic acid show a significant decrease in the oxygen partial pressure (after day 6), thus indicating that an oxygen consumption occurs.

However, the results concerning oxygen diffusion stand in good correlation to the literature data [2]. Especially if the fact of the higher diffusion rate concerning the storage in pure oxygen is taken into account (Figure 7).

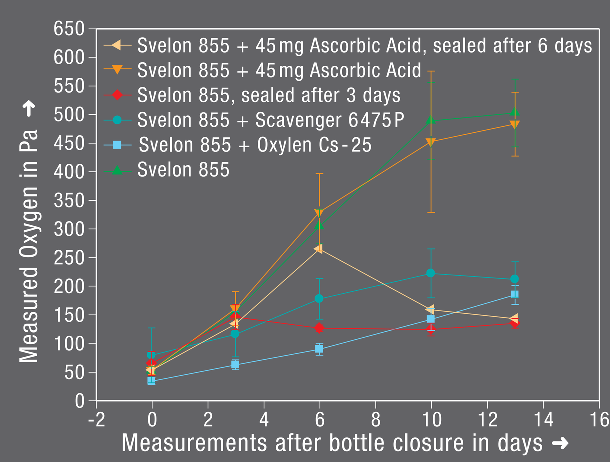

Figure 6: Oxygen measurement in beer bottles over time. The bottles were stored at ambient temperature and in 95 % oxygen atmosphere.

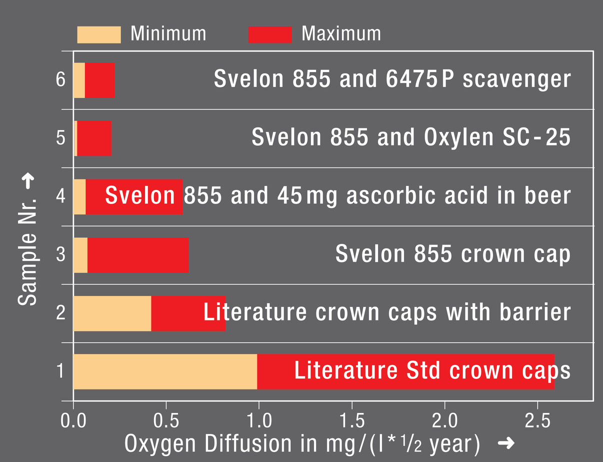

Figure 7: Charts of measured oxygen diffusion through crown caps compared with literature data. The measured values were calculated under the assumption of the validity of the ideal gas law and a 4.5 times lower diffusion rate at storage in ambient air (21 % oxygen).

Discussion

The results of the first set-up show good correlation to reference instruments. Furthermore an improvement concerning the oxygen diffusion was obtained by activated scavengers and by applying an overpressure in the bottle. The second set-up, which is a realistic approach for inline measurements at breweries, shows the influence of scavengers, barriers and ascorbic acid in beer.

The big advantage of this measurement is the possibility of observation of the oxygen diffusion process and oxidation processes of beer itself over a long period of time to determine also long time effects during storage of beer. It is therefore a tool of high importance for the brewery industry, since it can be used for on-line non-destructive quality controls at the processing line of ampoule filling factories and for leakage inspection of sealed bottles throughout the distribution chain from the manufacturer to the distributor. Furthermore, this method can also be profitably used in the packaging technology to investigate the oxygen diffusion of different types of crown caps and to gain thus valuable information for the optimization of packages.

www.joanneum.at/cpk

References

[1] Personal information from G. Zanker
[2] Müller K., Weisser H., Oxidative Processes, Barrier Properties of PET Bottles for oxygen sensitive Products, BBII, April 2003, p20–22