Ch. Huber, T.-A. Nguyen, Ch. Krause, H. Humele and A. Stangelmayer

Oxygen Ingress Measurement into PET Bottles using Optical-Chemical Sensor Technology

A new non-invasive and non-destructive fibre optic oxygen meter determines oxygen permeability of plastic bottles and containers via measuring trace concentrations of oxygen inside the package. Ideal for assurance, production and quality control applications, this system incorporates the latest state-of-the-art in optical-chemical sensor technology. Permeation rates can be confirmed without piercing the package or bottle. Oxygen ingress or seal integrity can be verified as it occurs in normal packaging processes. The sensing principle is based on a fluorescence quenching method enabling oxygen measurements in a non-destructive way. A trace oxygen sensor spot is placed on the inner wall of the transparent bottle or package and a fibre optic cable is positioned on the outside. The luminescence lifetime of the oxygen-sensitive spot changes with the oxygen concentration and is therefore acting as the oxygen dependent parameter. This internally referenced parameter is detected by the oxygen meter avoiding common problems provided by intensity based measurements. This measurement technique enables long-term studies with low amount of samples and highly reliable data. Concentration levels of gaseous or dissolved oxygen can be detected in parts per million to parts per billion ranges.
Measurement results of oxygen ingress into several different treated PET bottles are presented using the novel technology. The PET bottles differ from its barrier coatings (internal and external), multi-layer design and inclusion of different amount of oxygen scavenger materials.

Deskriptors: Oxygen permeation, oxygen measurement, PET bottles

1 Introduction

During the last few years PET (Polyethylene Terephthalate) bottles have – especially in Germany – successfully displaced cans as packages for beer and soft-drinks [1,2]. Leading discounters and beverage wholesalers have recognised the huge market potential of PET bottles; others will follow this trend [3]. Contrary to glass, PET shows several unbeatable advantages in being non-breakable, light in weight, flexible in design and easy to be recapped. A serious disadvantage, however, is the insufficient gas barrier against oxygen ingress and loss of CO_2 due to the molecular structure of PET. Oxygen causes chemical processes decreasing the shelf life and flavour quality of the beer [4,5]. Further factors affecting the shelf life of the product are shown in figure 1.

Increase of the shelf-life of products filled in plastic containers can be achieved by reducing the oxygen ingress e.g. by using monolayer bottles coated with high–barrier material to the inside or outside of a bottle [6], by incorporating one or more high-barrier layers in a multilayer structure [7], and by applying oxygen scavenger materials incorporated in the bottle wall [8]. To determine the oxygen barrier improvement factor (BIF) compared to the non-treated bottle, precise measurements of oxygen permeation under real conditions are required.

Traditional analysing techniques do not guarantee real conditions or non-destructive measurements [9,10].

Mocon Ox-Tran technology (Modem Control Company) is well-known and often used as standard for measurements of oxygen permeability of packaging films but also of empty packages [11]. Still, this method is invasive and the investigated packages have to be connected permanently to the equipment. Since only two bottles per device can be measured, this leads to a low through-put and assembling a multi-channel set-up will result in high costs. Additionally, information about the permeation of oxygen into an empty package does not describe sufficiently the oxygen ingress into a filled bottle (e.g. with carbonised water). Hence, for shelf life determination it is recommended to investigate the bottles under real conditions.

In contrast to the Oxtran technology, the Orbisphere analyzer (e.g. ORBISPHERE serie 3600, www.orbisphere.de, Hach Ultra Analytics, Buford, GA) does measure under real conditions but destruction of the PET bottle is necessary. Hence, the same bottle cannot be analysed over the complete investigation time. Package integrity has been verified by analysing samples of a production lot using invasive tests on a statistical basis. Usually seven bottles should be pierced and analysed to obtain one single average value. Carbonated water is sampled directly from the bottles, by drilling the cap with a rigid pipe to obtain a continuous flow through the analysis cell. For each measurement value an immense quantity of bottles have to be investigated separately. Consequently, this method is very laborious, time consuming and unreliable because randomly occurring defects are not necessarily detected and not all leaking packages are therefore rejected.

A new analysing technique is the measurement with optical-chemical sensors commercially available by PreSens (www.PreSens.de) and OXYSense (www.oxysense.com) [12–14]. These sensors eliminate disadvantages of the above mentioned electrochemical measurement processes [15,16]. PreSens offers optical-chemical sensors with a detection limit of 1 ppb of dissolved oxygen which can measure oxygen ingress continuously, non-destructively and non-invasively under real conditions over a long period of time. A sensor spot is placed on the inner wall of the bottle, package, or container and a fibre optical probe is positioned on the outside enabling a non-invasive measurement. Piercing the package is not needed, accordingly, continuous control of individual packages is possible and fewer samples are needed, compared to the destructive method. The measurement is passive; it does not interfere with contents of the package and does not consume oxygen. First correlation measurements between the PreSens equipment and the Mocon Ox-Tran technology are performed and discussed in [16].

Authors: Christian Huber, Tuy-Anh Nguyen, Christian Krause and Achim Stangelmayer, PreSens Precision Sensing GmbH, Josef-Engert-Strasse 11, 93053 Regensburg, Germany; Heinz Humele, Krones AG, Böhmerwaldstraße 5, 93073 Neutraubling, Germany.

Tables and figures see Appendix

2 Experimental Details

Measurement principle: dynamic quenching of luminescence

The principle of measurement is based on the effect of dynamic luminescence quenching by molecular oxygen. The following scheme, presented in figure 2, explains the principle of dynamic luminescence quenching by oxygen.

Collision between luminophore in its excited state and quencher (oxygen) results in radiationless deactivation and is called collisional or dynamic quenching. During collision, energy transfer takes place from the excited indicator molecule to oxygen which consequently is transferred from its ground state (triplet state) to its excited singlet state. As a result, the indicator molecule does not show luminescence and the total measurable luminescence signal decreases.

Therefore, a relation exists between oxygen concentration in the sample and luminescence intensity as well as luminescence lifetime which is expressed by the Stern-Volmer-equation (1). Here, τ_0 and τ are luminescence decay times in absence and presence of oxygen. $[O_2]$ corresponds to the oxygen concentration and K_{SV} is the overall quenching constant.

$$\frac{\tau_0}{\tau} = 1 + K_{SV} \cdot [O_2]$$

$$\tau = f([O_2]) \qquad (1)$$

τ: Luminescence decay time in presence of oxygen

τ_0: Luminescence decay time in absence of oxygen

K_{SV}: Stern-Volmer constant (quantifies quenching efficiency and therefore sensitivity of the sensor)

$[O_2]$: oxygen content

The oxygen-meter uses a blue-green light source for excitation, modulated with a frequency of 4.5 kHz to illuminate the sensor. An optical polymer fibre is used as signal transducer and leads the emission light to a photodiode.

The technique measures the luminescence lifetime, an intrinsically referenced parameter, as the oxygen dependent parameter to avoid common problems with intensity based measurements:

(a) The decay time does not depend on fluctuations in intensity of the light source and sensitivity of the detector;

(b) The decay time is not influenced by signal loss caused by fibre bending or by intensity changes caused by changes in the geometry of the sensor;

(c) The decay time is, to a great extent, independent of the concentration of the indicator in the sensitive layer; Photobleaching and leaching of the indicator dye has no influence on the measuring signal;

(d) The decay time is not influenced by variations in the optical properties of the sample including turbidity, refractive index and coloration.

A trace oxygen sensor spot is located within the PET bottle and the opto-electronical instrument is placed outside. Excitation and emission of the fluorescent dye can be performed through the PET wall provided that the luminescence decay time and not the luminescence intensity is measured as the oxygen-sensitive parameter (see fig. 3). Therefore, it is possible to measure the interior oxygen concentration of the closed filled PET bottle online, in a non-invasive and non-destructive way. Optical chemical sensors measure both in liquid and in gaseous (headspace) phase. They perform through transparent materials up to a thickness of 10 mm and even through turbid packaging. Gaseous or dissolved oxygen levels can be detected in parts per million to parts per billion ranges to determine permeability. Technical data of the trace oxygen sensor spot type PSt6 obtained from PreSens is listed in table 1.

Materials

The set-up of an oxygen-ingress measurement using this technique is very simple and includes the following items (see fig. 4):

1) trace oxygen meter
2) light guide with the fixed metal fibre holder
3) oxygen-tight cap or any other tight closure
4) safety screw for fixing the oxygen tight cap
5) trace oxygen sensor spot
6) PET bottle

The complete set-up for oxygen ingress measurement (except PET bottle) can be obtained from PreSens (PreSens Precision Sensing GmbH, 93053 Regensburg, Josef Engert Str. 11, Germany). PreSens offers single-channel trace oxygen meter but also multi-channel oxygen meter (four and ten channel devices) enabling simultaneous online characterization of the bottles (see fig. 5).

In this study, the trace oxygen sensor spot type PSt6 (5) is placed onto the transparent closure (3) which was adapted to the respective PET bottle. Three seals ensure the gas tightness of the closure which was confirmed measuring oxygen ingress in an oxygen-impermeable “metal bottle” sealed with this closure. A safety screw (4) adapted to the bottle thread is used to fix the closure (3). The reading is achieved by screwing the polymer optic fibre integrated in a metal holder on the outside of the package directly above the trace oxygen sensor.

Alternatively the sensor spot can be glued into the PET bottle which then can be closed with a standard closure. For this direct coating, the bottles should be transparent but the measurement is even possible through slightly coloured (e.g. greenish or yellowish) or turbid bottles. An assortment of acceptable bottles is displayed in figure 6. Dark brown PET bottles, however, are not suited for direct sensor coatings since they act like a filter diminishing excitation and emission light. Fluorescence intensity detection would be too low affecting the fluorescence lifetime reading. In this case a transparent optical window has to be integrated e.g. by using a transparent closure (3).

Filling procedure and measurement conditions

To obtain reliable results it is recommended to perform oxygen ingress measurements under realistic conditions. Measurements with the final product (beer, fruit juice) would give the best simulation of the ‘real-life’ situation, but beer will react with oxygen (like a scavenger), which makes it impossible to measure barrier properties of the packaging. Thus, the best simulant for beer is oxygen-free carbonated water. Adding of alcohol is not required because the influence is negligible. A carbonation level of the water similar to beer (app. 3 g/l) should be used since the packaging will be pressurised, which could influence the barrier properties of the packaging and the growth of oxygen consuming bacteria is prevented.

The filling process of the bottles is performed in a nitrogen-flushed glove box (see fig. 7). The oxygen content within the glove box is guaranteed to be < 0.1% oxygen. PET bottles are filled with nitrogen-saturated carbonated water (concentration of dissolved oxygen < 10 ppb) using a dosing pump adjusting the respective filling volume. For carbonization (app. 3 g/l) a pressure tablet containing sodium carbonate, sodium hydrogen carbonate and citric acid is used. In order to avoid bacteria growth, which will lead to oxygen consumption, silver nitrate is added in a concentration of 0.2 mmol/l by diluting a 0.1 N silver nitrate solution (Fluka, Germany). The bottles are sealed with oxygen tight closures coated with the trace oxygen-sensor spot type PSt6. The safety screw was added to fix the cap. The oxygen content after the filling procedure was < 50 ppb dissolved oxygen. The filled PET bottles were placed on a shaker which was located in a climate oven. Since the oxygen permeation rate is strongly dependent on temperature and humidity, measurements were performed in a controlled environment at 30 °C and 50% relative humidity. The bottles were conditioned for one hour within the climate oven to adjust the temperature of the filling before starting the measurement. The bottles were shaken during the complete measurement to assure equilibrium state in headspace and liquid of the bottle. Up to 10 bottles were measured simultaneously using the OXY-10 trace device.

Bottles tested

Several different treated PET bottles listed in table 2 obtained by Krones AG in Neutraubling were investigated with respect to their oxygen ingress rates. Monolayer bottles with outside coating (Bottle type 1) and an additional active barrier (bottle type 2), inside coated bottles (Bottle type 3) and multilayer bottles composed of three layers (bottle type 4) were used for this investigation.

Calculation of the total oxygen and determination of the Barrier Improvement Factor (BIF):

After permeation through the wall of the packaging, the oxygen will partly dissolve in water and partly appear in headspace. To determine the permeation rate, the TOTAL OXYGEN ingress in the packaging should be calculated as described in [18,19]

In case two comparable bottles are tested (size, shape) but with different oxygen barrier layers, the BIF (=barrier improvement factor) can be calculated dividing the oxygen transmission rate (OTR) of the uncoated bottle by the OTR of the coated bottle. This factor shows the superiority of the coated package to the reference package.

3 Results and Discussion

In the following, the measurement results of different treated bottles and the respective measurement bottle, as listed in table 2, are discussed.

The characterisation will include monolayer bottles with an external coating and additional oxygen scavenger, monolayer bottles with an internal coating and multilayer bottles containing oxygen scavenger.

Bottle type 1: LC2 external coated PET bottles compared to an identical non-coated PET bottle

In figure 9, the oxygen ingress into the LC2 coated and into the respective reference PET bottle without coating are shown over a period of more than 25 days. In the first 48 hours the increase of the oxygen concentration in non-coated bottles and bottles with LC2 external coating is high and non linear. Two reasons for the increase are (a) a desorption stage, where the matrix oxygen, dissolved in the PET bottle wall migrates out of PET into the liquid and (b) the "steady-state" permeation stage, where oxygen molecules move from the high concentration side (atmosphere) through the PET bottle wall to the low-concentration side (product).

After the bottle is filled with carbonated oxygen-free water, the partial pressure on the inside wall of this bottle is considerably lower than the partial pressure on the outside wall which is still in equilibrium with air. Therefore, at the beginning of the measurement, externally coated PET bottles display similar oxygen ingress rates as non-coated reference bottles up to the point when a new equilibrium is established within the polymer. After the new equilibrium between the matrix oxygen and the oxygen concentration within the liquid in the PET bottle has been established, the oxygen ingress shows a linear increase over time, and the slope gives the oxygen ingress in ppb/d. The rate of permeation now depends on the barrier properties of the polymer materials. The LC2 barrier coating reduces the rate of permeation, resulting in a significantly decreased slope compared to the slope observed for non-coated PET bottles.

The concentration of the dissolved oxygen has to be measured over time, and the total oxygen can be calculated from the slope of the curve according to equation 2. The increase of oxygen is expected to follow a straight line, as long as the saturation value is not reached. The slope within the linear range gives the oxygen permeation in mg O_2/l/day = ppm/day (or µg O_2/l/day = ppb/day).

Maximum oxygen concentration allowed in beer is 1 mg/l product (=1000 ppb), since higher concentrations affects the flavour of the product. If the maximum allowed concentration is divided by the slope of the oxygen increase, the theoretical shelf-life can be calculated. Results (mean value of seven bottles) are presented in table 3.

A shelf-life of app. 53 days is not sufficient since usually a shelf-life of at least six months is demanded. The use of oxygen scavenger in this type of externally coated PET bottles is needed to protect the oxygen-sensitive product against matrix oxygen. Even if the barrier of the coating is very high this matrix oxygen will stay in the PET material. Depending on the barrier of the coating the amount of scavenger material has to be optimised.

Bottle type 2: PET bottles with LC2 external coating and/or different contents of oxygen scavenger

A main disadvantage of externally coated bottles is the desorption of oxygen from the bottle wall into the product. For an empty bottle (500 ml, weight 38g) stored in air (0.21 bar O_2), the amount of oxygen at standard conditions (20 °C) within the polymer matrix (solubility of oxygen in PET 0.076 ml(O_2)/[ml(PET)xbar]) can be calculated to 0.44 ml/g PET assuming a density of 1.365 g/ml for the PET [20,21]. The matrix oxygen dissolved in the PET bottle can be removed by adding an oxygen scavenger into the PET material (e.g. Amosorb DFC^{TM} PET/polybutadiene copolymer, blended with PET from BP), protecting the product against this initial increase of oxygen. The goal is to reduce the amount of scavenger to a technological and economical efficient minimum and reach a shelf-life of at least six months.

In figure 10 oxygen ingress into four different-treated PET bottles of the same type is shown.

The addition of 2% Amosorb scavenger to the PET bottle (see curve (A)) is removing the matrix oxygen content within the PET bottle minimising the oxygen ingress at the beginning. However, after 8 days there is a significant increase of oxygen which can be attributed to the fact that the oxygen scavenger is started to be consumed. After 20 days the oxygen scavenger is consumed and the slope of the oxygen ingress is identical to that of the non-coated reference bottle shown in figure 9.

In comparison, the oxygen ingress curve of an external LC2 bottle without scavenger is shown in this graph (see curve (B)). As mentioned above, the increase of oxygen is high at the beginning due to the unresisted permeation of matrix oxygen into the product which is in the range of 0.3 mg/l for this bottle type. After 48 hours the equilibrium between matrix oxygen and oxygen dissolved in the product is reached resulting in a linear slope. After 40 days, the oxygen ingress curve of the LC2 coated PET bottle without scavenger subtends that of the uncoated bottle with 2% scavenger. Nevertheless, the oxygen ingress into both bottle types is too high and the maximum allowed oxygen pick up of 1000 ppb at 30°C is reached before 180 days which should be the minimum storage stability.

A combination barrier system has been devised to meet these criteria by adding Amosorb™ DFC oxygen scavenger as active oxygen barrier to the PET layer of LC2-coated PET bottles. Due to the limited oxygen solubility within the LC2 external coating and its passive oxygen barrier properties the scavenger, located in the inner PET layer, is protected from ambient oxygen. This inner-layer scavenger (a) is reacting with oxygen that has permeated through the outside coating, and (b) is available to diminish the headspace and dissolved oxygen integrated by the filling process.

The barrier synergism of an external coating and the oxygen scavenger material added to the inner PET layer is depicted in the figure 10. Adding 1% scavenger to a LC2 coated PET bottle results in an oxygen ingress rate which is significantly below 1000 ppb over a period of six month (see curve (C)). The significant decrease of the oxygen ingress rate compared to the non-coated bottle with 2% scavenger (see curve (A)) is attributed to the oxygen barrier layer which protects the oxygen scavenger within the bottle from ambient oxygen. Only the oxygen molecules which are diffusing through the oxygen barrier layer are able to react with the scavenger resulting in a significant longer lifetime of the scavenger. Even after 180 days the scavenger is still active and the total oxygen ingress is clearly below 1000 ppb. Consequently, oxygen scavengers, which have not to be activated e.g. by humidity, should be protected from atmospheric oxygen otherwise they would be spent within a short time.

Reducing the scavenger content from 1% to 0.5% is resulting in increased oxygen ingress over a period of 180 days. Nevertheless, the total oxygen concentration after 180 days is still clearly below 1 ppm. Consequently, there still exists the possibility to decrease the amount of scavenger within the bottle without exceeding the limit of 1 ppm oxygen. This measurement technology enables a simple possibility to control oxygen ingress by reducing the scavenger content as long as a compromise between a sufficient gas barrier and an economical efficient minimum is reached.

Bottle type 3: actis internal coating compared to a non-coated reference bottle

As an alternative, inorganic coatings can be applied to the inside of the bottle after blowing. The Sidel Actis coating technology produces a thin layer of amorphous carbon, typically 100 to 200 nm thick, on the inside surface of the bottle. This is deposited from high-energy plasma of acetylene gas within a high vacuum environment. Oxygen ingress curves of an Actis coated bottle compared to an identical non-coated bottle are shown in figure 11. The inner coating provides an efficient barrier to oxygen, and prevents oxygen desorption from the PET bottle wall into the product during the first few days of storage contrary to external coated bottles. A BIF factor of 9.9 was determined by comparing the slopes of oxygen ingress of coated and non-coated bottles. For both bottle types the sampling rate was adjusted to 30 seconds and the mean value was taken from seven bottles.

Bottle type 4: multilayer bottle containing oxygen scavenger

As shown in figure 13, the combination of a multilayer structure adding an active barrier within the middle layer decreases oxygen ingress significantly, something that could not be accomplished with a multilayer structure without active barrier.

4 Conclusion

This study presents the results of measurements of the oxygen ingress into different treated PET bottles using a novel, non-invasive, non-destructive analysing method based on an oxygen dependent measurement of the luminescence decay time.

The goal of the study was to find out whether a shelf-life of 180 days with a total oxygen concentration (dissolved and headspace) of less than 1 ppm is feasible applying the different barrier technologies. It was shown that the amount of oxygen that will enter the product depends on the location of the coating (external, internal, embedded) and whether an oxygen scavenger is used or not. A shelf-life of 180 days was not achieved with externally coated bottles due to oxygen desorption out of the matrix material. The best performance is shown by those bottles which use an active barrier (scavenger) additional to the passive barrier which is also acting as protection layer to prevent the reaction of the scavenger with atmospheric oxygen. A shelf-life of more than 180 days can be reached even when the amount of scavenger has been reduced.

5 References

1. Hertlein, J.; Bornarova, K.; Weisser, H.: Eignung von Kunststoffflaschen zur Bierabfüllung, Brauwelt **137**, no. 21/22, (1997), pp. 860–866.
2. Brody, A.L.: The plastic beer package: Why, how, but when?, Brew. Dig. **61**, (1986), pp. 12–17.
3. Unkrig, G.; Bartnick, H.: Aldi setzt auf Bier in PET, Neue Verpackung **11**, (2003), pp. 20–26.
4. Miedaner, H.: Praktikum Geschmacksstabilität, Brauwelt **131**, no. 27, (1991), p. 1181.
5. Miedaner, H.; Narziß, L.; Eichhorn, P.: Einige Faktoren der Geschmacksstabilität – sensorische und analytische Bewertung, Proceedings of the 23th Congress Lissabon 1991 of the European Brewery Convention, Oxford: Oxford University Press, (1991), pp. 401–408.
6. Briem, J.: Die Bombe ist geplatzt, Verpackungs-Rundschau **50**, no. 6, (1999), pp. 42–43.
7. Bichler, M.; Klotz, B.: Multilayer-Preforms, Kunststoffe **87**, no. 10, (1997), pp. 1290–1298.
8. Müller, K.: O_2-Durchlässigkeit von Kunststoffflaschen und Verschlüssen – Messung und Modellierung der Stofftransportvorgänge (Diss.), TU München, Lehrstuhl für Brauereianlagen und Lebensmittel-Verpackungstechnik, 2003.
9. Howard, G. A., Mawer, J. D. R.: The determination of dissolved oxygen in beer, J. Inst. Brew. **83**, (1977), pp. 144–152.

10. Demorest, R. L0.: Measuring oxygen permeability through today's packaging barriers, J. Pack. Technol., Oct./Nov., (1989), pp. 222–226.
11. DIN 53380 T 3: Prüfung von Kunststoffen; Bestimmung der Gas-durchlässigkeit; Sauerstoffspezifisches Trägergasverfahren zur Messung an Kunststoff-Folien und Kunststoff-Formteilen, Edition July, (1998)
12. Draaijer, A.: Optical sensor for measuring oxygen, WO0163264, (2001), pp. 08–30
13. Draaijer, A.; König, J. W.; De Gans, O., Jetten, J.; Douma, A.C.: A novel optical method to determine Oxygen in Beer Bottles, EBC Congress 1999, Cannes France, (1999)
14. Orzinski, M.; Weber, I.; Schneider, J.: New Conclusions in Measurements of Permeation through Plastic Bottles and Closures, World Brewing Congress, San Diego, (2004)
15. Orzinski, M.; Weber, I.; Schneider, J.: Hohe Genauigkeit und gute Reproduzierbarkeit, Permeationsmessung an der VLB Berlin, Brauindustrie **11**, (2004), pp. 66–71
16. Lundquist, L.; Pelletier, C.; Wyser, Y.: Oxygen permeability – Oxygen transmission rate measurement using oxygen sensitive fluorescent tracers, Verpackungs-Rundschau **11**, (2004), pp. 69–72
17. Vilacha, C.; Uhlig, K.: Die Messung niedriger Gesamtsauerstoffgehalte im abgefüllten Bier, Brauwelt **124**, no. 18, (1984), pp. 754–758
18. Pfenninger, H.: Brautechnische Analysenmethoden, Freising-Weihenstephan: Selbstverlag der MEBAK (Mitteleuropäischen Brautechnischen Analysenkommission), Band 2, (1993)
19. Dörr, C.: Polyesterflaschen für die Bierabfüllung I und II, Brauwelt **142**, no. 30, (2002), pp. 1044–1048 and no. 34/35, (2002), pp. 1196–1198
20. Dörr, C.: Untersuchung der Eignung von Kunststofflaschen für die Bierabfüllung (Diss.), TU München, Lehrstuhl für Brauereianlagen und Lebensmittel- Verpackungstechnik, (2003)

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Appendix

Table 1 Technical Data of the PSt6 type sensor spot

	Dissolved Oxygen	**Gaseous & Dissolved Oxygen**
Measurement range	0–1.8 mg/l (ppm) 0–56.9 µmol	0–20 % air-saturation 0–4.2 % oxygen-saturation 0–41.4 hPa
Limit of Detection (LOD)	1 ppb of dissolved oxygen	0.01 % air-saturation 0.002 % oxygen
Resolution at 20 °C and 1013 hPa	1 ± 0.30 µg/l (ppb) 10 ± 0.40 µg/l (ppb) 100 ± 0.50 µg(l (ppb) 1000 ± 4.0 µg/l (ppb)	0.002 ± 0.0007 % oxygen-saturation 0.02 ± 0.0009 % oxygen-saturation 0.2 ± 0.0015 % oxygen-saturation 2.0 ± 0.09 % oxygen-saturation
Accuracy (20 °C)	3% of the respective concentration	
Response time	<40 s; (<60 s with optical isolation)	<10 s; (<15 s with optical isolation)
Calibration	Conventional two-point calibration in oxygen-free environment (nitrogen) and a second calibration value, optimally between 1 and 2 % oxygen	
Temperature range	–10 to 50 °C	
Long-term stability	**100,000 data points** without drift	

Table 2 Bottle types investigated

		Coating	Weight	Volume	Scavenger
Bottle type	**1a**	No	38	500	No
	1b	LC2[a]	38	500	No
Bottle type	**2a**	No	38	500	2%
	2b	LC2	38	500	0%
	2c	LC2	38	500	1%
	2d	LC2	38	500	0.5%
Bottle type	**3a**	No	31	500	No
	3b	Actis™	31	500	No
Bottle type	**4b**	three layers	28	500	No
	4b	three layers	28	500	Yes

[a]) Double Liquid Coating consists of an oxygen barrier layer (polyvinyl alcohol) and a second, water and highly scratch resistant layer composed of a Nano-Varnish.

Table 3 Shelf-life increase of LC2-coated bottles

	LC2-coated	non-coated
Total bottle volume [ml]	518.00	518.00
Liquid [ml]	495.30	496.40
Headspace [ml]	22.70	21.60
Headspace [%]	4.58	4.35
Temperature [°C]	30.00	30.00
Z-value	2.64	2.55
Slope for dissolved O_2[a] [ppb/day]	7.13	38.33
Slope total O_2 [ppb/day]	18.80	97.90
Calculated shelf-life (days)	53.19	10.21
Average BIF	**5.21**	

[a]) The sampling rate was adjusted to 30 seconds; this value is the mean value of seven bottles

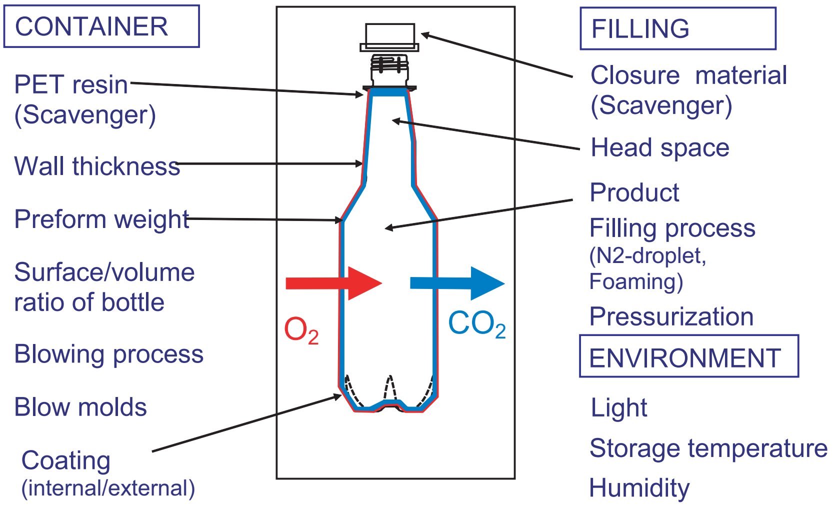


Fig. 1 Factors affecting the shelf life of the product filled in a PET bottle

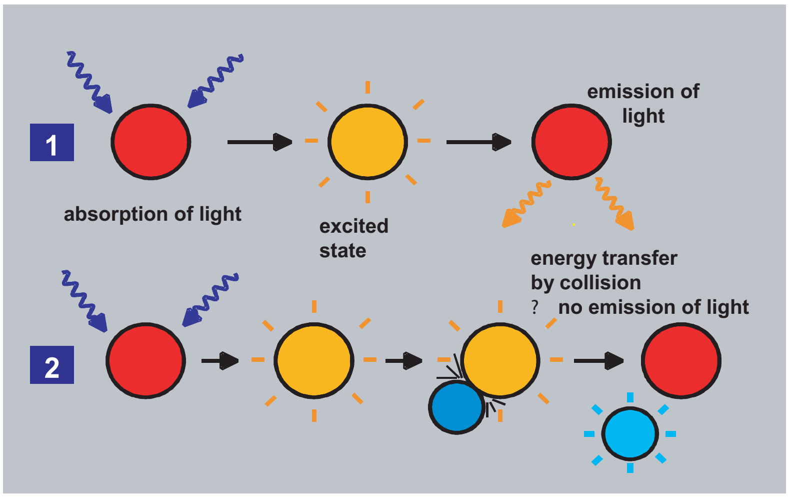


Fig. 2 Principle of dynamic quenching of luminescence by molecular oxygen
(1) Luminescence process in absence of oxygen
(2) Deactivation of the luminescent indicator molecule by molecular oxygen

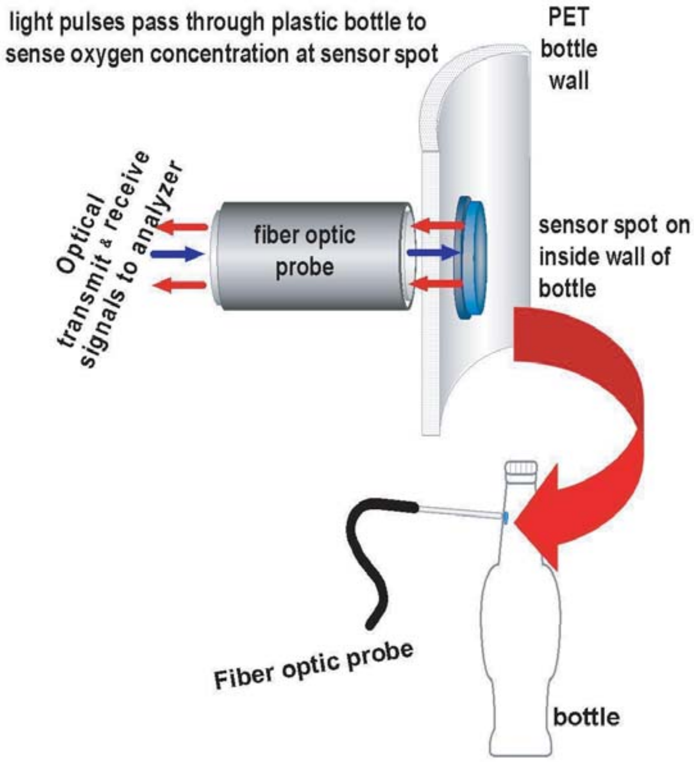
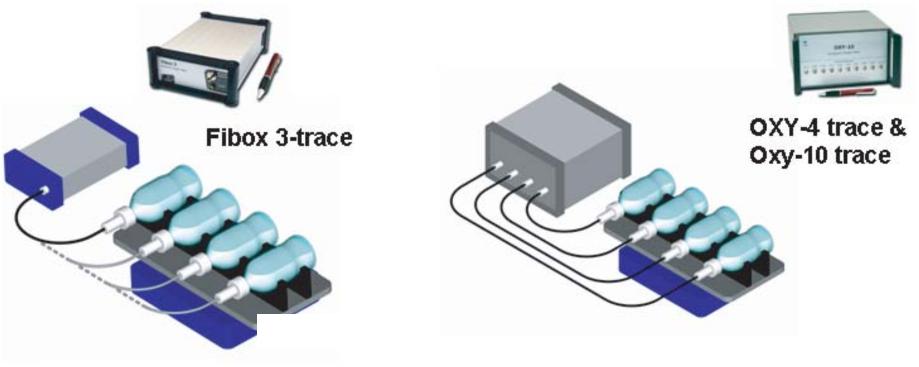


Fig. 3 Schematic presentation of non-invasive and non-destructive measurement of oxygen ingress into PET bottles

1 trace oxygen meter
2 light guide with the fixed metal fibre holder
3 oxygen-tight cap or any other tight closure
4 safety screw for fixing the oxygen tight cap
5 trace oxygen sensor spot
6 PET bottle

Fig. 4 Materials needed to perform oxygen ingress measurements



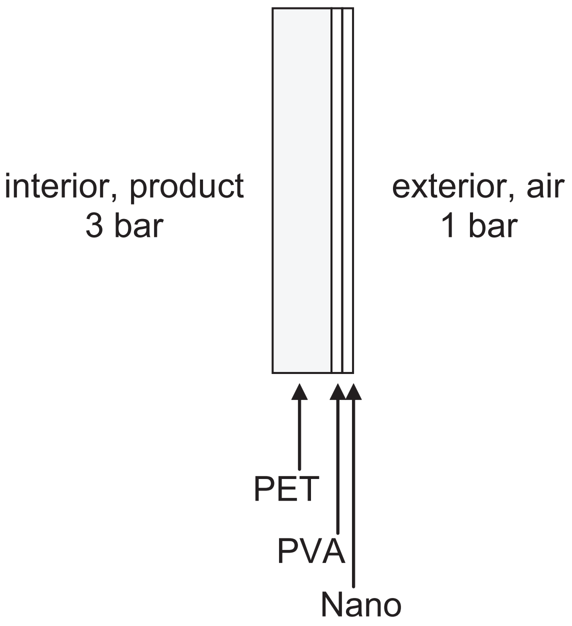
Subsequent measurement of Bottles

Simultaneous measurement of 4 or 10 Bottles

Fig. 5 Single-channel and multi-channel measurement set-up

Fig. 6 Acceptable bottle types for optical measurements

Fig. 7 A glove box filled with nitrogen is used for filling



The LC2 Coating (Double Liquid Coating) from Krones AG is a coating spread on the outside of the bottle. As shown in Figure 8, the first added layer consists of a poly-vinyl-alcohol layer (PVA) which is responsible for the oxygen barrier. Due to the water solubility of the PVA barrier coating, a second, water and highly scratch resistant layer composed of a Nano-Varnish is used as protection layer. Both coating layers have a thickness of app. 2 µm, providing a tough film, robust to filling and handling conditions.

Fig. 8 Composition of the external LC2 coating

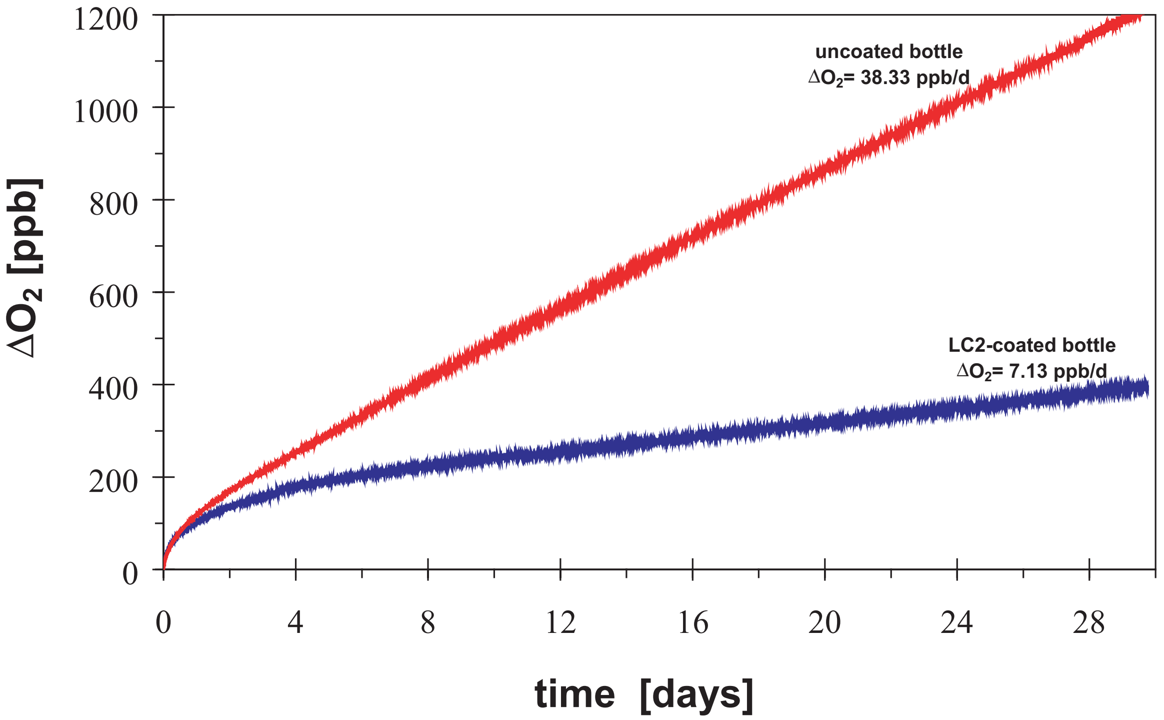


Fig. 9 Oxygen ingress into an externally LC2 coated PET bottle compared to the respective non-coated reference bottle

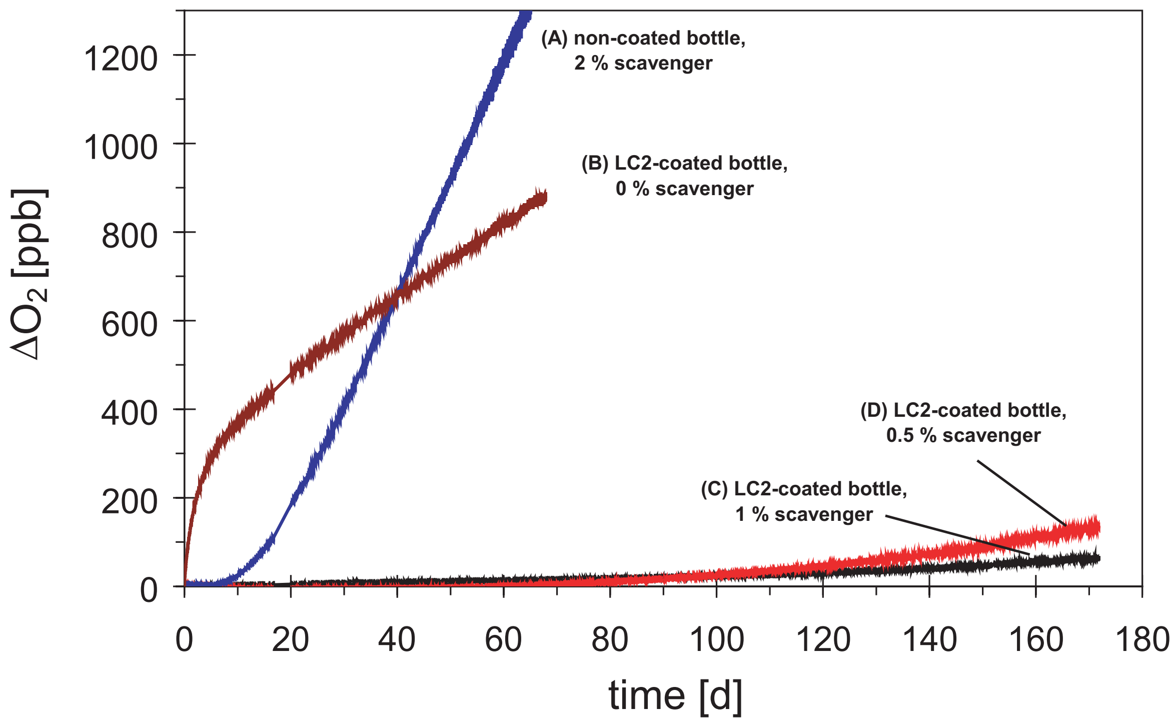


Fig. 10 Oxygen ingress into different treated PET bottles of the same type; (A) non-coated PET bottle with 2% scavenger, (B) LC2 coated PET bottle with no scavenger, (C) LC2 coated PET bottle with 1% scavenger, (D) LC2 coated PET bottle with 0.5 % scavenger. The combination systems (C) and (D) maintain the oxygen ingress to less than 1 ppm over six months, something that could not be accomplished with the active (scavenger, (A)) or passive barrier (LC2 coating, (B)) alone. The sampling rate was adjusted to 30 seconds

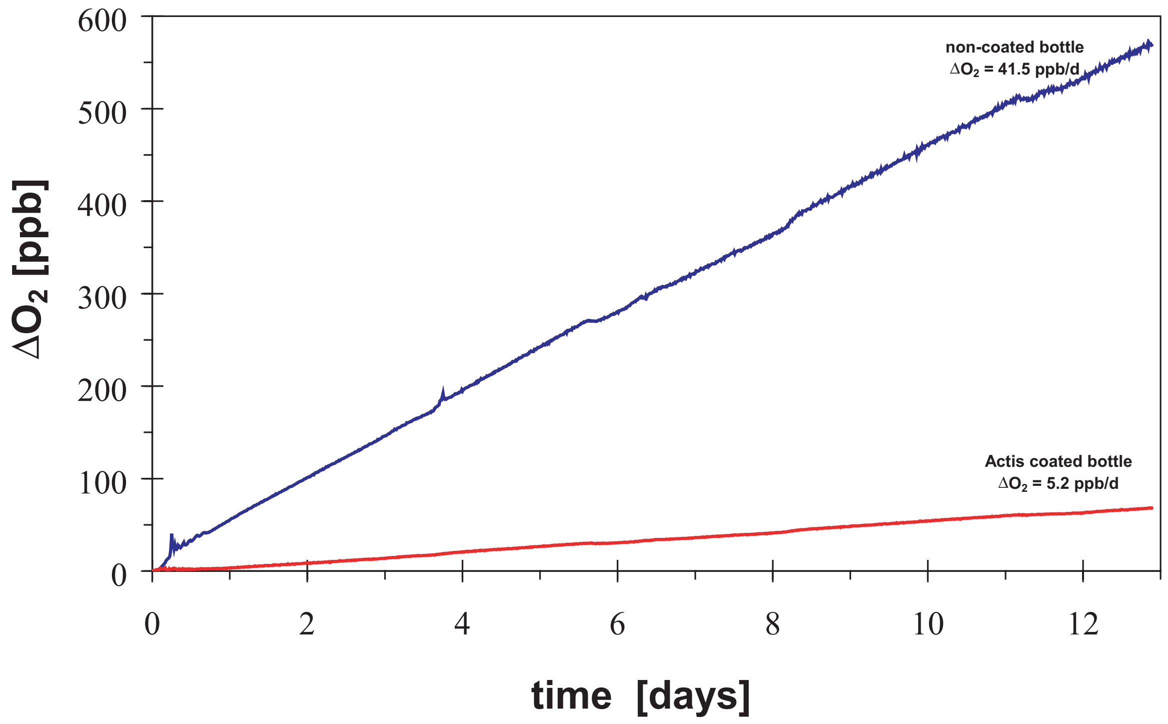
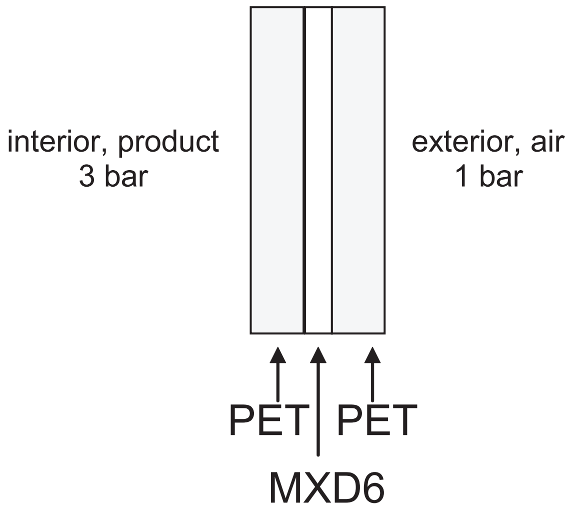


Fig. 11 Comparison of oxygen ingress into an Actis coated bottle and the respective non-coated reference bottle



The multilayer technology consists of a thin (3-10%) layer of high barrier plastic embedded within at least two layers of structural plastics.

Most common multilayer structures combine two layers of PET and a middle layer of Nylon MXD6 (metaxylylene diamine nylon) in three layer structures (see Figure 12). The high barrier material is present in separate layers which are made by simultaneous or sequential co-injection. The embedded barrier layer is also protected from abrasion and does not have direct contact to the product which is advantageous over exterior and interior coating technologies.

To extend the shelf-life by decreasing the oxygen ingress rate an oxygen scavenger can be embedded in the middle polyamide layer which reduces the level of oxygen present in PET walls and impedes its passage.

Fig. 12 Common multilayer structure

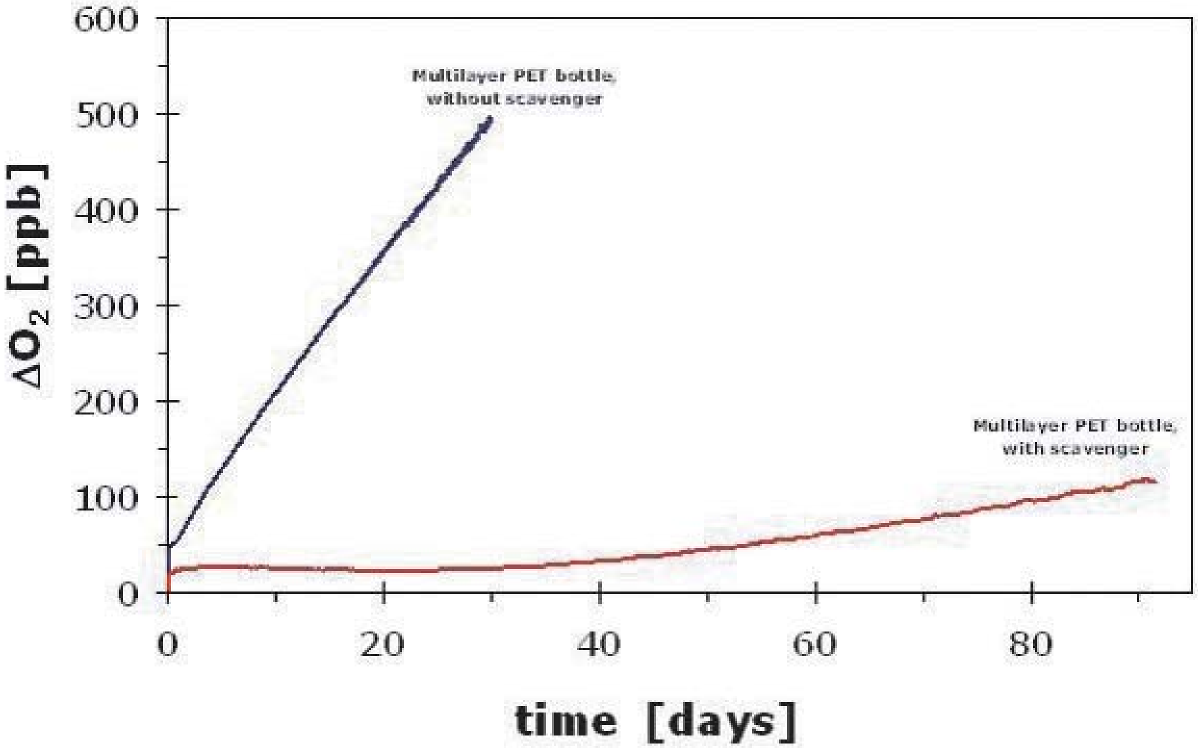


Fig. 13 Oxygen ingress in multilayer bottles; (A) without active barrier, (B) multilayer bottles containing proprietary sca vengers in the polyamide inner-layer. The sampling rate was adjusted to 30 seconds