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Measurement of Water Vapour Ingress in PET Bottles and Correlation with Oxygen and Carbon Dioxide Permeation

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. In order to overbear this difficulty methods are tested which use other gases or as in this instance water vapour. Instead of a complete permeation only the migration of water from PET into the bottle inner is measured. The ruggedness of the method meets the requirements of the practical measurement conditions. The correlation of the water vapour migration rate with the permeation of carbon dioxide and oxygen measured with a real-time method is linear. Active barriers employing scavenger material can not be detected by the water vapour ingress measurement.

Descriptors: multilayer, oxygen, PET bottle, permeation, quick test, water vapour

1 Introduction

This article is the second part of a study of which the first part has been published before [15]. The role of plastic bottles and the necessity of the quality control were discussed in the first paper already: 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 materials have 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]. Beside other difficulties as the creep effect (expanding of carbonised bottles) the problem is the minimum test time of this method. It is physically limited to about 2 days. Other so-called short-time tests are the manometric methods (absolute pressure method) which are 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 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 water vapour migration into PET bottles

The measuring apparatus was developed as a quick tester by the company SIG Corpoplast (Hamburg, Germany). A humidity sensor inside of a bottle measures the humidity that migrates from the bottle wall through a perhaps existing inner coating layer into the bottle inner (Fig. 1). With the help of the tester the barrier layer is supposed to be evaluated within a few minutes. The increase of humidity is measured. Water is comparably well soluble in PET and through a defined exposition of the bottle in a climatic chamber the moisture content can be increased and adjusted with a high precision. Afterwards the bottle is flushed with compressed air wile one minute in order to obtain a dry atmosphere in the inner of the bottle. At this point a dew point humidity sensor (Fa 300-2, CS-Messtechnik) is introduced according to Figure 1. The wor-

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Tables and figures see Appendix

king range is from –80 °C to 20 °C. Simultaneously the inner of the bottle is tightened to the environment. The measuring time including the flushing is 6 minutes. Every 20 seconds a measuring of the humidity takes place.

2.2 Real-time method

As a reference method the real-time measurement oxygen ingress and carbon dioxide loss is used. This method described separately [19, 15] has gained acceptance in the brewing industry because of its high reliability and the accordance to the product shelf-life.

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 in 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.

3 Results and discussion

3.1 Development of a measurement category

In Figure 2 two series of measurements demonstrate exemplary that the sensor can detect the changes in humidity properly. In the initial phase a steep raise of humidity is displayed through the measuring device. This is due to the technique of the measuring sensor and could not be avoided. The glass bottle was therefore exposed to a temperature of 23 °C and 50 % relative humidity for 1 h (repeated determination). The experiment with the glass bottles show in difference to plastic bottles (Fig. 3) a steady drop of humidity within the measuring time of 320 s. These measurements were used for the setting and the calibration of the drying of the bottle material.

During the exposition of the bottle in defined climatic conditions the PET takes up water according to the solubility. The curve progressing in Figure 3 represents the water that migrates out of the PET and that actually permeates through the internal coating layer. Apparently a time of 220 s is necessary before the linear increase of the humidity can be measured. It seems to make sense to use a fixed period between t_1 = 220 s and t_2 = 320 s as measuring time. The change of humidity in this period was set as the final measuring size "H" (water vapour migration rate) for the following experiments.

3.2 Repeatability (r)

Selected PET bottle (Coating 1 to 3) were measured daily and each measurement were repeated 25 times. The data shown in Figure 4 for the three selected bottles show a good repeatability between $r_{\text{Coating 1-3}}$= 0,069 and $r_{\text{Coating 1-3}}$= 0,095.

3.3 Impact of the conditioning parameters

The impact of the conditioning parameters (temperature, relative humidity, conditioning time) on the water vapour migration rate was investigated. These measurements were carried out with the coating bottle 2. As shown in Figure 5 there is no significant difference in the measuring result by varying the relative humidity between 50 % and 70 % (moisture of wet air 8 g/kg and 27 % higher). By varying the temperature between 23 °C and 40 °C (8 g/kg and 24 g/kg) the difference is as well not significant (Fig. 6) corresponding to a significance level of 95 % probability.

As soon as both conditioning parameters, temperature and relative humidity are varied a significant difference appears. As Figure 7 indicates that the incubation with a lower temperature and relative humidity results in a significantly smaller humidity migration compared with the conditioning on a higher level in temperature and relative humidity.

The conditioning time plays an important role as shown in Figure 8: whilst there is no significant difference in the cases of more than 30 min conditioning time the trial with 15 min incubation results in a significantly higher amount of migrated vapour.

3.4 Ruggedness of the method

The impact of these parameters was verified in a ruggedness test. 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. The effects documented too. The effects indicate a ranking of the factors concerning the extent of their influence.

The result discovers a greater influence of the conditioning time and the quantity of measuring points compared with the relative humidity and the temperature. The raise of the conditioning temperature from 95 min up to 105 min leads to mean increase of the measuring result by the factor 3 according to a significance level of 95 %. The confidence intervals of the effects range in the case of all factors in a span covering zero indicating that there is no significant impact on the measuring result and hence the method is rugged.

3.5 Measurement of selected bottles and correlation with the oxygen and carbon dioxide permeation measurements

In Figure 9 a comparison of the water vapour migration and the real-time-permeation measurements (oxygen and carbon dioxide) is shown. There is a clear tendency of qualitative correspondence of the compared methods. A quantitative correlation between water vapour and oxygen or carbon dioxide ingress can not derived from these results. Regarding the coated bottles (coating 1, coating 2 and coating 3) a significant difference between the bottles is revealed with the reference method but has not been detected with the proposed method. Multilayer bottle 1 indicates a high water vapour ingress in difference to the permeation of oxygen a carbon dioxide. In case of the oxygen the explanation can be found in the active barrier which influences the oxygen permeation but not the water vapour. The correlation analysis by Bravais-Pearson discovers a linear dependency between both methods. The correlation coefficient is r_{xy}= 0,67 for the comparison of water vapour migration and oxygen permeation. If the results for multilayer bottle 1 (active barrier) is taken out of account the correlation coefficient is r_{xy}= 0,94 for the comparison with the oxygen and r_{xy}= 0,96 with the carbon dioxide permeation.

4 Conclusion

A new quick method for the determination of the gas barrier of plastic bottles measures the water vapour migration out of the plastic material through the inner surface into the inner of a bottle. The bottles must be incubated under defined climatic conditions in order to obtain constant moisture in the plastic material. The ruggedness and repeatability allow the use of the new method considering the deviation of the influencing parameters under practical conditions. The comparison with an established real-time-permeation measurement (oxygen and carbon dioxide) reveals a linear correlation. The water vapour migration test can physically not be sensitive to active barriers. The test can be alternatively be employed in case of incoming good test or in the process control of bottle coating machines.

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Appendix

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

bottle identification	description[1]	body diameter [mm]	height [mm]	weight [g]	base thickness	wall thickness [mm]	barrier material[2] [mm]
Multilayer 1	PET/PA+Sc/PET	65.5	238.3	27.9	0.24	0.32	10 %
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

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	48	52	%	–0,9	–39,7	37,9
temperature	21	25	°C	–1,1	–39,9	37,7
time	95	105	min	2,9	–35,9	41,7
quantity of measuring points	6	8	quantity	2,6	–36,2	41,4

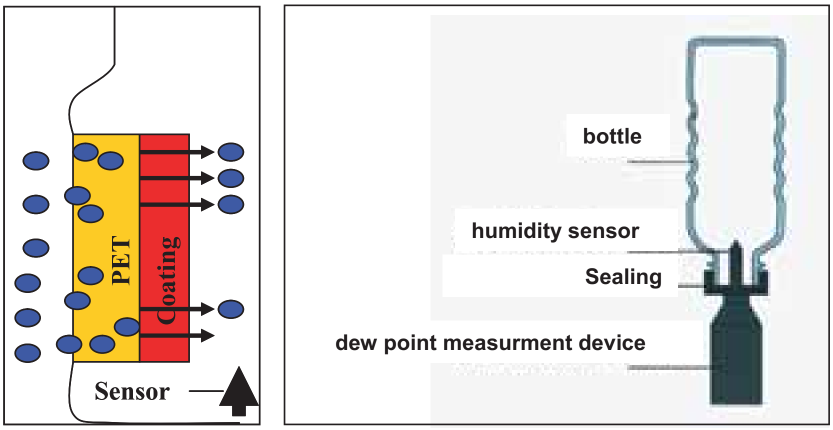

Fig. 1 **Principle of the water vapour migration (left) and detection with a humidity sensor (right) [16]**

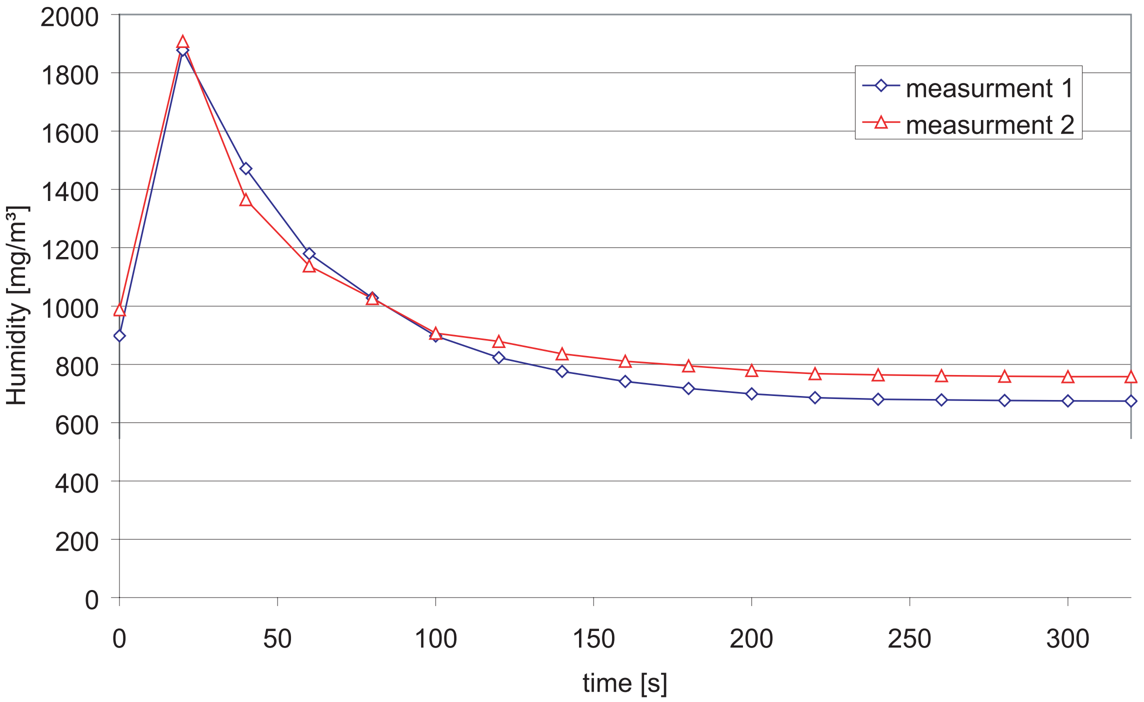

Fig. 2 Humidity measurements in the inner of 0.5 liter glass bottle (NRW) after a treatment in climatic chamber (23 °C, 50 % relative humidity)

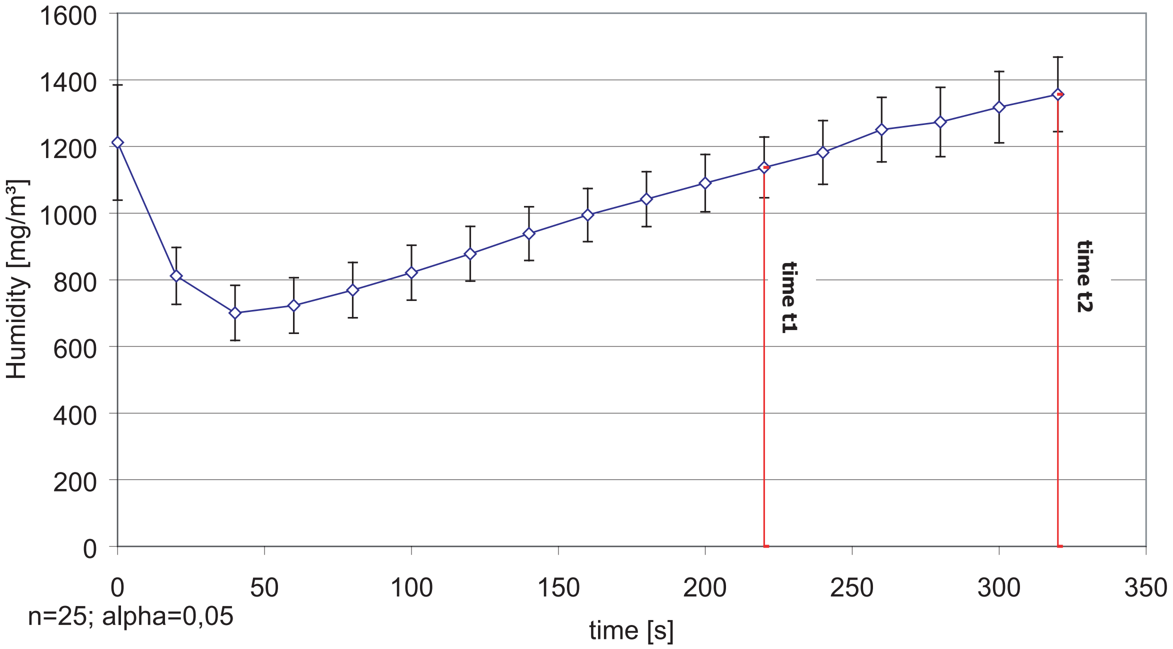

Fig. 3 humidity measured inside of an exemplary PET bottle with a internal coating barrier after a treatment in climatic chamber (23 °C, 50 % relative humidity); confidence intervals (n = 25, α = 5 %)

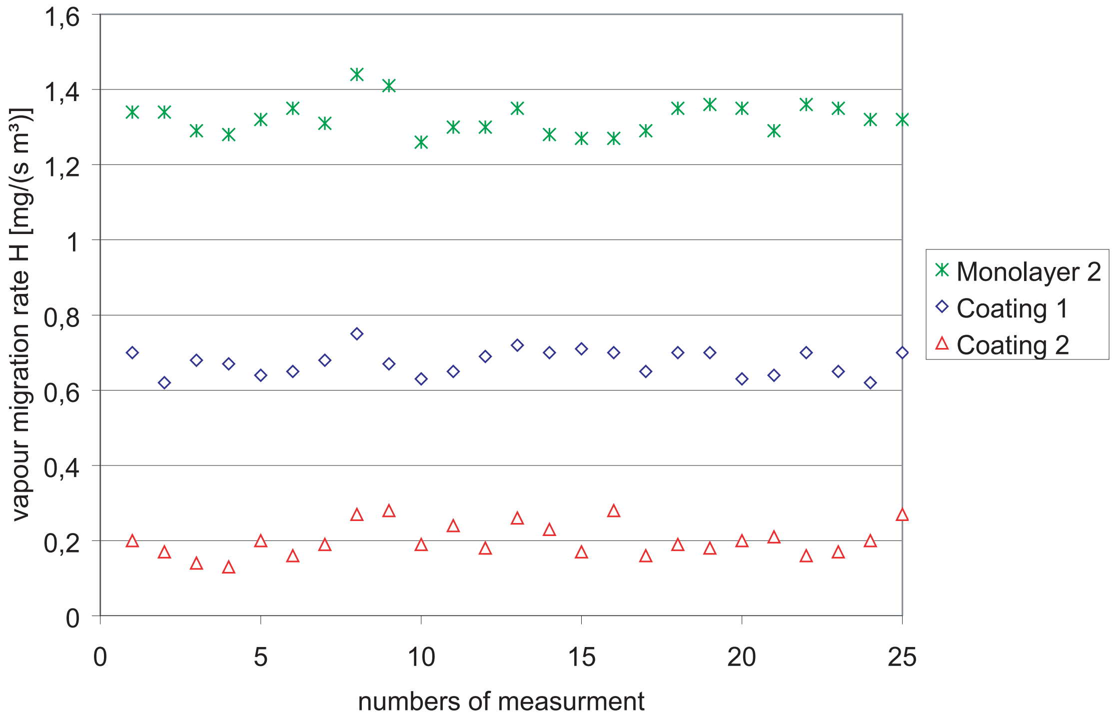

Fig. 4 **Repeatability (r) measurements of the water vapour migration rate H**

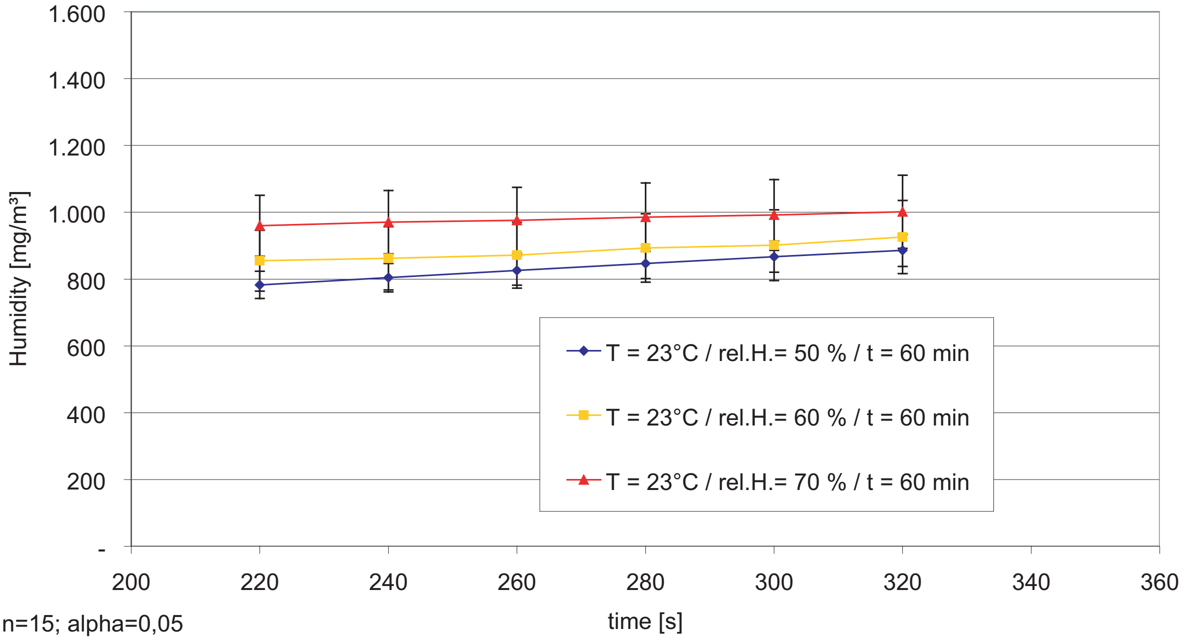

Fig. 5 **Impact of conditioning with different relative humidity on the migrated water vapour; conditioning time: 1 h, temperature: 23 °C**

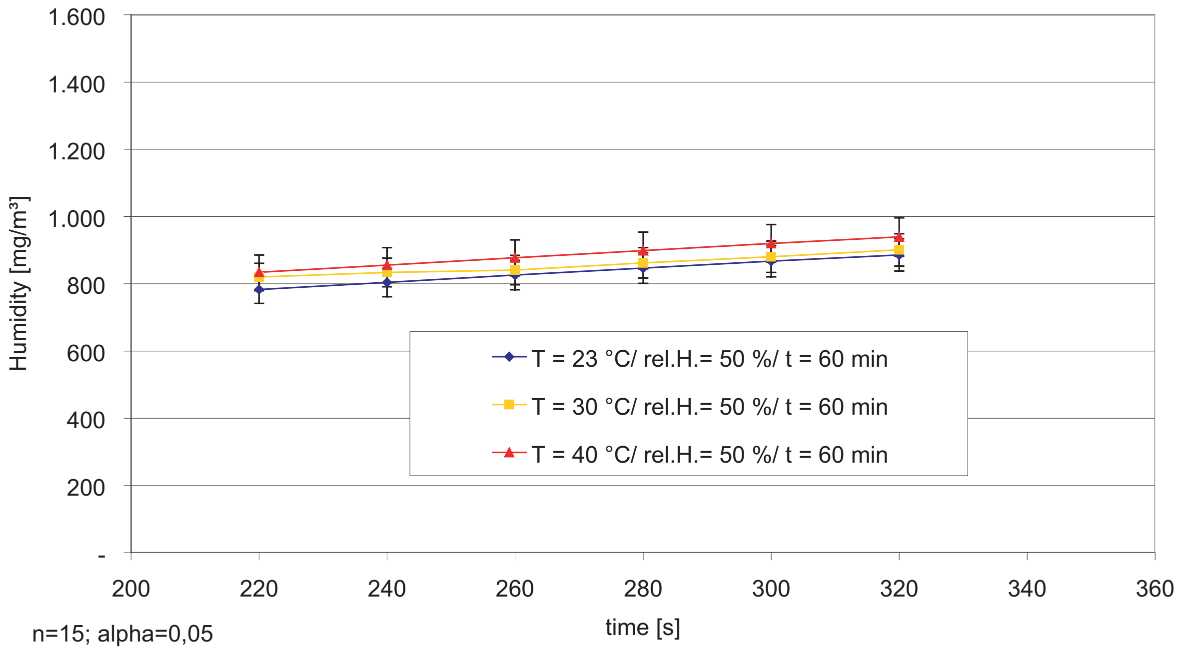

Fig. 6 Impact of the conditioning temperature on the migrated water vapour; conditioning time: 1 h, relative humidity 50 %

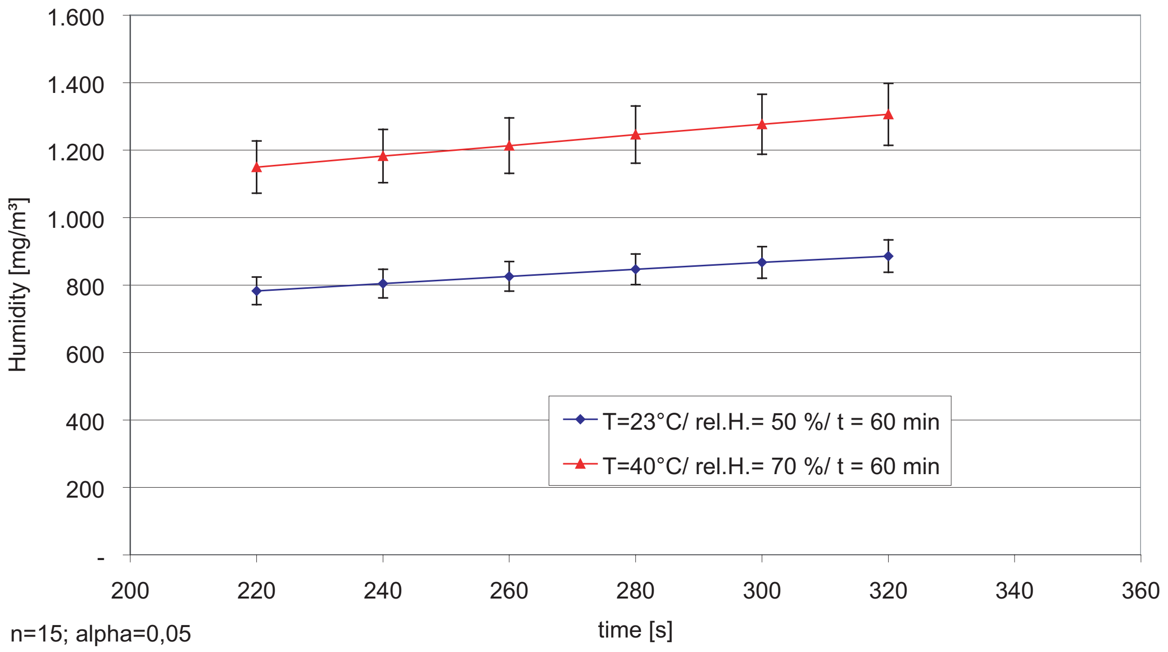

Fig. 7 Impact of the combined variation of the conditioning parameter temperature and relative humidity on the migrated water vapour, conditioning time 1 h

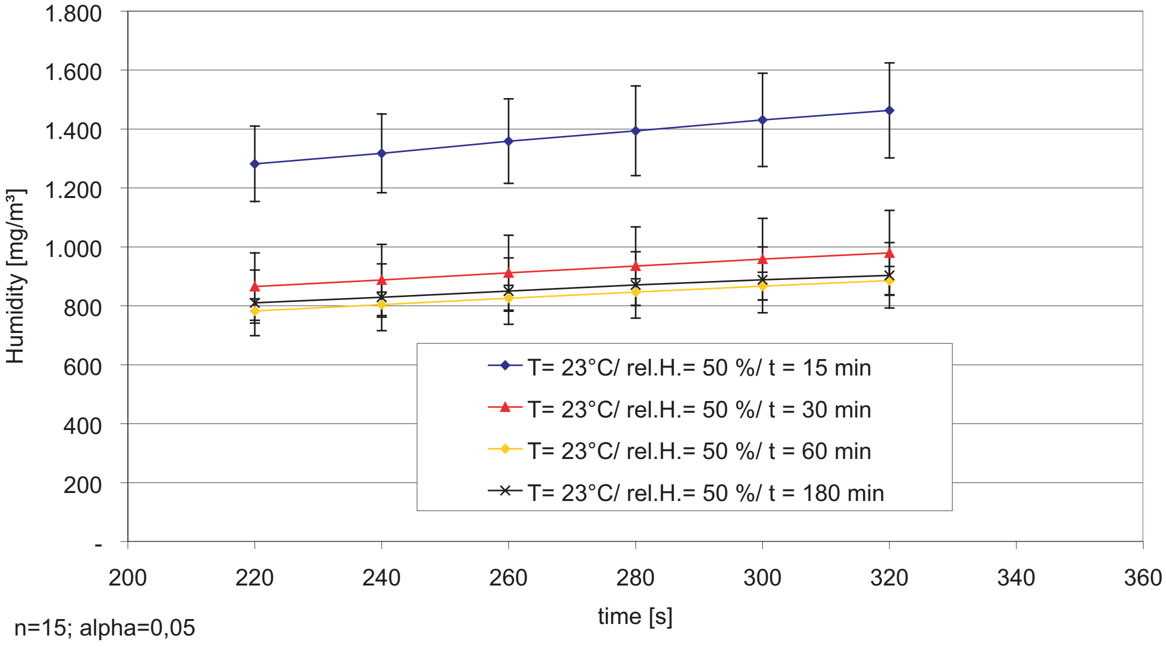

Fig. 8 Impact of the conditioning time on the migrated water vapour; conditioning temperature: 23 °C, relative humidity 50 %

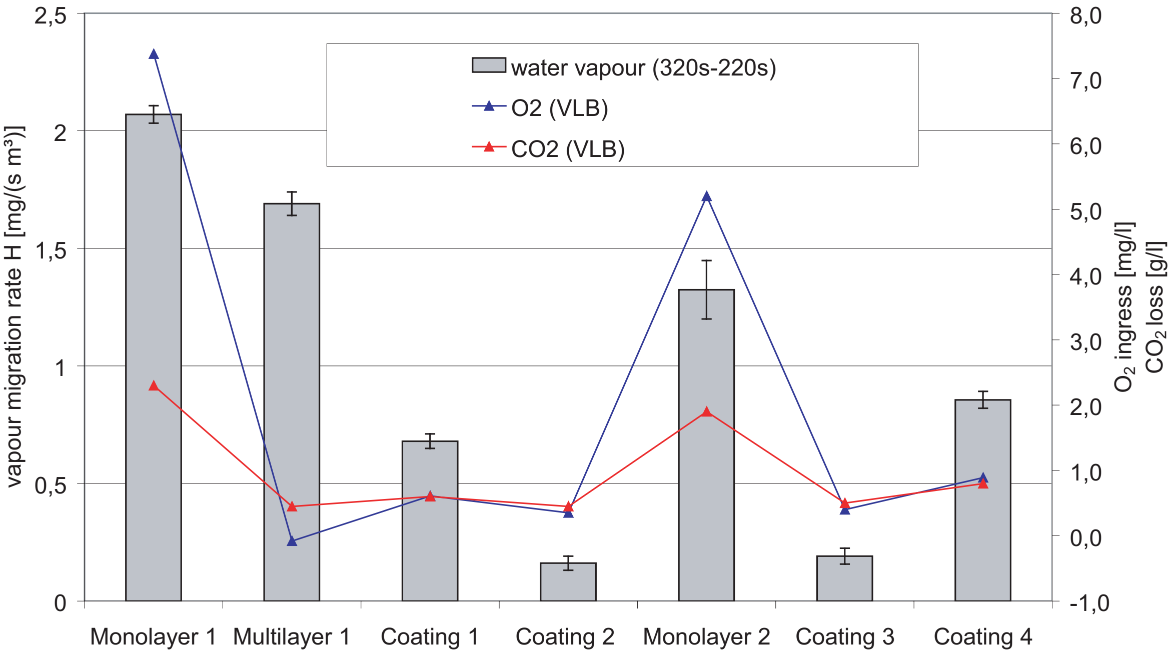

Fig. 9 Results of the water vapour ingress measurements as beside the oxygen and carbon dioxide permeation measurements by VLB method at selected bottles