

## **Oxygen Transmission Rate Measurement Using Oxygen Sensitive Fluorescent Tracers**

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### **Abstract**

Measurement of oxygen transmission rate through finished packaging by the use of Fibox fluorescent tracer technology is evaluated against reference values obtained on a Mocon Oxtran 2/20 MH. The Fibox has the advantage of allowing samples to be dissociated from the measurement device. This permits running a large number of specimens simultaneously. In addition, the oxygen sensitive foils used are temperature resistant up to 130°C, thus permitting measurement of oxygen uptake during retorting.

A method for intermittent measurement of oxygen partial pressure in gaseous headspace of nitrogen flushed beverage bottles is presented. A metal bottle closure integrating an oxygen sensitive foil was developed and characterised in terms of its permeability to oxygen. The evolution of the gross oxygen transmission rate (GOTR), i.e. the total oxygen transmission rate of the sample, including the bottle closure, with the time of measurement was investigated for three different sensor foil calibration routines: individual calibration of sensor foils, the average values from individual calibration and the values supplied on the factory calibration sheet delivered with the sensor foil. After 27 days of measurement using individual sensor spot calibration the GOTR's measured on the Fibox were found to overshoot the Oxtran results of 0.0068 and 0.0027 cc/(pack·day) by 36% and 106% for high and very high barrier bottles respectively. The OTR values for the three calibration routines, i.e. deducing the bottle closure permeability from GOTR, can be considered equal to Oxtran results for all three calibration routines. Statistical analysis of means and variances showed that the use of individual calibration values resulted in equal performance as the reference method after 11 days of measurement, whereas the average calibration value as well as the factory calibration only reached equal performance to the reference method after the full measurement period of 27 days. The labour intensity and the time frame within which reliable results can be obtained is higher than that of the reference method. Nevertheless, although currently not yet at par with the measurement performance of the reference method, the Fibox shows interesting potential, especially for laboratories with a limited financial resources, and will with further experience and development become a viable alternative for oxygen transmission rate measurements.

### **Introduction**

Mocon Oxtran technology is arguably the most widespread equipment used nowadays to measure the oxygen permeability of packaging films and finished packs. The test is invasive, and investigated samples are thus connected permanently to the equipment during the entire period of testing. Whereas sample preparation and the testing time required to obtain reliable results is reasonably short, e.g. 2-3 days, this technology presents a few drawbacks. Despite the fact that results are obtained in short time, the fact that only two samples can be tested per piece of equipment accounts for a reasonably low through-put. Increasing throughput can only be achieved by acquisition of additional units, which is associated with relatively high cost. Whereas testing under varying conditions of temperature and relative humidity is possible with such equipment by means of dedicated climatic chambers, they do not permit attaining conditions of harsh processing steps such as retorting.

An additional disadvantage with Oxtran equipment is that the permeability of finished packs can only be measured by means of a sample-mounting device, which has its own inherent permeability or tightness. In a case such as a beverage bottle mounted onto a metal plate by means of an epoxy seal, the permeability to oxygen of the seal can most likely be considered to be close to zero, or at least negligible compared to the permeability of the tested specimen itself. In other cases, such as a bottle with bottle closure, or flexible packaging, mechanical clamps equipped with rubber washers ensure tightness. Such a device is not necessarily oxygen tight and its permeability

would ideally have to be characterised separately and deduced from the measurement value in order to get reliable results.

Whereas a permeability value on a film or a bottle without its cap gives a performance indication to the user this value is not as useful as a permeability value of the finished pack would be. In the case of high-barrier bottles, the permeability of the bottle cap may contribute significantly to the overall permeability of the pack and it should thus ideally be tested with its closure as it is assembled in the manufacturing process in order to be of maximum utility with respect to its final application.

One potential alternative capable of measuring oxygen transmission rates on samples dissociated from the measuring device, while permitting measurement of the finished pack as a whole without the use of complicated sample mounting devices is the use of oxygen sensitive fluorescent tracers [1-5]. Several systems exist on the market and are used for measurement of oxygen concentration in permanent gases as well as in liquids. This technology is based on the quenching of luminescence of a luminophore by molecular oxygen. The luminophore can either be present on the tip of an optical fibre, or be embedded in a sensor spot, which can be attached onto the interior surface of a package. The latter has the advantage of making it possible to dissociate the investigated package from the measurement device, thus theoretically permitting an unlimited amount of specimens to be analysed simultaneously by means of intermittent measurements. By illumination with a light source the luminophore is excited and emits light until it encounters a molecule of oxygen. The luminescence life time and intensity is mathematically related to the oxygen concentration through the Stern-Volmer equation [6;7].

The only requirement on the packaging material for intermittent measurements by oxygen sensitive fluorescent tracers is that at least a portion of the packaging wall be capable of transmitting the light wavelength which is inherent to the source of illumination, or that a transparent surface on which the oxygen sensitive luminophore is attached can be integrated into the package prior to or in conjunction with its sealing. In the case of opaque packaging, these techniques will thus encounter the same problems as those encountered with flexible packaging using conventional equipment.

The overall goal of the project, of which the present study constitutes the initial part, was to first evaluate the performance of the fluorescent tracer technology against a well-established reference method, in our case Mocon Oxtran technology, second to develop a measurement methodology permitting the measurement of oxygen transmission rates on flexible as well as rigid packaging during harsh conditions such as retorting. The first step of the project, which will be presented in the following, thus details the development of an intermittent measurement methodology using oxygen sensitive fluorescent tracers on nitrogen flushed rigid packaging dissociated from the measuring device and the evaluation of the results against measurements performed using Oxtran technology.

## **Experimental**

### **Samples**

Two types of 0.5 L PET beverage bottles with Actis Lite™ and Actis™ treated interior surfaces, henceforth referred to as “L” and “A”, supplied by Sidel, le Havre, France, were used for this investigation. The treatment consists in plasma coating of the bottle interior with highly hydrogenated amorphous carbon. The L bottle has barrier properties suitable for, e.g. juices, teas and sparkling water, whereas the A bottle has very high barrier properties, and is intended for extremely oxygen sensitive products, such as beer and ciders.

### **Oxtran reference method measurements**

Oxygen transmission measurements were performed according to ASTM F1307-02 using a Mocon Oxtran MH 2/20. The bottles were glued onto metal sample holders using epoxy glue as depicted in Fig. 1. After connection to the apparatus they were conditioned during 24 hours at  $23\pm 1$  °C,  $50\pm 2$  % RH prior to testing. Testing was performed under the same climatic conditions. Ambient air was used as the test gas. The carrier gas composition was 98% nitrogen and 2% hydrogen. Gas flow was regulated at 25 ml/min. Five cycles of measurements were performed

without individual zeroing. The analysis time of each cycle was 50 min. The used instrument has an integrated pressure transducer and automatically corrects the measurement values to a sea-level pressure of 1013 mbar with the pressure reading at the time of measurement. The tests were performed by Ecole d'Ingénieur du Canton de Vaud (EiVd), Yverdon, Switzerland.



**Figure 1:** Oxttran bottle mounting set-up.

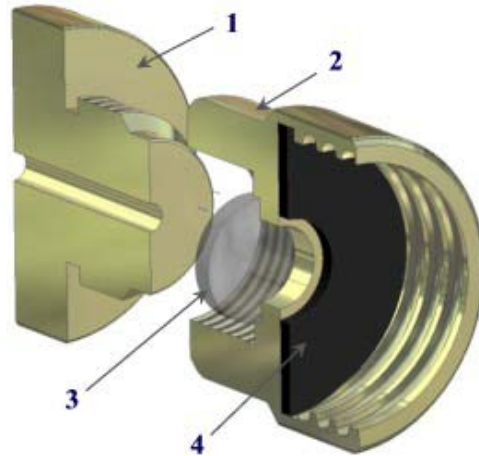
### Fluorescent Tracer (FT) Measurements

**Equipment.** A Fibox 3 fiber-optic oxygen meter supplied by PreSens Precision Sensing GmbH, Regensburg, Germany, was used for the fluorescent tracer measurements. The Fibox 3 measures the luminescence decay time of an immobilized luminophore. The luminophore is excited with a sinusoidal intensity-modulated monochromatic light and its decay time causes a time delay in the light signal emitted by the luminophore. This decay time, or phase angle,  $\Phi$ , decreases in the presence of oxygen. According to the equipment supplier the measurement of luminescence decay time presents numerous advantages to intensity-based measurements using fluorescent tracers, namely:

- Independence of intensity fluctuations in the light source as well as of detector sensitivity;
- Insensitivity to signal loss induced by fiber bending or intensity changes provoked by changes in sensor geometry;
- Independence to a great extent of the concentration of luminophore in the sensitive layer, and thus independence of the measurement signal on photobleaching.

The decay time is not influenced by variations in sample optical properties, e.g. turbidity, refractive index and coloration [6].

Planar oxygen sensitive MEF14 foils integrated in stainless steel bottle closures, as depicted in Fig. 2, designed for the purpose of the measurement, were used for the intermittent measurements of oxygen partial pressure in the bottles. The bottle closures consist in four parts. The optical fiber guide, annotated as 1 in the figure, which also shuts out incident light, having a detrimental effect on the measurements, holds the optical fiber in place during the measurement. The bottle closure (2) has a PCO 28 threading to fit the investigated bottle samples. A glass center piece (3) with the MEF14 foil, glued onto it with a non-interfering silicon glue, is fitted into the slot in the bottle closure and an epoxy resin is cast around it to the height of the glass surface to form an oxygen tight seal. A rubber washer (4) is fitted into the bottle closure in order to form a tight seal against the bottle brim. In the experiments the rubber washer used was made from natural rubber.



**Figure 2:** Stainless steel bottle closure with optical fibre guide (1), closure (2), glass substrate for oxygen sensitive foil (3) and rubber washer (4).

**Sensor foil calibration.** The sensor foils are calibrated using a conventional two-point calibration with temperature compensation. The calibration set-up, depicted in Fig. 3, allows controlling the gas pressure in the headspace of the bottle closure holder in order to have constant pressure regardless of atmospheric pressure variations between calibrations. A pressure transducer is connected to the headspace in order to permit recording the gas pressure used for the calibration. In this case nitrogen gas was used for the zero reading and a gas containing  $2.01 \pm 0.04$  % oxygen was used for the second calibration point. The calibration was performed at a pressure of 950 mbar.



**Figure 3:** Calibration set-up showing gas inlet (1), pressure transducer connection (2), bottle closure holder (3), and flowmeter (4) permitting pressure control for the calibration and pressure display (5).

A calibration sheet is also delivered with the sensor foil. If no means of calibration are available, these values can be used. The factory calibration of the sensor foil used was performed at an atmospheric pressure of 995 mbar at  $20^{\circ}\text{C}$  using pure nitrogen and a gas of 6% oxygen air saturation. The corresponding phase angles were  $67.7^{\circ}$  and  $28.27^{\circ}$ . The equipment supplier nevertheless recommends a specific calibration at the place of measurement. In total the effect of three different calibration routines, individual calibration values for each bottle closure, the average value of 19 individual bottle closure calibrations and the values from the factory calibration sheet, were evaluated. The

recorded phase angles of the bottle closures as well as the average values of the calibration are represented in Table 1. The advantage of using average values, such as the factory calibration or the average of several sensor spot calibrations, is strictly practical in the sense that it avoids having to enter new calibration values when changing the specimen and thus the risk of erroneous entries associated with this. At any rate, the data file contains information on the entered calibration values, which permits at any time to go back and verify the validity of the calibration used for each single measurement.

**Table 1:** Two-point calibration values for oxygen sensitive foils in bottle closures.

Oxygen concentration [%]	0%		2.01%	
Cap#	Phase angle [°]	T [°C]	Phase angle [°]	T [°C]
1	66.54	23.2	19.06	23.2
2	66.51	23.2	19.49	23.2
3	66.50	23.2	19.17	23.2
4	66.58	23.2	19.02	23.2
5	66.66	23.2	19.08	23.2
6	66.56	23.2	18.93	23.2
7	66.82	23.2	19.07	23.3
8	66.02	23.2	19.10	23.2
9	66.05	23.2	19.80	23.2
10	65.72	23.2	19.14	23.2
11	66.40	23.2	18.88	23.3
12	66.73	23.3	19.31	23.3
13	66.20	23.2	19.31	23.3
14	66.60	23.3	19.11	23.3
15	64.50	23.2	20.64	23.2
16	64.39	23.0	20.02	23.0
17	65.08	23.2	20.23	23.2
18	66.82	23.2	19.14	23.2
19	66.91	23.3	19.11	23.2
<b>AVG</b>	<b>66.19</b>	<b>23.2</b>	<b>19.35</b>	<b>23.2</b>

**Measurement procedure.** Prior to measurements bottles were placed in a vacuum chamber with the closures loosely screwed onto the neck. The vacuum chamber was flushed three times with nitrogen with intermediate vacuum of a pressure of approximately 1 mbar. The initial oxygen partial pressure in the headspace of the gassed bottles was thus in the vicinity of 3.5 mbar. The atmospheric pressure at the moment of bottle gassing was recorded to the nearest mbar using a Cerabar PMC 130 pressure gauge. The inner pressure of the bottle is required in order to calculate the volume of oxygen in the container since the measurement device measures a concentration.

In contrast to the reference method, the fluorescent tracer method does not consume the oxygen entering the tested membrane, i.e. the concentration of oxygen inside the tested pack will increase with time. It is well known that the rate of transfer,  $F$ , in the steady state, of a chemical species through a given membrane of permeability,  $P$ , is proportional to the partial pressure difference  $p_1-p_2$ , between the two sides of the membrane as  $F = P(p_1-p_2)$  [8]. The measured rate of transfer at a given moment must thus be normalized with the actual partial pressure inside the container in order to give a correct value of the permeability. The partial pressure increase during a typical test period, however, only gives rise to a change in driving force for permeation of approximately 0.1-0.2 % and was consequently not applied to the measurement results.

The testing conditions were  $23 \pm 1$  °C and  $50 \pm 2$  % RH. Six specimens were tested per sample. The samples were conditioned for 24 hours prior to testing. Measurements were made at varying intervals during 12 days with

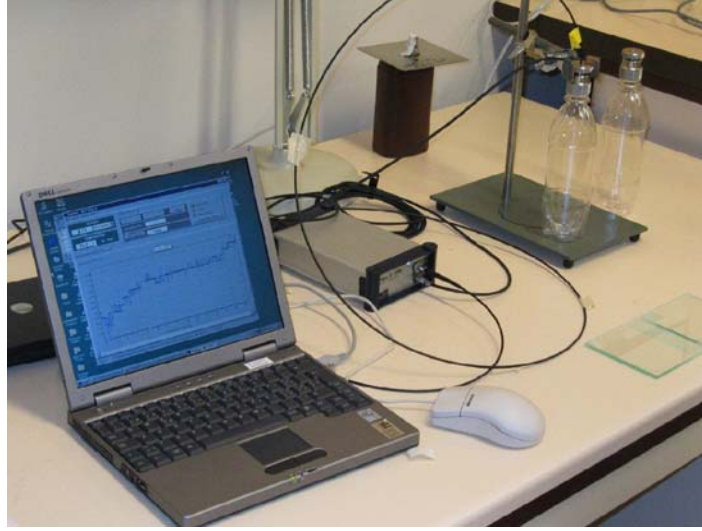
interruptions during weekends. A last measurement was made after 27 days in order to evaluate the evolution of the measurement value and its dispersion with time. The atmospheric pressure was recorded at each measurement and the average of the pressures recorded during measurements was used to normalize the resulting OTR values to the sea-level pressure of 1013 mbar.

Due to the presence of the rubber washer forming the seal between the bottle closure and the bottle brim the bottle closures cannot be considered as impermeable to oxygen. The oxygen transmission rate values obtained are thus constituted by the contribution of the bottle itself as well as of the bottle closure. This value will hereafter be referred to as the gross oxygen transmission rate (GOTR) and is not comparable to the reference method, which yields a value representative of the bottle alone.

The permeability of the bottle closures was evaluated by measuring the oxygen transmission rate of the bottle closure mounted onto a threaded stainless steel container with a brimful headspace volume of 15 cc as depicted in Figure 4. Six different washers were tested per sample on one and the same bottle closure. In addition to the natural rubber washer used for the present measurements fluoroelastomer washers were also evaluated. The oxygen partial pressure in the headspace of the stainless steel container was measured twice a day during a period of approximately 7 days. In all other aspects the measurement procedure was the same as that used for the bottle samples. The complete experimental set-up is depicted in Fig. 5.



**Figure 4:** Bottle closure permeability measurement device.



**Figure 5:** View of the fluorescent tracer set-up during measurement.

The partial pressure measurements [mbar] were made at an acquisition rate of 1/s with dynamic averaging of four values. The average of the ten consecutive measurements following an initial acquisition period of 90 seconds were used as the measurement value. The atmospheric pressure at the time of measurement was recorded to the nearest mbar and entered into an Excel® spreadsheet. The oxygen volume,  $V_{O_2}$  [cc], was calculated as:

$$V_{O_2} = \frac{P_{O_2} \cdot V_b}{P_G} \quad (1)$$

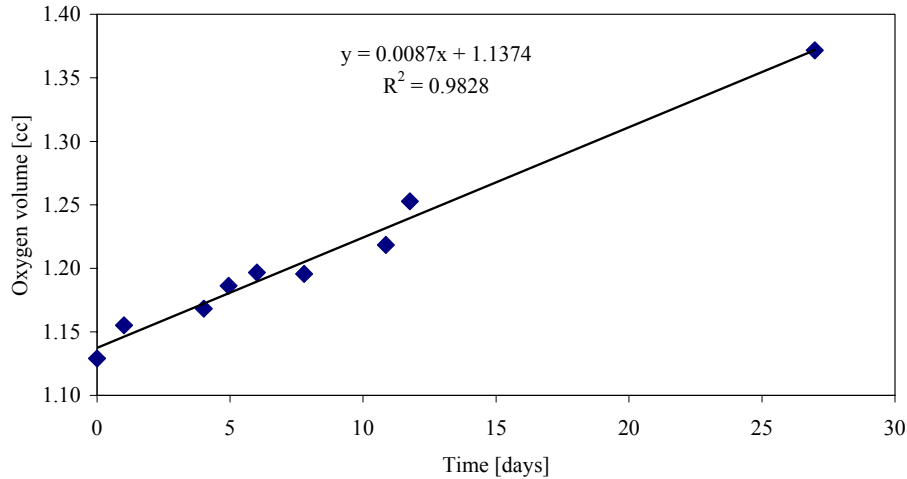
where  $P_{O_2}$  is the measured partial oxygen pressure [mbar],  $V_b$  the brimful bottle volume [cc], and  $P_G$  the pressure in mbar at the time of sealing of the nitrogen flushed specimen.

As the FT equipment measures relative oxygen content and not absolute, the volume of the bottles has to be known. The brimful bottle volume was evaluated by gravimetric measurement of bottles filled with degassed demineralised water. The weighing was performed in a climatic chamber at 20°C and 65% RH. The water used for the weighing was conditioned to temperature during 48 hours prior to weighing. The bottle volumes were calculated according to

$$V_b = \frac{M_w}{\rho_w} \quad (2)$$

where  $M_w$  is the weight of the water in grams and  $\rho_w$  the density of water at 20°C, i.e. 0.99823 g/cc [9]. A total of ten bottles were measured per specimen. The volumes of the bottles were found to be 518.77 (SD 0.23) cc and 518.80 (SDP 0.34) cc for the L and A bottles, respectively.

The recorded oxygen volume was plotted against time in days, whereupon a linear regression was applied to the data points as depicted in Fig. 6. The slope of the linear regression was then normalised to a sea level atmospheric pressure of 1013 mbar using the average value of the atmospheric pressure readings during the measurements to yield the GOTR value in cc/(pack·day). The same procedure was applied to the measurements of bottle closure permeability.



**Figure 6:** Oxygen volume in bottle headspace as a function of time for one specimen of bottle type “A”.

## Results and Discussion

### Reference OTR Values

The OTR values obtained by measurement using the Oxtran equipment are displayed in Table 2. The relative standard deviation of the mean (RSD) for the L bottles is approximately 5%, whereas that of the A bottle is 29%.

**Table 2:** Oxtran oxygen transmission rate measurement results for Sidel L and A beverage bottles (\*standard deviation of the mean, \*\*relative standard deviation of the mean).

Sample	Transmission rate [cc/(pack·day)]	
	L	A
	0.0063	0.0028
	0.0071	0.0016
	0.0068	0.0029
	0.0070	0.0034
<b>AVG</b>	<b>0.0068</b>	<b>0.0027</b>
<b>SD*</b>	<b>0.0004</b>	<b>0.0008</b>
<b>RSD**</b>	<b>0.05</b>	<b>0.29</b>

### Fluorescent Tracer OTR Results

**Bottle closures.** The OTR of the bottle closure in conjunction with natural rubber washers was found to amount to 0.0023 cc/(pack·day) with a standard deviation of the mean (SDP) of 0.0002 cc/(pack·day). The fluoroelastomer washers were found to exhibit a much lower permeability of 0.0006 cc/(pack·day) with a SDP of 0.0002 cc/(pack·day). It is believed that the use of the fluoroelastomer washers will improve method performance. For all regressions the correlation factor,  $R^2$ , was higher than 0.98 and the residuals were randomly distributed, suggesting that the assumption of linearity is correct.



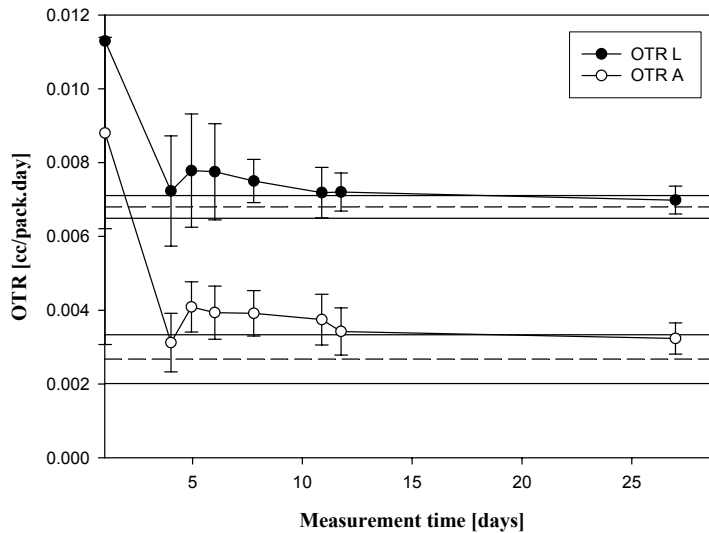
**Bottles.** The gross oxygen transmission rate values at the end of the measurement after 27 days as well as the OTR values are displayed in Table 3. As the OTR value is obtained by deducing the OTR of the bottle closures from the GOTR value, the sum of squares of the two standard deviations is used for the comparison.

A Student / Aspin Welch comparison of means and variances shows that the values obtained with the fluorescent tracer technique are not different from those obtained with the reference method at a 5% significance level.

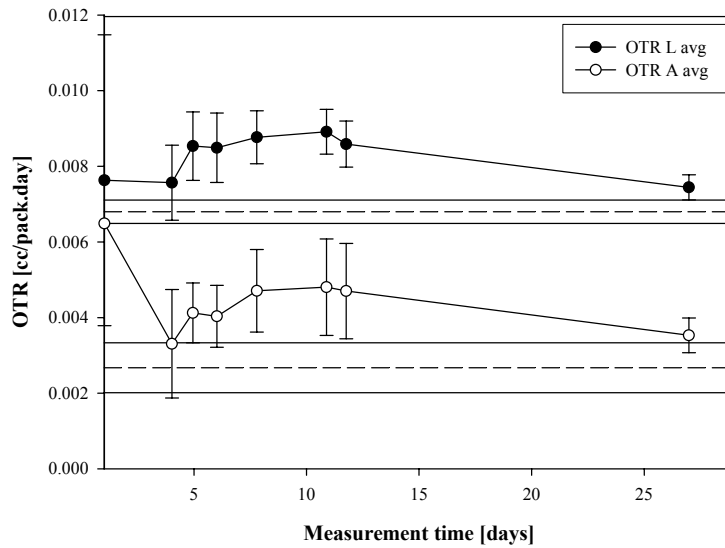
**Table 3:** Fibox 3 results after 27 days of measurement.

Bottle type	L	A
Calibration	Individual	Individual
GOTR	0.0093	0.0054
OTR	<b>0.0070</b>	<b>0.0031</b>
SD	0.0004	0.0004
RSD	0.054	0.131

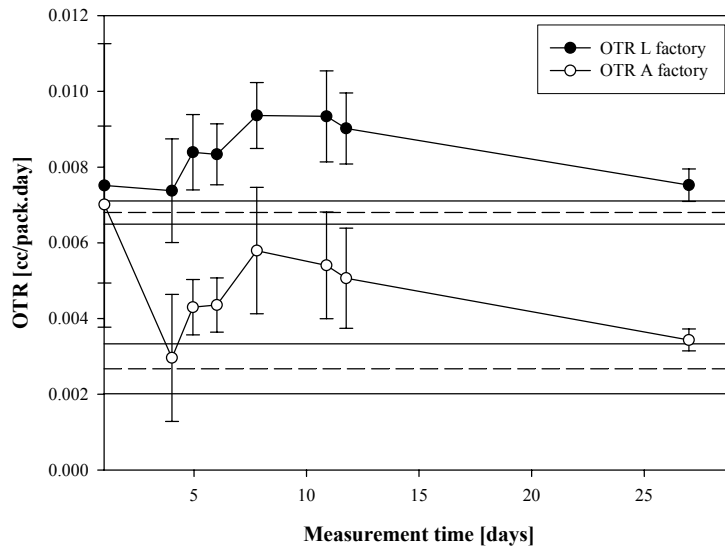
**Effect of measurement time and calibration.** Figures 7-9 show the evolution of the FT method results as a function of measuring time for individual, average and factory calibration values respectively. In all figures, the mean value of the reference method is denoted by the dashed horizontal line, whereas the interval defined by the standard deviation of the mean is denoted by the solid lines above and below the dashed line. For all results the average OTR values are close to the reference values already after a measurement period of four days. The spread of the results is however not small enough to consider these values as similar to that of the reference method. Subsequently, the measured OTR values deviate considerably from the reference values before slowly approaching the values of the reference method as the measurement time increases. One possible reason for this would be that these variations are due to the fluctuation in atmospheric pressure between measurements. As atmospheric pressure was only recorded at the time of measurement, no information is available on the evolution of atmospheric pressure and thus the driving force for permeation between measurements.



**Figure 7:** Evolution of FT OTR values with measurement time in days. The dashed horizontal lines represent the average values of the reference method, whereas the solid lines delineate the upper and lower bounds defined by their standard deviation.



**Figure 8:** Evolution of FT OTR values with measurement time in days using average calibration. The dashed horizontal lines represent the average values of the reference method, whereas the solid lines delineate the upper and lower bounds defined by their standard deviation.



**Figure 9:** Evolution of FT OTR values with measurement time in days using factory calibration. The dashed horizontal lines represent the average values of the reference method, whereas the solid lines delineate the upper and lower bounds defined by their standard deviation.

In order to determine the measurement time required for obtaining comparable results with the reference method in terms of the average reading as well as in terms of standard deviation a Student / Aspin Welch comparison of means with different variances was applied to the measurement results. Table 4 shows the results of testing the hypothesis of similarity at 5% significance level for the three different calibrations used as compared to the average and standard deviation of the reference method. Only the results from day 11 and onward are shown in the table. For the individual calibration the measurement values, as well as their dispersion, are not different from those of the

reference method neither for the L- nor for the A bottle. Using the average and factory calibrations, on the other hand, results in a considerable overshoot compared to the reference method, regardless of the barrier level of the tested bottle. Only after the full measurement period of 27 days can they be considered to be comparable to the reference method. The average calibration is nevertheless closer to the reference values than the factory calibration, thus underlining the importance of calibrating the sensor spots prior to measurements. The numerical values of the OTR values obtained with the three calibrations for both bottle types after 27 days are shown in Table 5.

**Table 4:** Results of Student / Aspin Welch comparison of means and variances of average results of fluorescent tracer results as compared to the reference method.

Calibration / bottle	Measurement time [days]	Different	t	t <sub>95</sub>	t <sub>99</sub>
IND / L	11	No	1.255	2.3646	3.4995
	12	No	1.5492	2.3060	3.3554
	27	No	0.8430	2.3060	3.4995
IND / A	11	No	2.2704	2.3646	3.4995
	12	No	1.7096	2.4469	3.7074
	27	No	1.4633	2.5706	4.0321
AVG / L	11	Yes	7.3710	2.3060	3.3554
	12	Yes	6.1071	2.3060	3.3554
	27	Yes	3.1360	2.3646	3.4995
AVG / A	11	Yes	3.2211	2.4469	3.7074
	12	Yes	3.0984	2.4469	3.7074
	27	No	2.1984	2.5706	4.0321
FAC / L	11	Yes	4.9353	2.4469	3.7074
	12	Yes	5.389	2.4469	3.7074
	27	Yes	3.1007	2.3060	3.3554
FAC / A	11	Yes	3.8338	2.4469	3.7074
	12	Yes	3.5845	2.4469	3.7074
	27	No	2.0419	2.7765	4.6041

**Table 5:** Comparison of measurement results as a function of used calibration for measurement after 27 days.

Bottle type	L			A		
	Individual	Average	Factory	Individual	Average	Factory
<b>GOTR</b>	0.0093	0.0097	0.0098	0.0055	0.0059	0.0055
<b>OTR</b>	<b>0.0070</b>	<b>0.0074</b>	<b>0.0075</b>	<b>0.0032</b>	<b>0.0035</b>	<b>0.0034</b>
<b>SD</b>	0.0004	0.0003	0.0004	0.0004	0.0005	0.0003
<b>RSD</b>	0.054	0.045	0.085	0.131	0.130	0.057

**Measurement time comparison:** With the present Oextran capacity in our laboratory we can measure the permeability of four bottles of the investigated permeability range within 48 hours. During a period of 12 days, if measurements are started on a Monday morning, it is practically possible to measure the permeability of 20 bottles, while already having trustworthy OTR value on the second day. For the developed methodology the present results indicate that reliable measurements can be obtained after a minimum of 12 days upon the sealing of nitrogen flushed containers of this size and permeability. In this sense at its present state, the developed method falls short of the performance of the reference method. That is, if fast results are required the reference method is more suitable. If many specimens are available, on the other hand, given that there is no limitation on the number of specimens which can be measured with the developed method, it is possible to get permeability values on a very high number of specimens in a reasonable time, thus improving statistics.

**A comparison of labour intensity:** The reference method involves little work. The specimens have to be glued onto the specimen holders and mounted on the measuring device. In direct hours, 20 measurement results would require approximately 2.5 man-hours, representing five sample mounting operations.

The FT method is more labour intensive. The calibration procedure for 20 bottle closures requires approximately 3 hours. Since sensor calibration is not performed prior to each measurement series, but would rather be performed a couple of times a year, only 30 minutes are allocated to the measurement of 20 bottles. The gassing of the bottles takes approximately 10 minutes per bottle, accounting for approximately 4 hours. In addition to this, a measurement of one bottle takes approximately 3 minutes. Every bottle was measured 7 times. Consequently, for the 20 bottles this accounts for 6 hours of work. In total the work involved in measuring 20 bottles with the developed method would thus amount to 10.5 man-hours. The developed method is thus significantly more labour intensive.

**Possibilities of improvement:** Continuous measurement of atmospheric pressure in order to compensate for effects of driving force. The atmospheric pressure was only recorded at the time of measurement. The atmospheric pressure variations between the measurements are thus not taken into account in the calculation of the normalised result. Continuous measurement of atmospheric pressure would permit a more accurate determination of the driving force for permeation and thus give a more accurate final result.

It is clear that the tighter is the bottle closure, the less will be the influence of the bottle closure on the end result. Nevertheless, this contribution will never be zero and will thus at any rate have to be deduced from the GOTR value in order to obtain a value comparable to that of the reference method. It is thus more important to measure the permeability on a large number of washers in order to have a statistically relevant value on its permeability. A one-time measurement of a large number of washers would thus contribute to higher measurement precision.

## **Summary**

The present investigation compares the measurement of four specimens using the reference method with the measurement of six specimens using the method developed based on fluorescent tracers. For both the L and A bottles, representing high and very high barrier properties, the measurement results of the developed method were shown not to be different from those of the reference method using individual calibration values of the oxygen sensitive foils, provided that measurements are carried out for at least 11 days. For average calibration values as well as for the factory calibration values, the results were equivalent only for the values obtained after 27 days. It may well be that the equivalent performance could have been observed at an even earlier stage due to the fact that no measurements were performed between the 12<sup>th</sup> and the 27<sup>th</sup> day. Nevertheless, measurement times exceeding 14 days are not desirable.

Based on the present results, the fluorescent tracer method proposed here is highly competitive to the reference method in terms of performance, provided that testing times are sufficiently long. Although it is more demanding in time, improvements can be made which may contribute to a reduction in the required testing time for equal performance. These improvements would be better characterisation of the permeability of the bottle closure and continuous measurement of the atmospheric pressure during testing. Despite its labour intensity and the time required for measurements for the developed method it remains a very interesting alternative to the Oxtran equipment due to its wide potential of application as well as the low acquisition and maintenance cost. The present method is directly applicable to measurements of packaging film permeability by means of a permeation cell integrating an oxygen sensitive sensor spot. Development is under way to adapt the present method to measurements on flexible finished packs. As fluorescence-based measurements do not consume oxygen and measure oxygen concentration an additional hurdle to overcome in this development will be the measurement of flexible package volume.

## **Acknowledgement**

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