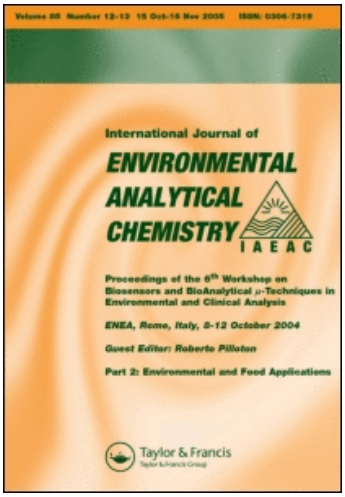
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of oxygen permeability of food wrapping films by an amperometric sensor

Luigi Campanella[a]; Riccarda Antiochia[b]; Roberto Dragone[c]; Irma Lavagnini[b]
[a] Department of Chemistry, University of Rome 'La Sapienza', 00185 Rome, Italy [b] Department of Chemical Sciences, University of Padova, 35131 Padova, Italy [c] Istituto dei Sistemi Complessi (ISC) CNR - Department of Chemistry, University of Rome 'La Sapienza', 00185 Rome, Italy

To cite this Article Campanella, Luigi , Antiochia, Riccarda , Dragone, Roberto and Lavagnini, Irma(2005) 'Determination of oxygen permeability of food wrapping films by an amperometric sensor', International Journal of Environmental Analytical Chemistry, 85: 12, 959 — 969
To link to this Article: DOI: 10.1080/03067310500151359
URL: http://dx.doi.org/10.1080/03067310500151359

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Environ. Anal. Chem.
Vol. 85, No. 12–13, 15 October–15 November 2005, 959–969

Taylor & Francis
Taylor & Francis Group

Determination of oxygen permeability of food wrapping films by an amperometric sensor

LUIGI CAMPANELLA*†, RICCARDA ANTIOCHIA‡, ROBERTO DRAGONE§ and IRMA LAVAGNINI‡

†Department of Chemistry, University of Rome 'La Sapienza', Piazzale Aldo Moro 5, 00185 Rome, Italy
‡Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy
§Istituto dei Sistemi Complessi (ISC) CNR – Department of Chemistry, University of Rome 'La Sapienza', Piazzale Aldo Moro 5, 00185 Rome, Italy

Downloaded At: 15:04 17 January 2011

(*Received 8 October 2004; in final form 23 December 2004*)

A new method for measuring the oxygen permeability (*Dk*) of common polymer membranes based on an amperometric sensor was developed. The system was successfully applied to food wrapping and storing films. The method is based on measurement of oxygen concentration variations in time, by means of an amperometric oxygen sensor (Clark electrode), covered with the polymer film and secured with a proper cap. Measurements were carried out under a constant flow of oxygen in order to be independent of initial oxygen concentration. The oxygen permeability of various commercially available food wrapping films was determined according to Fick's first law of diffusion. The method was tested using a reference material of different thickness, Hydrofilcon-43, with a known permeability value. This method gave more reproducible results compared with the ISO measurement systems. The influence of time, use and hydration degree on oxygen permeability was also tested by exposing the tested films for 36 h to UV radiation and keeping them for 50 days in a dryer under vacuum. Results showed that oxygen permeability is proportional to the degree of hydration of the film.

Keywords: Oxygen permeability; Oxygen transmissibility; Food wrapping films; Clark electrode

1. Introduction

In recent years, considerable attention has been paid to improving the characteristics of food wrapping and storing films. Oxygen permeability is one of the most important parameters to be optimized. It must be sufficiently low in films for food, in order to prevent oxidative degradation caused by reactions with oxygen. It is well known that the growth of bacteria, fungi and other micro-organisms occurs in aerobic conditions and that oxygen is responsible for the fat oxidation which causes rancidity. The major

*Corresponding author. Fax: +39-06-49913725. Email: luigi.campanella@uniroma1.it

International Journal of Environmental Analytical Chemistry
ISSN 0306-7319 print: ISSN 1029-0397 online © 2005 Taylor & Francis
DOI: 10.1080/03067310500151359

role of good food packaging is to retard the natural processes that lead to food spoilage by avoiding contact with oxygen. Reproducible, low-cost measurement of the oxygen permeability of food wrapping films is therefore absolutely necessary [1, 2].

Nowadays the most used packaging materials are derivates of cellulose and of melaminic, epossidic and phenolic polymers. Small amounts of polyvinyl chloride (PVC) are often added to these polymers in order to enhance the elasticity of the material.

Determination of oxygen transport through polymer membranes is based on the measurement of two important physical parameters: oxygen permeability (Dk, where D and k are respectively the diffusion coefficient and the solubility coefficient of Henry's law) and oxygen transmissibility (Dk/L, where L is thickness of film). Dk is an inherent property of the membrane, independent of the shape or thickness of the film. Parameter Dk/L depends on film design and thickness.

Several different methods have recently been developed to measure the oxygen transport characteristics of polymer membranes. The most commonly used are the single-chamber 'polarographic' technique developed by Fatt *et al*. [3–5] and the coulometric carrier gas method (ISO measured systems) [6–8]. The Fatt method, which is based on an amperometric oxygen sensor (Clark electrode), became standard in determining the oxygen permeability of soft hydrogel contact lenses, whereas the coulometric method is more suited for rigid contact lenses [9].

However, measurement of oxygen permeability and transmissibility present some difficulties, largely arising from the dependence of the signal on the initial partial pressure of oxygen in solution, edge effects, and boundary layer resistances [9–11].

This article reports new static and dynamic methods for measuring the oxygen permeability of food wrapping films, which give more reproducible results compared with the ISO measurement systems [5, 6]. The methods were successfully tested using a reference material. The influence of time, use and hydration degree on oxygen permeability are also discussed.

Downloaded At: 15:04 17 January 2011

2. Experimental

2.1 *Materials*

The following commercially available food wrapping films were used: Cuki, Domopak, Rotofresh, Coop, La Valle, Ottimo Casa Idea. Hydrofilcon-43 was kindly supplied by Schalcon. All experiments were carried out in distilled water solutions. Distilled water was produced by a Milli-Q system (Millipore, Bedford, MA, USA).

2.2 *Apparatus*

The Clark electrode was purchased from Orion 97-08-99. An Orion SA720 potentiostat was used with an AMEL 868 X-Y recorder. The cathode was poised at 0.65 V *versus* a silver anode. The electrode was carefully calibrated before each use. All measurements were carried out at $21.0 \pm 0.2^{\circ}$C using a thermostatic bath.

Each food wrapping film was carefully placed directly on the gas-permeable membrane of the Clark electrode and tightly secured with a Teflon cap, thereby avoiding the formation of air bubbles between sensor membrane and film.

Films were artificially aged by placing them in a Panel Accelerated Weathering Tester (Q-Panel Company, Cleveland, OH, USA). Samples were irradiated by eight mercury lamps with a power of 40 W each, which simulate solar radiation up to 370 nm.

Films were dried by placing them in a dryer kept under vacuum.

2.3 *Measurement procedure*

The assembled electrode was initially immersed in 20 mL of a distilled water solution, kept under stirring for 10 min in order to reach equilibrium between the oxygen present in solution and in the film in direct contact with the Clark electrode membrane ('static method'). An alternative method consisted of the use of the Clark electrode in a solution maintained under a constant oxygen flow, suitably mixed with nitrogen, in order to increase the oxygen partial pressure and therefore its concentration in the bulk solution ('dynamic method').

Oxygen passing from the solution to the cathode of a Clark electrode involves the oxyreduction process:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
$$4Ag \rightarrow 4Ag^+ + 4e^-$$

Oxygen transmissibility (Dk/L) is related to total current diffusion in the steady state by:

$$\frac{Dk}{L} = \frac{I}{nFAp}$$

where I is steady-state current intensity, n the number of electrons exchanged in the electrodes for each molecule of oxygen ($n = 4$), F the Faraday constant, A the surface of the cathode, and p the O_2 partial pressure difference across the film.

Downloaded At: 15:04 17 January 2011

3. Results and discussion

3.1 *Static measurements*

We first measured the amount of oxygen passing through six commercially available food wrapping films after reaching the equilibrium condition. This static method yielded a first rank of oxygen permeability of the various polymer films (table 1, column 1). The values reported are the averages of ten consecutive measurements carried out on fresh membranes for each film tested. Reproducibility was quite good, with a relative standard deviation (RSD) of about 10% for each film, in good agreement with the results obtained with the ISO methods [5, 6].

3.2 *Dynamic measurements*

In order to increase the reproducibility of the method, we measured oxygen content variations as a function of time by blowing a gentle oxygen flow over the solution. This creates an oxygen gradient between the outer and inner parts of the membrane and a passage of oxygen through the film. Oxygen variations measured by the Clark electrode were proportional to the increasing oxygen rate on the inner part of the film. A change in the slope of oxygen contents *versus* time after adding the

Table 1. Oxygen permeability of commercial food wrapping films expressed in terms of oxygen contents (column 1) and slope of oxygen contents *versus* time (column 2). Measurements were performed with Clark electrode.

Food wrapping film	Oxygen contents (ppm)[a,b]	Slope (ppm min^{-1})[a,c]
Domopak	6.17 ± 0.44	0.63 ± 0.04
Cuki	6.26 ± 0.52	0.69 ± 0.03
Rotofresh	6.33 ± 0.63	0.73 ± 0.05
La Valle	6.35 ± 0.58	0.74 ± 0.05
Coop	8.01 ± 0.78	0.75 ± 0.05
Ottimo Idea Casa	8.40 ± 0.74	0.91 ± 0.06

[a] Mean of ten measurements.
[b] In equilibrium conditions.
[c] Under a constant oxygen/nitrogen flow maintained over solution.

oxygen flow over the solution was observed. The oxygen flow was maintained over the solution and not blown into the solution, in order to obtain a lower oxygen concentration gradient. Therefore, slower passage of the oxygen through the film gave rise to a lower slope of the curve. This result was also favoured by blowing oxygen, suitably mixed with nitrogen, over the solution.

Comparisons of the results for the various commercial films was carried out by using the slopes of oxygen contents *versus* time shown in figure 1. Actually, these slope values represent an estimate of the oxygen permeability of the films. The slope of each curve was calculated by using the points recorded between the first and sixth minutes of measurement, because of the straight trend shown by the curves during this interval.

The resulting scale of oxygen permeability of the films is shown in table 1, column 2. Each slope value is the average of 10 consecutive measurements with an RSD not higher than 7%. Note that no significant change appears, compared with the scale obtained with the static method, but the reproducibility is better.

Downloaded At: 15:04 17 January 2011

3.3 *Calculation of* Dk *values*

Fick's law of diffusion was used to determine the oxygen permeability of the films. As already mentioned, the driving force for the passage of oxygen through a membrane of thickness L and area A is the concentration difference across the membrane. According to Henry's law, the concentration of a dissolved gas is proportional to its partial pressure above the solution, in absence of reactions. Thus, a direct correlation between flux J, defined as flow rate per unit area, and the partial pressure difference across the membrane is given by:

$$J = \frac{pDk}{L}$$

where J is oxygen flux (mL O_2 (STP)/s cm^2), D is the diffusion coefficient of oxygen ($cm^2\,s^{-1}$), k is the solubility coefficient of oxygen in the membrane (mL O_2/cm^3 mmHg), L is the thickness of the membrane (cm) and p is the difference of partial pressures of oxygen across the membrane (mmHg) (the 'STP' abbreviation has its usual meaning). Oxygen permeability Dk of a film is usually expressed in 10^{-11} ($cm^2\,s^{-1}$) (mL O_2/mL mmHg), and oxygen transmissibility Dk/L in 10^{-9} ($cm\,s^{-1}$) (mL O_2/mL mmHg).

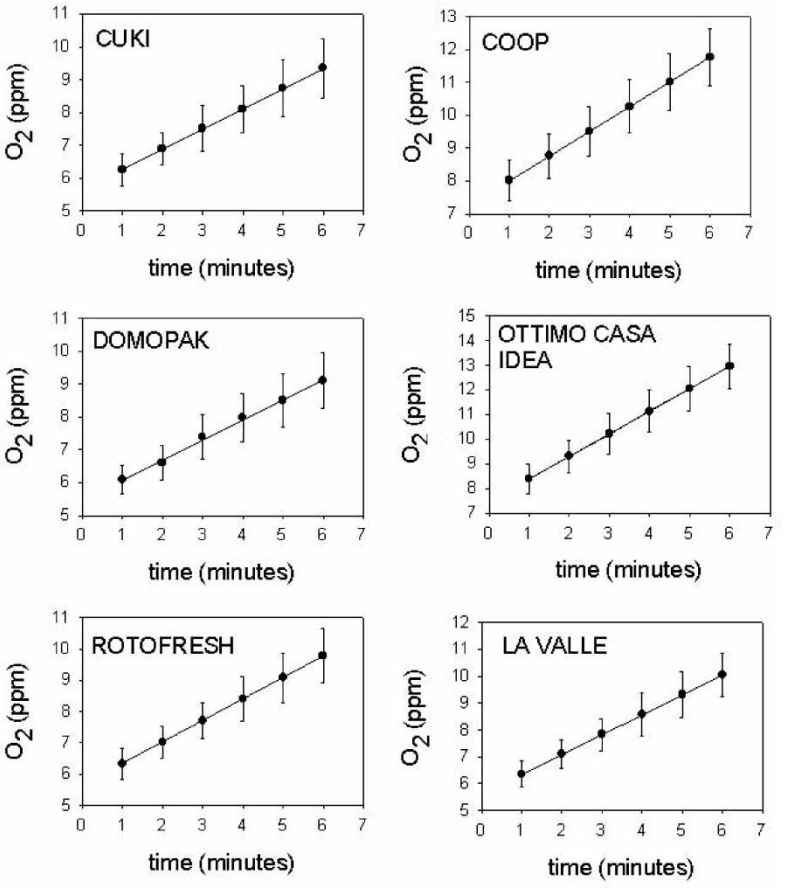


Figure 1. Oxygen content *vs*. time plots of six commercial food wrapping films: Domopak, Cuki, Rotofresh, La Valle, Coop, Ottimo Casa Idea. Continuous lines: fitted straight lines. Error bars: standard deviations of ten replicates. Experimental conditions: Clark electrode; distilled water solutions maintained under oxygen/nitrogen flow.

Application of Fick's law to a film with known thickness and to a fictitious membrane of water of the same thickness (blank) and obtaining the ratio of the two equations, yields the expression:

$$Dk = \frac{J(Dk)_{\text{blank}}}{J_{\text{blank}}}$$

where $(Dk)_{\text{blank}}$ is the oxygen permeability of water, which is 79×10^{-11} $(\text{cm}^2\,\text{s}^{-1})$ $(\text{mL O}_2/\text{mL mmHg})$ [4]. Fluxes J and J_{blank} may be expressed in terms of either oxygen content (expressed in ppm units) measured by the Clark electrode (static method) or slope of oxygen contents *versus* time (dynamic method) for films and blanks, respectively.

The resulting Dk value is named 'apparent' $(Dk)_{\text{app}}$, because it is related to the system formed of the membrane plus the solution. The diffusion resistance of the solution

Downloaded At: 15:04 17 January 2011

layers (surface effects) between membrane and sensor must also be taken into account. Consequently, determination of the true permeability of the film (Dk) requires measurements of the apparent oxygen permeability $(Dk)_{app}$ of several membranes of known thickness placed in series configuration. True transmissibility is related to apparent transmissibility by the equation [12–14]:

$$\left(\frac{L}{Dk}\right)_{app} = \frac{L}{Dk} + R_{bl}$$

where R_{bl} is boundary layer resistance (surface effects). According to this equation, the plot of the reciprocal of measured oxygen transmissibility $(L/Dk)_{app}$ *versus* film thickness L results in a straight line, and the Dk value of the material can be derived from the inverse of the slope of the line.

In order to test the method, we calculated the Dk value of Hydrofilcon-43 by using both oxygen content values (table 2, column 2) and the slopes of the curves shown in figure 2 (table 2, column 4). Figure 2 shows the dependence of oxygen permeability

Downloaded At: 15:04 17 January 2011

Table 2. Comparison of $(Dk)_{app}$ values obtained with static and dynamic methods for Hydrofilcon-43 films at three thickness values. Column 2 shows measured oxygen contents and column 4 calculated slope values of curves in figure 2.

	Static method		Dynamic method	
Hydrofilcon-43 thickness (cm)	Oxygen content[a] (ppm)	$(Dk)_{app}$ ($cm^2\,s^{-1}$) (mL O_2/mL mmHg)	Slope[a] (ppm min^{-1})	$(Dk)_{app}$ ($cm^2\,s^{-1}$) (mL O_2/mL mmHg)
0.012	6.00 ± 0.54	$52.1 \pm 7.0 \times 10^{-11}$	0.91 ± 0.06	$75.3 \pm 7.2 \times 10^{-11}$
0.023	5.39 ± 0.51	$46.8 \pm 6.4 \times 10^{-11}$	0.80 ± 0.04	$66.8 \pm 5.7 \times 10^{-11}$
0.030	4.87 ± 0.44	$42.3 \pm 5.7 \times 10^{-11}$	0.48 ± 0.03	$39.8 \pm 3.7 \times 10^{-11}$

[a] Mean of four measurements.

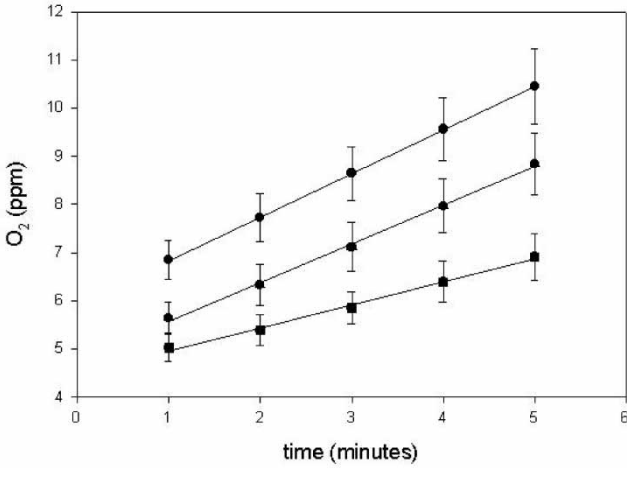


Figure 2. Oxygen content *vs.* time plots for Hydrofilcon-43 films with thickness values equal to 0.012 cm (●), 0.023 cm (▲), 0.030 cm (■). Continuous lines: fitted straight lines. Error bars: standard deviations of ten replicates. Experimental conditions as in figure 1.

Table 3. Oxygen permeability values of commercial food wrapping films obtained with dynamic method.

Food wrapping film	Dk ($cm^2\,s^{-1}$)(mL O_2/mL mmHg)
Cuki	$11.7 \pm 2.6 \times 10^{-11}$
Domopak	$12.4 \pm 2.2 \times 10^{-11}$
Rotofresh	$15.8 \pm 1.6 \times 10^{-11}$
La Valle	$17.8 \pm 2.8 \times 10^{-11}$
Coop	$19.2 \pm 2.1 \times 10^{-11}$
Ottimo Casa Idea	$24.5 \pm 2.2 \times 10^{-11}$

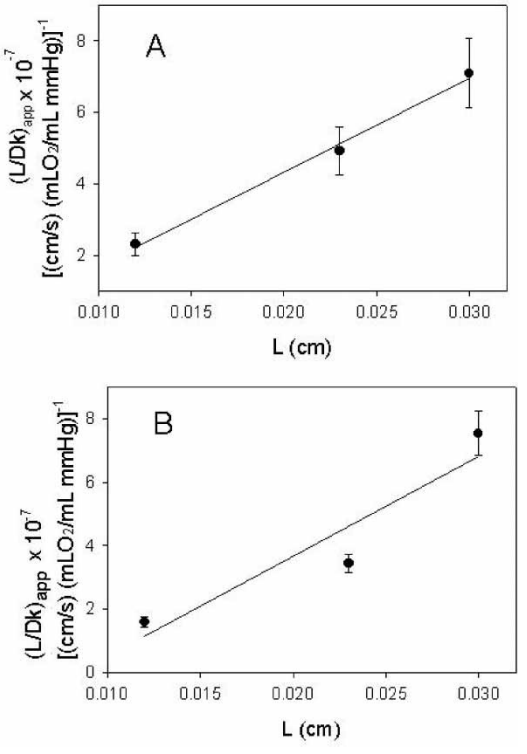


Figure 3. Inverse transmissibility *versus* Hydrofilcon-43 film thickness plots obtained with static (A) and dynamic (B) methods. Error bars: standard deviations calculated from four replicates.

on time of three Hydrofilcon-43 films with differing thicknesses. Clearly, the membrane with lower thickness has higher oxygen permeability and therefore a higher slope of the curve. Table 3 also lists the $(Dk)_{app}$ values calculated by using, for the blank, an oxygen content value of 9.1 ppm in the former case and a slope value of 0.95 ppm min^{-1} in the latter. Figure 3 shows the dependence of inverse transmissibility $(L/Dk)_{app}$ on film thickness. The slope of the first plot (figure 3A) yields a Dk value of $(37.9 \pm 2.8) \times 10^{-11}$ ($cm^2\,s^{-1}$) (mL O_2/mL mmHg). This value is about three times that of the Dk, 14.5×10^{-11} ($cm^2\,s^{-1}$) (mL O_2/mL mmHg), given by the manufacturer. The slope of the second plot (figure 3B) yields a Dk value of $(31.7 \pm 11.3) \times 10^{-11}$ ($cm^2\,s^{-1}$) (mL O_2/mL mmHg) which is in better agreement with the value reported in the

Downloaded At: 15:04 17 January 2011

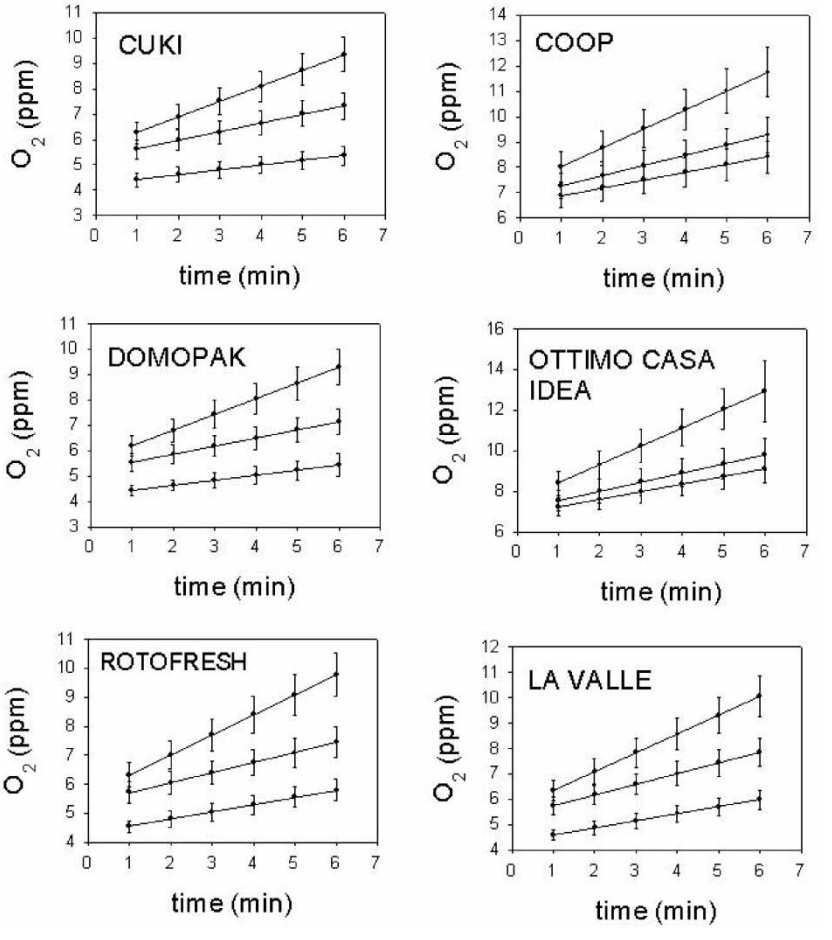


Figure 4. Oxygen content *vs.* time plots for stacked commercial food wrapping films: 1, film (♦); 2, stacked films (■); 3, stacked films (▲). Experimental conditions as in figure 1.

manufacturer's brochure. An improved value of 17.1×10^{-11} ($cm^2 s^{-1}$) (mL O_2/mL mmHg) was obtained by neglecting the first point of the plot in figure 3B, which corresponds to the lowest thickness. This point is the most affected by convective movements, which cause a passage of oxygen through the membrane larger than that obtained by diffusion only [4].

The dynamic method was then applied to determine the *Dk* values of six commercial food wrapping films. Figure 4 shows oxygen contents *versus* time plots for stacked food wrapping films. Figure 5 shows inverse transmissibility *versus* number of films stacked for each film. Table 3 lists the oxygen permeability values of all films thus obtained. Cuki and Domopak films gave the best results, showing the lowest values of oxygen permeability.

It is interesting to note that the Coop film is the only commercial film without polyvinyl chloride (PVC), which may be dangerous if it is put in contact with fatty and alcoholic foods. Nevertheless, this film had a quite good *Dk* value, not much

Downloaded At: 15:04 17 January 2011

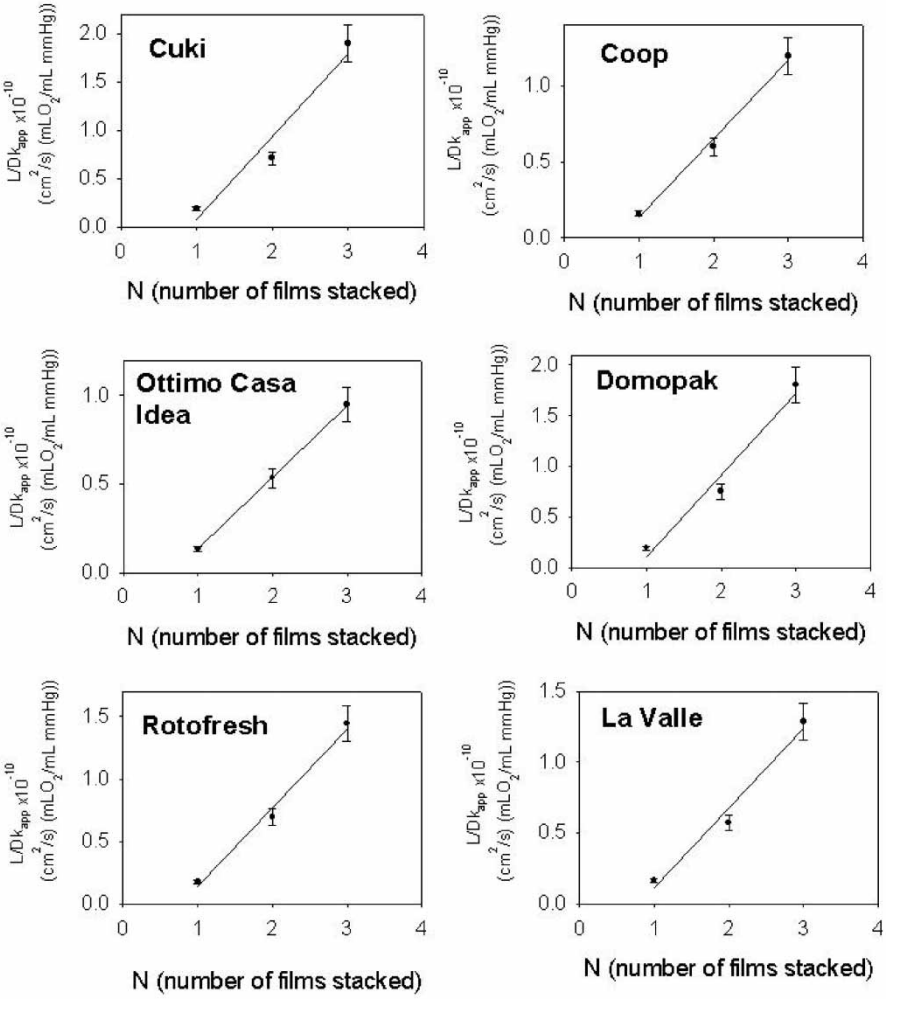


Figure 5. Inverse transmissibility *vs.* number of films stacked for six commercial food wrapping films. Error bars: standard deviations calculated from four replicates.

larger than those of other films, and smaller than the Ottimo Casa Idea film, which contains PVC, like all the other films tested.

3.4 *Influence of time and use*

In order to study the influence of time and use on the oxygen permeability of commercial food wrapping films, samples were photodegraded by exposing them for 38 h to UV lamps which perfectly simulate 1 month of UV solar radiation. Table 4 (column 2) lists the $(Dk)_{app}$ values obtained after exposing a single layer of each food wrapping film to photodegradation. Despite the quite large uncertainties about the Dk_{app} values, their increasing trend (column 3) in the range 4.5% (Coop film) and 10.4% (Domopak film) is clearly observed.

Downloaded At: 15:04 17 January 2011

Table 4. Effect of photodegradation and drying on apparent oxygen permeability of commercial food wrapping films. $(Dk)_{app}$ values calculated with one single film (instead of stacking experiments) as means of four measurements.

Food wrapping film	$(Dk)_{app}$ before treatment $\times 10^{11}$ ($cm^2 s^{-1}$) (mL O_2/mL mmHg)	$(Dk)_{app}$ after photodegradation process $\times 10^{11}$ ($cm^2 s^{-1}$) (mL O_2/mL mmHg)	Difference *versus* mean values (%)	$(Dk)_{app}$ after drying process $\times 10^{11}$ ($cm^2 s^{-1}$) (mL O_2/mL mmHg)	Difference *versus* mean values (%)
Cuki	51.1 ± 4.8	55.4 ± 5.2	7.4	38.0 ± 3.6	−26.4
Domopak	51.9 ± 4.9	57.3 ± 5.3	10.4	36.8 ± 3.5	−29.0
Rotofresh	57.4 ± 5.5	60.7 ± 6.0	5.7	46.4 ± 4.5	−19.2
La Valle	61.5 ± 5.9	65.7 ± 6.4	6.8	43.6 ± 4.1	−29.2
Coop	62.4 ± 6.0	65.2 ± 6.2	4.5	40.7 ± 4.0	−34.8
Ottimo Casa Idea	75.7 ± 7.4	82.9 ± 8.0	9.5	59.3 ± 5.7	−21.7

3.5 *Effect of hydration*

The degree of hydration of film is another important parameter to be checked when studying the oxygen permeability of food wrapping films. Films were kept in a dryer for 50 days and oxygen permeability was measured as soon as the films were removed from the dryer. Table 4 (column 4) shows the $(Dk)_{app}$ values obtained after exposing a single layer of each film to drying. The values clearly indicate a strong decrease in apparent oxygen permeability (column 5), ranging from 19.2% (Rotofresh) to 34.8% (Coop). This result confirms that the oxygen permeability of a material is directly proportional to its degree of hydration.

Downloaded At: 15:04 17 January 2011

4. Conclusions

The present work demonstrates that the oxygen permeability of food wrapping films can be successfully determined using a simple amperometric sensor based on a Clark electrode. This new method is more reproducible, faster, and more versatile than the ISO methods. It does not require any complicated instrumentation, because it is independent of oxygen partial pressure difference across the film. It is simple, rapid and inexpensive and therefore, in principle, may become a good alternative to the reported high-cost ISO methods for monitoring of oxygen permeability of commercial food wrapping films.

Acknowledgements

Financial support from the EU and Italian Ministry of Education University and Scientific Research (PRIN 2002) is acknowledged.

References

[1] F. Charles, J. Sanchez, N.Gontard. *J. Food Eng.*, (2004) (In press).
[2] C. Yoshida, A. Antunes, C. Alvear, A.J. Antunes. *Int. J. Food Science Techn.*, **40**, 41 (2005).
[3] I. Fatt, J. Chaston. *Int. Contact Lens Clin.*, **9**, 76 (1982).
[4] I. Fatt, St. Helen. *Am. J. Optom. Arch. Am. Acad. Optom.*, **48**, 545 (1971).

[5] ISO 9913-1. 1996 Ophtalmic Optics-Contact Lenses-Part 1: Determination of oxygen permeability and transmissibility by the FATT [polarographic] method (German version prEN ISO 9913-1 : 1997).
[6] ISO/DIS 9913-2. Ophtalmic Optics-Contact Lenses-Part 2: Determination of oxygen permeability and transmissibility by the coulometric method (German version peen ISO 9913-2 : 1997).
[7] L.C. Winterton, J.C. White, K.C. Su. *Int. Contact Lens Clin.*, **15**, 117 (1988).
[8] I. Fatt. *Int. Contact Lens Clin.*, **16**, 226 (1989).
[9] D. Obendorf, M. Wilhelm. *Anal. Chem.*, **75**, 1374 (2003).
[10] V. Compañ, J.Guzman, E. Riande. *Biomaterials*, **19**, 2139 (1998).
[11] V. Compañ, A. Andrio, A. Lopez-Alemany, E. Riande, M.F. Refojo. *Biomaterials*, **23**, 2767 (2002).
[12] S.-T. Hwang, T.E.S. Tang, K. Kammermayer. *J. Macromol. Sci.*, **5**, 1 (1971).
[13] V. Compañ, J. Garrido, J.A. Manzanares, J.S. Esteve, M.L. Lopez. *J. Opt. Vis. Sci.*, **69**, 685 (1992).
[14] V. Compañ, M.A. Villar, E. Valles, E. Riande. *Polymer*, **37**, 101 (1996).

Downloaded At: 15:04 17 January 2011