M. Orzinski, J. Schneider and W. Hunger

Determination of oxygen ingress and carbon dioxide loss through plastic bottles using permeation simulation with hydrogen

The beer and beverage industry is using ever more barrier enhanced plastic bottles for the filling of its products. The quality of the products can be considerably affected by the permeation of oxygen into the bottle and carbon dioxide out of it. The quality control of the bottles with particular emphasis on the gas barrier is thus of great importance. However, the conventional gas permeation measuring method needs too much time. In order to respond effectively and quickly to barrier defects, bottle production or incoming goods inspection measuring time must be shortened, for example by 2 hours. A physical problem of a quick measurement of oxygen is the comparably long unsteady state of permeation due to desorption of oxygen into the bottle after filling. Hydrogen as a test gas can overbear this difficulty because of its high molecular mobility and low viscosity so a method for the use of hydrogen was established. The ruggedness of the method meets the requirements of the practical measurement conditions. The correlation of the hydrogen ingress rate with the permeation coefficient of carbon dioxide and oxygen measured with a real-time method is not linear but can be used to differentiate between bottles with good or poor passive barriers. Active barriers employing scavenger material can not be detected by the hydrogen ingress measurement.

Descriptors: hydrogen, PET bottle, permeation, quick test, packaging

1 Introduction

Plastic containers and closures have taken on a predominant role as packaging materials for the beverage industry, and are still gaining ground. Alongside the many well-known advantages there is the problem of plastic's inherent permeability to gases. This has a negative impact, principally in terms of oxygen and CO_2 permeation. An objective comparison of the barrier properties of various bottles and closure types is an important prerequisite in being able to forecast a product's shelf life, and hence in selecting the most appropriate container-cap combination, as several authors dealing with this topic agree [7, 14, 18].

Since in the food packaging industry plastic packaging material has been used for a long time a carrier gas method for flexible food packaging has become a matter of a German standard (DIN 53380-3) [3, 19]. A modification of this method permits the measurement of packaging systems such as bottles [14]. Unlike the real conditions, the permeation here is not measured in contact with a liquid phase but in contact to a carrier gas. The creep effect (expanding of carbonised bottles) is also not measured here. The minimum test time of this method is physically limited to about 2 days. Other so-called short-time tests are the manometric method (absolute pressure method) which is not specific to a specific kind of gas, and a method that employs gas chromatography after taking samples [4, 5, 9, 10, 11, 12, 13, 16, 19].

In order to investigate PET bottles with a high degree of accuracy, a so-called real time method can be used today [14, 19]. Real time means that the test time corresponds to the real time of the product shelf-life. In the case of PET bottle production or purchase thereof no useful tool is existent. Even a test time of 2 days as is possible with the DIN method is not quick enough. The content of this paper is the investigation of a so-called quick method to determine the oxygen ingress and the carbon dioxide loss indirectly (Figure 1). The aim is to provide a method that is fast, rugged and accurate enough for decisions in either bottle production control or incoming goods control.

2 Equipment and methods

2.1 Measurement of hydrogen ingress into PET bottles

The test time for the measurement of hydrogen ingress into a bottle takes less than 2 hours and is thus much faster than all existing

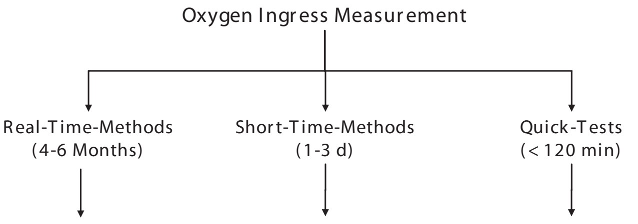

Fig. 1 Classification by test time of methods for the evaluation of PET bottles concerning oxygen ingress

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Dr. Martin Orzinski, Research Institute for Engineering and Packaging in the Beverage Industry, VLB Berlin, Seestrasse 13, D-13353 Berlin, Germany, Tel.: +49/30/45080-238; E-mail address: orzinski@vlb-berlin.org; Prof. Dr. Jan Schneider, University of Applied Science Lippe and Höxter, Technology of Beverages, Liebigstr. 87, D-32657 Lemgo, Germany; Winfried Hunger, SensorData Instruments, Stüttinghauser Ringsstrasse 33, D-58515 Lüdenscheid, Germany

methods determining oxygen. The reason can therefore be explained by the lower weight and the mobility of the hydrogen molecule. Following the solution-diffusion model for the mass transfer through material, a permeating gas dissolves after adsorption inside the plastic material. The concentration of gas in the bottle wall corresponds to the gradient of partial gas pressure. Initially the partial oxygen pressure is constant over the thickness of the bottle wall. After filling with beer, a slope from the outer to the inner bottle wall is formed. The concentration of dissolved oxygen follows this rapid change with a time lag that depends on the mobility of the gas. This unsteady state takes approximately 2 days for oxygen in PET and less than 2 hours for hydrogen in PET.

Assuming that the diffusion coefficient of oxygen and hydrogen under equal conditions in terms of packaging material and climatic data relate proportionally to each other, a correlation between hydrogen and oxygen must be measurable. This correlation can eventually be utilised for a quick evaluation of PET bottles and barrier enhanced PET bottles.

The hydrogen ingress measuring equipment is a prototype (Sensor Data Instruments, Lüdenscheid, Germany). The device consists of a five sample ports for bottles, a hydrogen sensor and a data receiving unit (Figure 2). The bottles are turned upside down and individually connected to the sensor. In this position the bottles are exposed to the test gas (5 % hydrogen and 95 % nitrogen provided by Air Liquide Deutschland, Düsseldorf) in a tight chamber (Figure 3). The sensor consists of transistor with a gate electrode and a hydrogen absorbing alloy. The absorbed hydrogen molecules dissociate into ions and diffuse into the metal. The surface potential of the metal is influenced and the gate potential changes proportionally to the ion concentration. The background hydrogen concentration in the atmosphere is small with about 0.5 ppm and does not noticeably affect the result.

In the test performance the test chamber is flushed with inert gas at a flow of 2 l/min for 20 min. In timed intervals, gas from the insides of the bottles is transferred to the sensor so that an almost simultaneous measurement is possible. The calibration is carried out with a test gas (10 ppm Hydrogen in Nitrogen, provided by Air Liquide Deutschland, Düsseldorf)

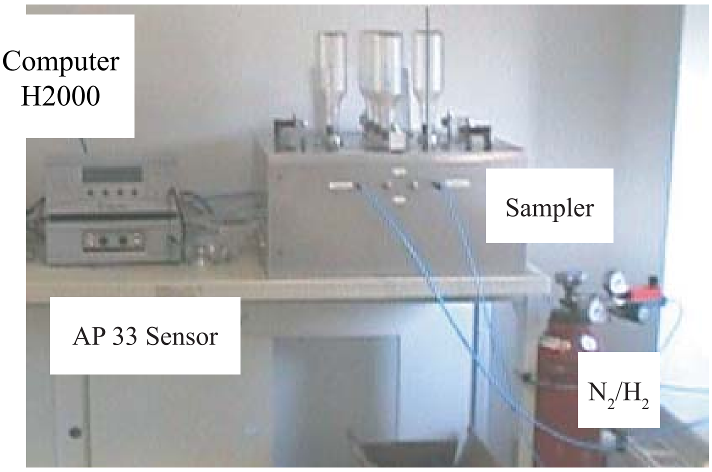

Fig. 2 **Hydrogen ingress measurement apparatus for the simultaneous test of 5 bottles**

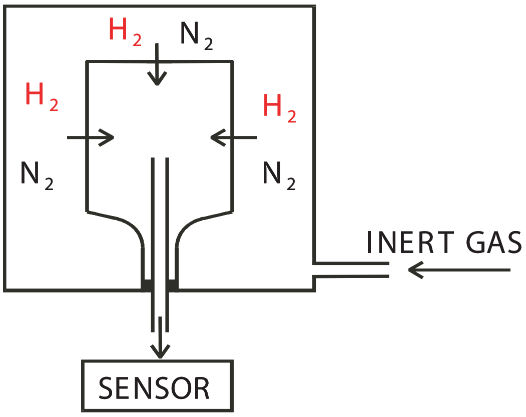

Fig. 3 **Principal of the hydrogen ingress measurement**

2.2. Real-time method

As a reference method the real-time measurement oxygen ingress and carbon dioxide loss is used. This method described subsequently has gained acceptance in the brewing industry because of its high reliability and the accordance to the product shelf-life.

For this test, plastic bottles are filled with water which has been de-oxygenated by heating in a test chamber, and subsequently carbonated. The test bottles are not filled with beer because the oxygen would be converted by the reducing components in the beer before it could be measured. The workflow of the real-time test is described in a separate paper [19]. At time t_0 the oxygen and carbon dioxide concentrations are measured in a defined number of the bottles. The remaining bottles are stored at a temperature of 23 ± 2ºC and at a relative humidity of 50 %. At clearly defined intervals, a specific number of bottles are removed and oxygen and CO_2 concentration measured again, so that a statistical evaluation of the changes in concentration levels can be established. The influence of various parameters – product in the container, oxygen content, carbon dioxide content (creep effect) and test period – are all taken into account. This method is therefore a simulation of real conditions and covers the real-time period of the shelf life being tested.

2.3. Tested PET bottles

A number of exemplary monolayer and barrier enhanced PET bottles were used in order to challenge the test method with a wide spread of measuring values. The characterisation of the bottles is described in Table 1. Multilayer bottles consist of more than one layer, typically 3 or 5 layers. The inner and outer layers provide the mechanical stability and the enclosed layer or layers represent the gas barrier. Active barriers (scavengers) are also implemented additionally to the passive barrier. Scavengers are able to chemically bind passing oxygen. However an active carbon dioxide barrier is not available. Bottles subsequently called “coating” consist of a monolayer PET bottle with the addition of an inorganic (used here) or organic coating such as a gas barrier [2, 15].

3 Results and discussion

3.1 Development of a measurement category

The data measured with the hydrogen test apparatus is hydrogen concentration in the inner of the bottles as a function of the time

Table 1 **PET bottles used as measuring objects**

Bottle identification	**description**[1]	**body diameter [mm]**	**height [mm]**	**weight [g]**	**base thickness [mm]**	**wall thickness [mm]**	**barrier material**[2]
Multilayer 1	PET/PA+Sc/PET	65.5	238.3	27.9	0.24	0.32	10 %
Multilayer 2	PET/PA+Sc/PET	63.8	247.3	27.9	0.27	0.29	2 %
Multilayer 3	PET/PA+Sc/PET/PA+Sc/PET	65.6	238.3	28.8	0.28	0.30	5 %
Multilayer 4	PET/PA+Sc/PET	64.0	247.1	27.9	0.28	0.28	5 %
Multilayer 5	PET/PA+Sc/PET	64.0	247.3	27.8	0.28	0.29	7 %
Coating 1	PET + internal coating	66.5	239.4	27.8	0.24	0.38	0.14 µm
Coating 2	PET + internal coating	63.4	238.5	27.6	0.25	0.34	0.15 µm
Coating 3	PET + internal coating	65.4	238.1	27.8	0.28	0.32	0.15 µm
Coating 4	PET + internal coating	65.0	238.6	27.8	0.27	0.35	0.15 µm
Monolayer 1	PET	63.4	247.0	28.0	0.28	0.29	
Monolayer 2	PET	63.4	245.0	28.0	0.29	0.28	

1) PET (poly ethylene therephthalat), PA (poly amide), Sc (Scavenger)
2) Barrier material: mass percentage or thickness of coating layers

exemplary shown in Figure 4. Because the exact value of the hydrogen concentration in the exposition chamber is not measured, a permeation coefficient can not be calculated. As a measurement category the (almost linear) slope in the graph of Figure 4 in a defined span of time (first 120 min) is taken. The slope represents a hydrogen flow rate under defined conditions and is subsequently abbreviated as F_{H2}. The example in Figure 4 results in

Hydrogen Ingress Rate: $$F_{H2} = \frac{\Delta c_{H_2}}{\Delta t} = \frac{19\ \text{ppm}}{120\ \text{min}} = 0.158\ \frac{\text{ppm}}{\text{min}}$$

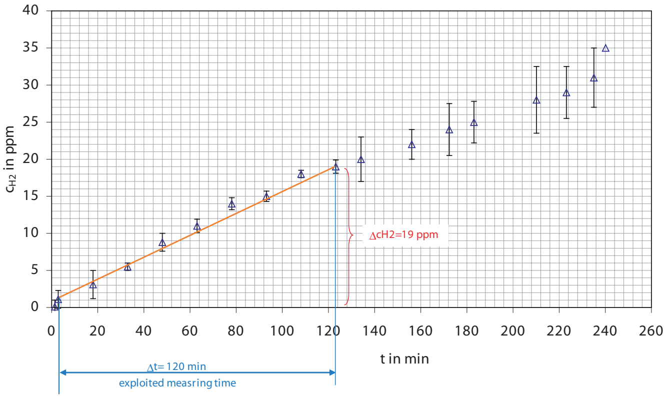

Fig. 4 **Exemplary course of measuring data: hydrogen concentration as function of the time (multilayer bottle 3) resulting in a measurement category "hydrogen ingress rate", a= 0.05, n = 25**

Since it is not the aim to determine a permeation coefficient, because of the new correlation factor but rather a size for a comparative evaluation of bottles, it is not necessary to employ a preconditioning time or to wait for a stationary state. However, the linearity of the graph in Figure 4 is an indication that the permeation of hydrogen is already in a stationary state. The temperature affects the permeation of gases and is thus a sensitive parameter of the measurement. Figure 4 shows an increase of F_{H2} that becomes steep when exceeding a temperature of 30 °C.

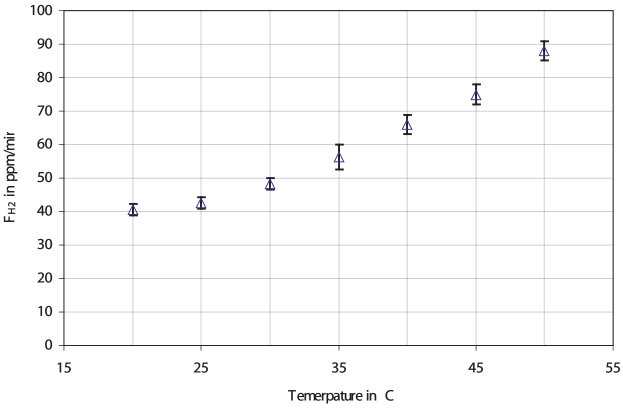

Fig. 5 **Hydrogen Flow F_{H2} plotted versus Temperature (monolayer bottle 1), n = 12, α =0.05**

It is supposed that for the practical application a maximum temperature of 30 °C can be warranted. In addition to the temperature some of the influencing parameters can not entirely be controlled to be constant. The impact of these parameters was verified in a ruggedness test [1, 6]. A rugged method must provide reliable results even in the case of expected deviation in the influencing parameters. In Table 2 the factors are listed with their adjusted variation and the effects documented. The effects indicate a ranking of the factors concerning the extent of their influence. The results in Table 2 show that the relative humidity and the quantity of measuring have a stronger effect than measurement duration and the temperature. The confidence intervals of the effects range in the case of all factors in a span covering zero indicating that

Table 2 Ruggedness verification on the measurement category F_{H2}; significance level 95 %

	variation of the influencing parameters			ruggedness (effects)		
Factor (influencing parameter)	**lower limit -**	**upper limit +**	**unit**	**effect [ppm/min]**	**lower confidence limit [ppm/min]**	**upper confidence limit [ppm/min]**
relative humidity	40	60	%	0.003	–0.028	0.034
temperature	20	30	°C	0.000	–0.031	0.031
time	116	123	min	0.004	–0.027	0.035
quantity of measuring points	12	16	quantity	0.000	–0.031	0.031

there is no significant impact on the measuring result and hence the method is rugged.

3.2 Correlation of the hydrogen ingress with oxygen and carbon dioxide barrier in the real time method

The measurement category F_{H2} is a measure for the ingress of hydrogen under defined conditions into a bottle. Keeping all other parameters constant this measurement depends only on the barrier of the bottle which is thus characterised. Whether the hydrogen barrier relates proportionally to the permeation of oxygen and carbon dioxide was the matter of investigations. Oxygen ingress and carbon dioxide loss were measured with the real time method in a period of 8 months. The data were converted in a permeation rate. For the calculation an oxygen partial pressure in the environment of 21,000 Pa and a carbon dioxide partial pressure of 0 Pa were used. 20 bottles of each type were measured with both methods resulting in confidence bands shown in Figure 6.

The results of the hydrogen test allow the distinction of the bottles in the same order as the measurements with the real time method. However, the proportionality differs between bottles with a poor barrier and those with a high gas barrier. The differences of good barriers are wider spread in the real time method whilst the "monolayer bottle" together with "multilayer bottles 3 and 4" can only be differentiated by the hydrogen method. It must be assumed that both results represent the physical reality for the kind of gas employed. A direct conversion of hydrogen ingress rates into permeation coefficients for carbon dioxide is not possible by multiplication with one factor. But Figure 6 enables the estimation of the carbon dioxide barrier from the hydrogen ingress rate with sufficient precision for practical application such as bottle production control or incoming goods acceptance tests.

The scavenger is specifically effective only for oxygen and the hydrogen ingress test is insensitive to detect its activity. This represents the problematic aspect of the correlation of hydrogen ingress rate with the permeation coefficient of oxygen measured with the real-time method. In Figure 7 the data of both methods are plotted.

Bottles without a scavenger such as the "monolayer bottle" and "Coating 1" show a comprehensible relation between the oxygen

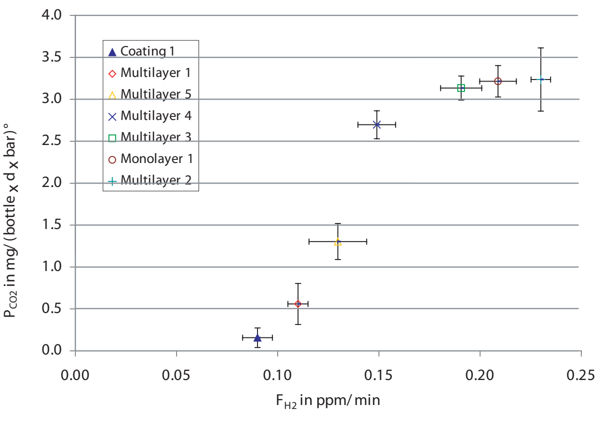

Fig. 6 Correlation of the carbon dioxide loss measured with the real-time method and expressed as permeation coefficient with the hydrogen ingress rate, confidence intervals n = 20, α = 0.05

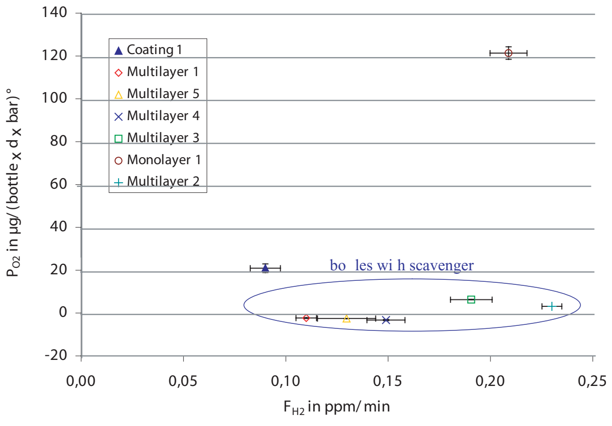

Fig. 7 Correlation of the oxygen ingress measured with the real-time method and expressed as permeation rate with the hydrogen ingress rate, confidence intervals n = 20, α = 0.05

permeation coefficient and hydrogen ingress rate. Bottles with a scavenger seem to have a more or less low passive barrier identified by the hydrogen ingress rate. However the actual ingress of oxygen is controlled by the active barrier.

4 Conclusion

The hydrogen ingress rate can be measured with a method that is rugged in regard to the application in the PET bottle production or incoming goods control. The hydrogen ingress rate is not a permeation coefficient but a flow rate through a packaging material under defined conditions, and thus an adequate measure in order to evaluate bottles under production conditions in the practice of filling. The comparison of bottles with passive barriers illustrated that there is a relation between the barriers against hydrogen on the one hand and the technological interesting gases oxygen and carbon dioxide on the other. The physical reality may not be the same for gases of different chemical nature but similar enough in order to make distinctions of bottles for practical purposes. Active barriers for oxygen can not usually be detected by the hydrogen ingress measurement.

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