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Oxygen transfer into wines through different types of PET bottles

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The oxygen transfer into empty, nitrogen-flushed PET bottles with different construction and compositions as well as into bottled wines was examined in comparison with the one into glass bottles. Three white and two red wines were bottled and the oxygen transfer into bottles was monitored under two different storage conditions. Using a new non-invasive method of oxygen measurement (PreSens™) a differentiation of oxygen permeation into empty bottles of different PET types and glass could be documented over a period of 427 days. The results of the chemical and sensory analysis of the bottled wines showed that depending on the PET bottle type and storage conditions a shelf life of up to 24 months was possible. PET bottles with specific barrier technologies developed for lower oxygen, carbon dioxide and sulphur dioxide permeation (e. g. PolyShield®/MXD6, Plasmax, APPE (multilayer PET-bottles)) are an interesting alternative for wine packaging and storage especially regarding the ecological aspects of lower transportation weight. Consumer studies should be done to clear up the general or individual acceptance of PET bottles for wine bottling and storage.
Keywords: wine in PET, PreSens™, oxygen transfer (OTR), shelf life

Sauerstoffeinbruch in Weine bei verschiedenen Typen von PET-Flaschen. *Bei PET-Flaschen unterschiedlicher Bauart und Materialzusammensetzung wurde der Sauerstoffeinbruch in leere, mit Stickstoff gespülte Flaschen sowie in mit Wein befüllte Flaschen untersucht und mit dem in Glasflaschen verglichen. Drei Weiß- und zwei Rotweine wurden in diese Flaschen gefüllt und der Sauerstoffeinbruch unter zwei verschiedenen Lagerbedingungen aufgezeichnet. Unter Verwendung einer neuen, nicht-invasiven Methode zur Sauerstoffmessung (PreSens™) konnten die unterschiedlichen Sauerstoffeinbrüche in leere PET-Flaschen und Glasflaschen über eine Zeitdauer von 427 Tagen dokumentiert werden. Die Ergebnisse der analytischen und der sensorischen Analysen der abgefüllten Weine zeigten, dass, abhängig vom PET-Flaschentyp und den Lagerbedingungen, ein shelf life von bis zu 24 Monaten möglich ist. PET-Flaschen mit speziellen Barrieretechnologien für niedrigere Sauerstoff-, Kohlendioxid- und Schwefeldioxideinträge (z. B. PolyShield®/MXD6, Plasmax, APPE (multilayer PET-Flaschen) sind eine interessante Alternative für die Abfüllung und Lagerung von Wein, speziell unter Berücksichtigung der ökologischen Aspekte auf Grund des geringeren Transportgewichts. Untersuchungen zur Konsumentenakzeptanz sollten durchgeführt werden, um die allgemeine oder individuelle Akzeptanz von PET-Flaschen für die Abfüllung und Lagerung von Wein abzuklären.*
Schlagwörter: Wein in PET-Flaschen, PreSens™, Sauerstoffeinbruch (OTR), shelf life

Le transfert d'oxygène dans les vins à travers différents types de bouteilles PET . *La pénétration d'oxygène dans les bouteilles PET vides et remplies de vin, présentant des formes et des mix de matériaux différents, rincées à l'azote, a été étudiée et comparée à celle dans les bouteilles en verre. Trois vins blancs et deux vins rouges ont été versés dans ces*

bouteilles et la pénétration d'oxygène a été enregistrée sous deux conditions de stockage différentes. Une nouvelle méthode non invasive de mesure de l'oxygène (PreSens™) a permis de documenter les différentes pénétrations d'oxygène dans les bouteilles PET vides et dans les bouteilles en verre sur une période de 427 jours. Les résultats des analyses analytiques et sensorielles des vins embouteillés montrent qu'en fonction du type des bouteilles PET et des conditions de stockage, une durée de conservation (shelf life) allant jusqu'à 24 mois est possible. Les bouteilles PET dotées de technologies de barrière spéciales destinées à minimiser les pénétrations d'oxygène, de dioxyde de carbone et de dioxyde de soufre (telles que PolyShield®/MXD6, Plasmax, APPE (bouteilles PET multicouches)) sont une alternative intéressante pour l'embouteillage et le stockage du vin, compte tenu des aspects écologiques, notamment du faible poids de transport. Des études devraient être menées afin de déterminer l'acceptation générale ou individuelle des bouteilles PET pour l'embouteillage et le stockage de vin.
Mots clés : vin dans bouteilles PET, PreSens™, pénétration d'oxygène (OTR), shelf life

Oxygen transfer into wines can be primarily influenced by using different bottling systems and procedures, but also the choice of wine packaging has a significant influence on the sensory development of wine compounds and on shelf life. Alternative packaging systems have been used in different sectors of the beverage industry for many years. Besides "Bag in Box (BiB)" packaging, bottles made of polyethylene terephthalate (PET) with different scavenging and barrier systems were developed to reduce the oxygen transfer into the bottled product. PET bottles are very common for alcohol-free and carbonated beverages like water and soda products. For beer and beer-mix beverages PET bottles have a certain market share but can only be used for a limited shelf life because of the oxygen sensitivity of beer. Wine generally is a very "traditional" alcoholic beverage which can be stored for a longer time before it is consumed. These "stored" wines certainly are only a small part of the total wine consumption. Nowadays wines are bought and directly consumed mostly because consumers prefer "fresh" wines (white and rosé wines) and wines which were already stored in the winery (red wines) since private households often do not possess a suitable place to store a wine under appropriate conditions.

The main advantage of PET bottles is the breaking resistance, the low weight and consequently the saving capacities during the transport of bottled wines. This positive environmental impact together with the improved oxygen barrier and scavenging technologies, but also the concentration of companies in the glass-producing industry made PET bottles a realistic alternative packaging material, also for the "traditional" product wine (Hamdorf, 2009).

In three experiments newly developed PET bottles were tested with empty bottles flushed with nitrogen (Trial 2) and with bottled white ('Riesling', 'Gewürztraminer', 'Pinot blanc') and red wine ('Frühburgunder', 'Regent') (Trials 1 and 3). For comparison all wines were also bottled in glass. The experiments started in 2007 and included analytical (colour, carbon dioxide, gazeous and dissolved oxygen, free and total sulfur dioxide) and sensory analyses during the storage time of 12 months (Trial 1) and 24 months (Trial 3), respectively. Furthermore the oxygen transmission rate (OTR) into the product was examined (Lay, 2009; Seckler, 2009).

Material und Methods

Trial 1

In order to test the storage behaviour of wine in PET bottles in comparison to glass bottles two white ('Riesling' 2007, 'Gewürztraminer' 2007) and two red wines ('Frühburgunder' 2007, 'Regent' 2007) were bottled and closed with 30 x 60 mm BVS aluminium screw caps with saranex liner (CSI - Europe). 50 % of the bottles were stored at 15 °C and 50 % at 20 °C to 25 °C.The weight of the empty PET bottle was 54.1 gramm whereas the glass bottle weighed 500 gramm. In the PET material of the bottle a O2-Scavenger ("Amosorb dfc", ColorMatrix) was included to minimize "matrix-oxygen" (desorption) from the PET material itself as well as the oxygen coming from the wine. For the first time the oxygen permeation through the material during the storage was measured. After one, three, six and twelve months of storage the wines from PET and glass bottles were analysed and the sensory quality evaluated. Ten bottles from each variant

were opened to analyse colour, free and total SO_2 and the content of CO_2.
Colour measurement was done with a Dr. Lange Cadas200 Spectrum-Photometer between wavelengths of 380 nm and 770 nm in intervals of 20 nm. The contents of free and total SO_2 were measured with FOSS FiaStar 5000 Analyser based on Flow Injection technology (www.foss.dk/industry-solution/products/fiastar-systems).
CO_2 contents were determined with a Mettler Toledo 965D Carbon Dioxide Analyser. Sensory tests were done with a trained panel of 14 panelists as difference tests in form of triangular tests according to DIN 10951.

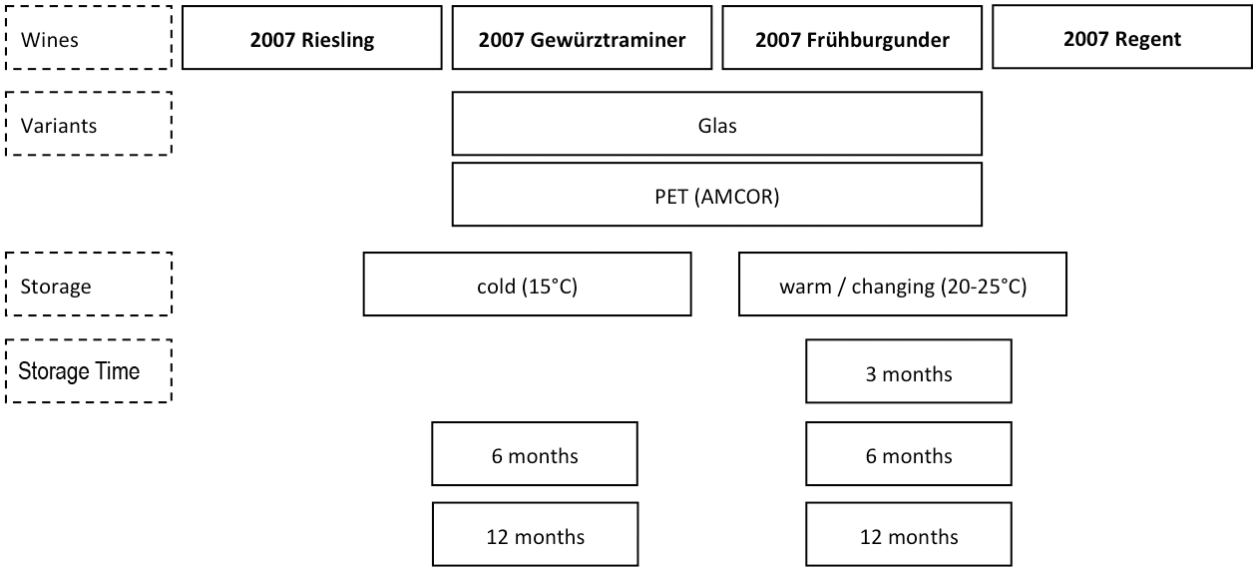

Fig. 1: Experimental Plan Trial 1, comparative trial PET versus glass with four wines from vintage 2007

Figure 1 shows the experimental design for the comparative Trial 1 with four wines.

Trial 2

In the second experiment the oxygen transmission of five transparent PET bottles of different production and composition was tested and compared to that of glass bottles (Table 1). Oxygen sensitive spots (PreSens™ PST3, PreSens) were glued into five empty bottles per variant with a silicon glue. Before closing the bottles with a 30 x 60 BVS screw cap closure (sealing liner: saranex) they were flushed with nitrogen quantitatively.
Oxygen measurement with PreSens™ is based on a photo-luminescence technology which allows a very accurate and non-destructive oxygen measurement in gas or liquid phase. It can be used in the lab, in the cellar or at the bottling line. The PreSens™ can be used as an invasive tool (using a dipping probe) or as a non-invasive tool (based on sensor spots glued inside bottles, sight-glasses or hose-connectors). The methodology is illustrated below:
As illustrated in Figure 2, a blue LED light is beamed at an oxygen sensor spot which emits a red light back in an intensity which is directly related to the oxygen concentration in the wine or in the air (empty bottle or headspace). The oxygen sensor spots are pre-calibrated and can be reused several times. (Huber et al, 2008). The measurement with PreSens™ allows a continuous monitoring of oxygen concentration in a bottle sample or tank.
The PreSens™ luminescence technology was used in Trial 2 with empty bottles but also to follow the actual oxygen consumption over time in sealed bottles with wine in Trials 1 and 3 (results for Trials 1 and 3 not shown).

Trial 3

In this experimental series to a large extent the same bottle variants which were already examined in Trial 2

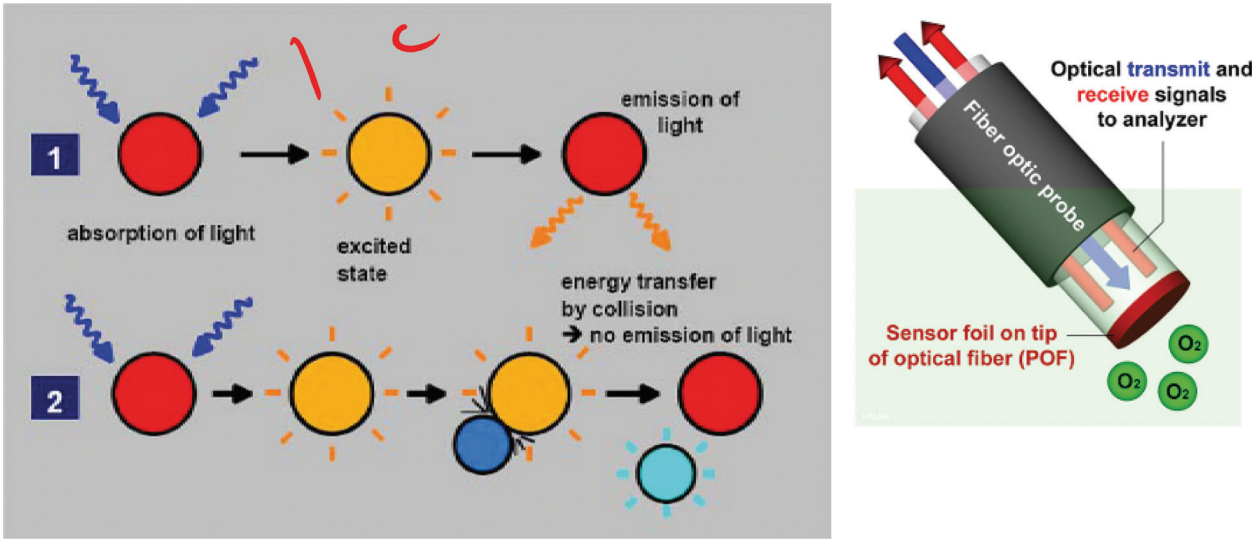

Fig. 2: PreSens™ luminescence technology (Source: PreSens™ Precision Sensing)

were used. Additionally two light green coloured PET variants were included in the bottling trial (Poly-Shield® resin + 3 % and 5 % MXD6 + colorant, resp.). In this experiment PET bottles with different barrier materials and coatings were used for the storage of a 2007 'Pinot blanc' quality wine from Rheingau. It was the aim of the experiment to monitor the oxygen transfer (OTR) through these bottles into the wine over a longer storage period. In total seven PET bottle variants were examined in this storage trial, again in comparison to glass bottles (Table 1). The storage conditions were identical to those in Trial 1 (50 % of bottles stored at 15 °C and 50 % stored at 20 °C to 25 °C). Also the same analytical and sensory testing procedures were applied after a storage time of 6, 12, 18 and 24 months.

Table 1: PET bottles used in a) Trial 2 and b) Trial 3

No.	Bottle code	Bottle material	Bottle colour	Bottle features	Bottle used in trial
1	P3 %Mc	Blend of Polyshield® Resin 2300 & 3 % MXD6	Colourless (clear)	Combined barrier properties against oxygen ingress and loss of CO_2	2 & 3
2	P3 %Mg	Blend of Polyshield® Resin 2300 & 3 % MXD6	Green	Combined barrier properties against oxygen ingress and loss of CO_2	2 & 3
3	P5 %Mc	Blend of Polyshield® Resin 2300 & 5 % MXD6	Colourless (clear)	Combined barrier properties against oxygen ingress and loss of CO_2	2 & 3
4	P5 %Mg	Blend of Polyshield® Resin 2300 & 5 % MXD6	Green	Combined barrier properties against oxygen ingress and loss of CO_2	2 & 3
5	P2 %Ocb	Blend of Polyshield® Resin 2300 & 2 % OxyClear® barrier resin	Blue / green	Barrier properties against oxygen ingress	2 & 3
6	PlasC1	SiOx covered PET (Plasmax technologie)	Colourless (clear)	Combined barrier properties against oxygen ingress and loss of CO_2	2 & 3
7	PlasC2	SiOx covered PET (Plasmax technologie)	Colourless (clear)	Combined barrier properties against oxygen ingress and loss of CO_2	3
8	PlasU	Uncoated PET	Colourless (clear)	No barrier	2
9	Glass		Colourless (clear)		2 & 3

Results and discussion

Trial 1

The results for the contents of CO_2, free and total SO_2 as well as the data from sensory difference testing after the storage period of twelve months of final 1 are documented in Figure 3. Comparing glass bottles to. PET bottles with "Amosorb dfc" it was obvious that the contents of CO_2 in the bottled wines with 'Riesling', 'Gewürztraminer', 'Frühburgunder' and 'Regent' varied significantly. The wines in glass bottles showed higher contents of CO_2 in the wines in every case. The effect of storage temperature was less important than the effect of the bottle material. This may be the case, since the PET bottle used in this trial had no special barrier to avoid CO_2 permeation. Other technologies, e. g. PolyShield® or Plasmax coating should be appropriate to reduce this loss of CO_2.

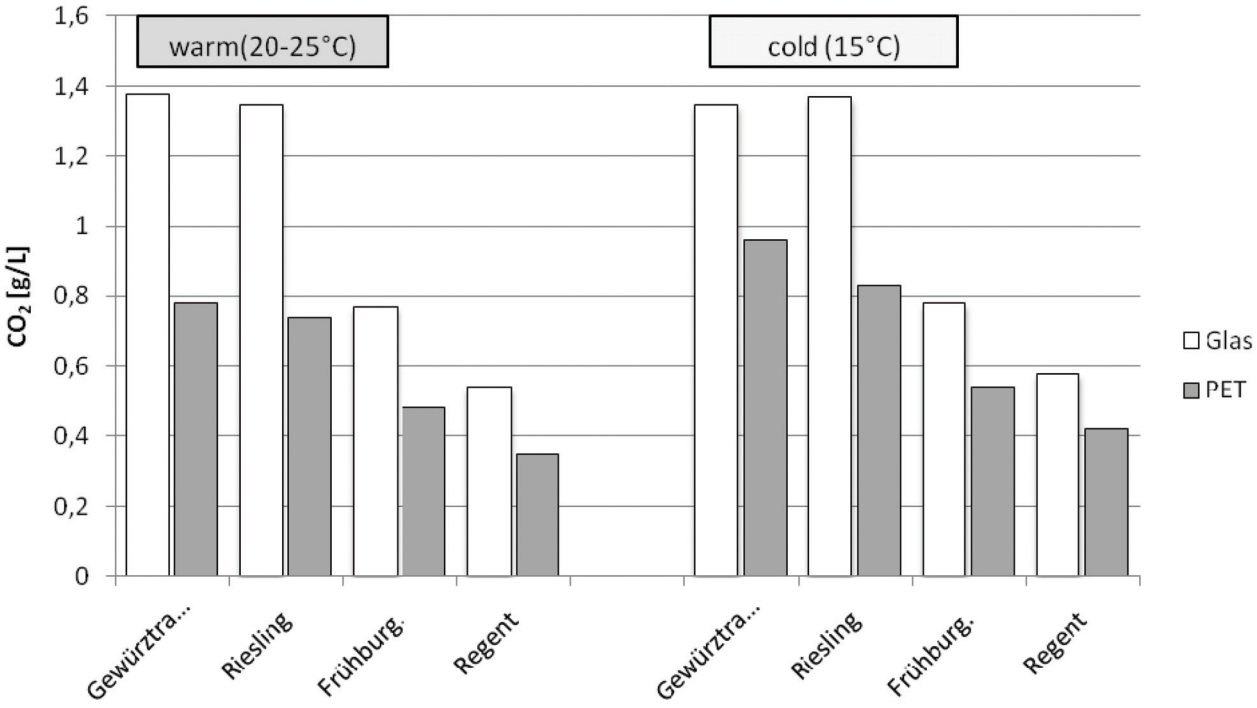

Fig. 3: Carbon dioxide in wines of different varieties from vintage 2007 in PET bottles with "Amosorb dfc" and glass bottles after 12 months of bottle storage, average from n = 2

After one year of storage the contents of free and total SO_2 were reduced in all bottle variants of Trial 1 (Fig. 4 and 5). Especially for the white wines under "warm" (20 °C to 25 °C) storage conditions the difference in the SO_2 contents between PET and glass bottles was striking. In the PET bottles with "Amosorb dfc", the content of free SO_2 was partly reduced to a content at which oxidation of wines was possible (variants Gewürztraminer-warm, Gewürztraminer-cold and Riesling-warm). For the red wines the contents of free and total SO_2 stayed on a high level over the whole storage period even under high temperature storage conditions.

After one year of bottle storage only in some variants sensory differences between the wines in the different bottle types could be examined by the testing panel (14 well trained employees of the Geisenheim Research Center). To have a significant difference in triangular testing at least 9 of the 14 panelists had to pick the different sample correctly (α = 0,05 %), for significance levels of α = 0,01 % and α = 0,001 % 10 and 11 correct answers were needed, respectively.

In triangle tests no significant difference could be detected between glass and PET bottles for the two white ('Riesling', 'Gewürztraminer') and two red

wines ('Frühburgunder', 'Regent') which were stored under a constant temperature of 15 °C
In contrary the triangular test of the warm stored wines showed significant different results after one year. The wines of 'Gewürztraminer', 'Frühburgunder' and 'Regent' exhibited significant differences between the PET bottles with "Amosorb dfc" and glass bottles. A preference test with the differentiated bottle variants did not show a clear result for one or the other bottle type.

Trial 2

In the tests with empty bottles flushed with nitrogen the effect of barriers on the oxygen transfer into PET bottles could be clearly demonstrated.In Figure 6 the quantity of oxygen measured with PreSens™ sensor spots (PST3) in the empty bottles over the time of 427 days is documented. The highest quantity of oxygen could be analyzed in the PET bottle without any barrier ("PlasU"). After 427 days, the PreSens™ measure-

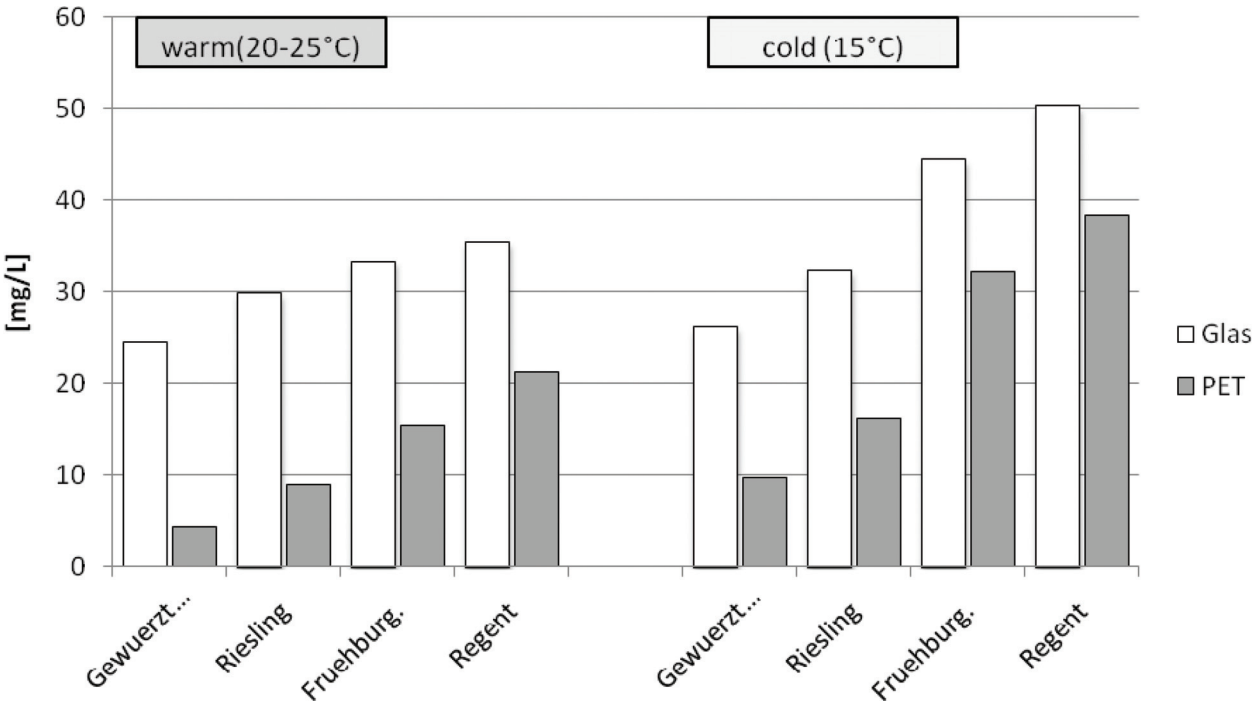

Fig. 4: Free Sulfur dioxide in wines of different varieties from vintage 2007 in PET bottles with "Amosorb dfc" and glass bottles after 12 months of bottle storage, average from n = 8

Table 2: Sensory triangular difference tests, glass vs. PET bottle, storage at 15 °C and 20 to 25 °C, 12 months

Wine	Given answers	Right answers		Preference (in case of right answers)
		Storage at 15 °C	Storage at 20-25 °C	
Gewürztraminer	14	5 n. s.	12 ***	No
Riesling	14	7 n. s.	7 n. s.	-
Frühburgunder	14	5 n. s.	11 ***	No
Regent	14	5 n. s.	9 *	No

Significance levels: 9, 10**, 11****

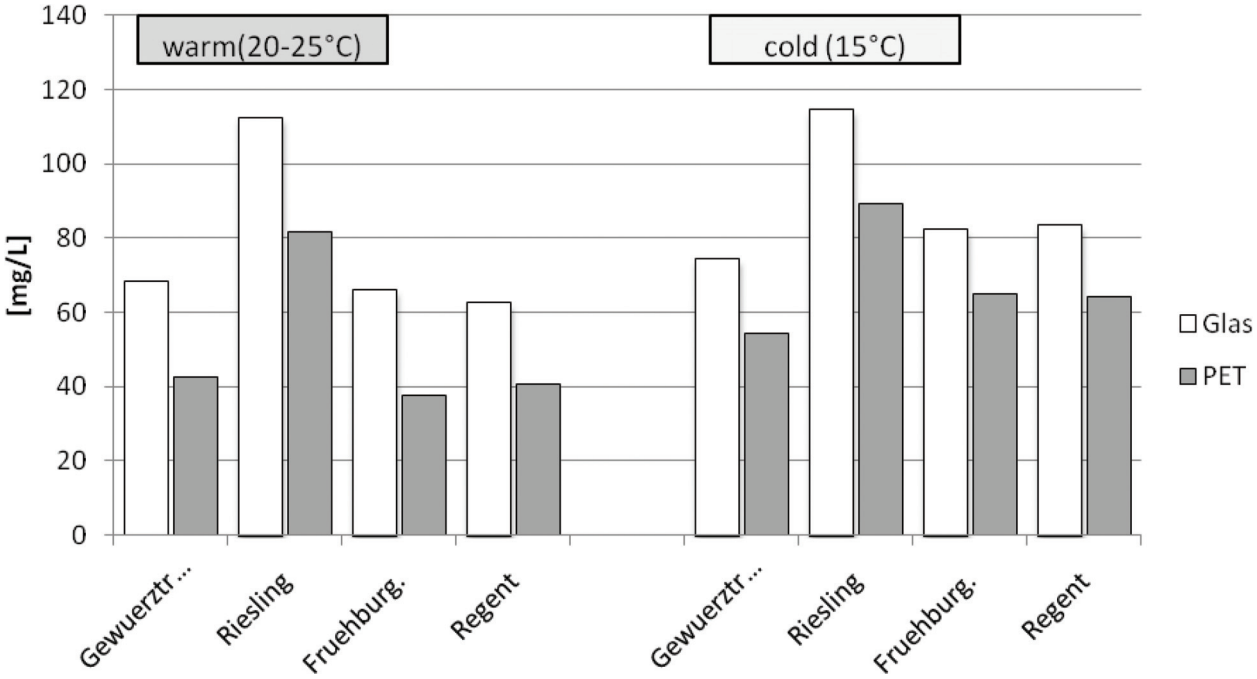

Fig. 5: Total Sulfur dioxide in wines of different varieties from vintage 2007 in PET bottles with "Amosorb dfc" and glass bottles after 12 months of bottle storage, average from n = 8

ment showed a result of 7,4 %. This means that 1,5 % of the gas volume in the bottle of this variant was oxygen because the PreSens™ system uses the maximum air content of 21 % of oxygen as 100 %. In most of the nitrogen flushed PET bottles only low oxygen ingress was documented (Fig. 6). PET bottles with a low OTR were such with "Plasmax" treatment inside (a treatment which creates a nanoscaled glass surface inside the bottle), as well as bottles with MXD6 (crystallised polyamide) in "monolayer bottles". The integration of "OxyClear® barrier resin" in PET bottles also helped to prevent the oxygen transfer into the bottle, but showed a slight increase compared to the other PET bottle variants. In total all PET bottles with barriers showed a good performance in OTR and low variation in the direct comparison.

Trial 3

In Trial 3 the bottle variants listed in Table 1 were used for storing a 2007 'Pinot blanc' with the glass bottle used for comparison. After 24 months of bottle storage significant differences concerning the oxygen transfer through bottles and consequently wine ageing could be determined. Whereas no significant difference in the contents of carbon dioxide could be found between the wines in different bottle variants, the analysis of free and total sulfur dioxide showed significant differences.

The contents of free SO_2 in the wines in different bottles stored at 15° are depicted in Figure 7, showing the development over 24 months, from bottling onwards. Using "coated" PET bottles or "monolayer" PET-bottles with PolyShield® resin, a reduced oxygen transfer into the bottles could be documented during the ageing of the 'Pinot blanc' wine. Wines filled in PET-bottles with inner nanoscaled glass coatings (PlasC1 and PlasC2) exhibited a SO_2 reduction which was comparable to that in glass bottles. Wine in monolayer bottles with PolyShield® resin and MXD6 showed even lower reduction rates of free SO_2 than in glass bottles. Generally the results of opto-chemical oxygen measurement in empty, nitrogen flushed bottles in Trial 2 could be confirmed with the results from "bottle-ageing" and reduction of sulphur dioxide in Trial 3.

Also a sensory examination in form of triangular difference tests was performed with the wines stored at

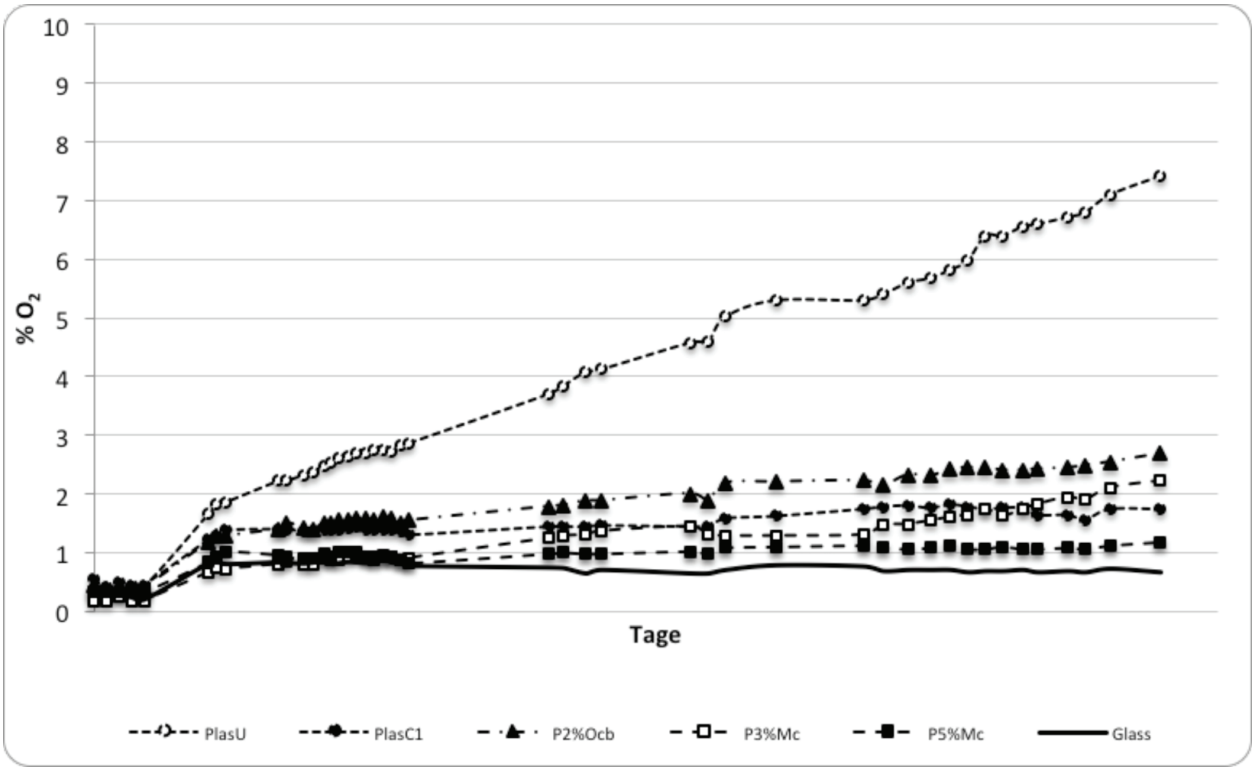

Fig. 6: Oxygen permeation into empty PET bottle types flushed with nitrogen, average from n = 5

Table 3: Sensory triangular difference tests, 'Pinot blanc' (2007), storage at 15 °C, 24 months (bottle variants: Table 1)

Glass or PET variant	Given answers	Right answers	Signi-ficance
Glass vs. PET, (IP5 %Mg)	12	4	n. s.
Glass vs. PET, (P5 %Mc)	12	3	n. s.
PET, (P5 %Mg) vs. PET, (P5 %Mc)	12	6	n. s.

Significance levels: 8, 9**, 10****

15 °C in the different PET bottle types. After 24 months of stored wines in monolayer-PET-bottles with Polyshield® technology and MXD6 barrier were compared sensorily to wines in glass bottles (Table 3). The panel consisted of twelve trained employees of the Geisenheim Research Center. To have a significant difference in triangular testing at least 8 of the 12 panellists had to pick the different sample corrects (α = 0,05 %), for significance levels of α= 0,01 % and α = 0,001 % 9 and 10 correct answers were needed, respectively. As shown in Table 3 the triangular tests gave no significant differences between any wines. The panelists could neither differentiate between the 'Pinot blanc' wines from glass and PET bottle types nor between wines in the different PET bottle types.

PET bottles with specific barrier technologies developed for lower oxygen, carbon dioxide and sulphur dioxide permeation (e. g. PolyShield®/MXD6, Plasmax, APPE (multilayer PET-bottles)) are an interesting alternative for wine packaging and storage especially regarding the ecological aspects of lower transportation weight.
Consumer studies should be done to clear up the general or individual acceptance of PET bottles for wine bottling and storage.

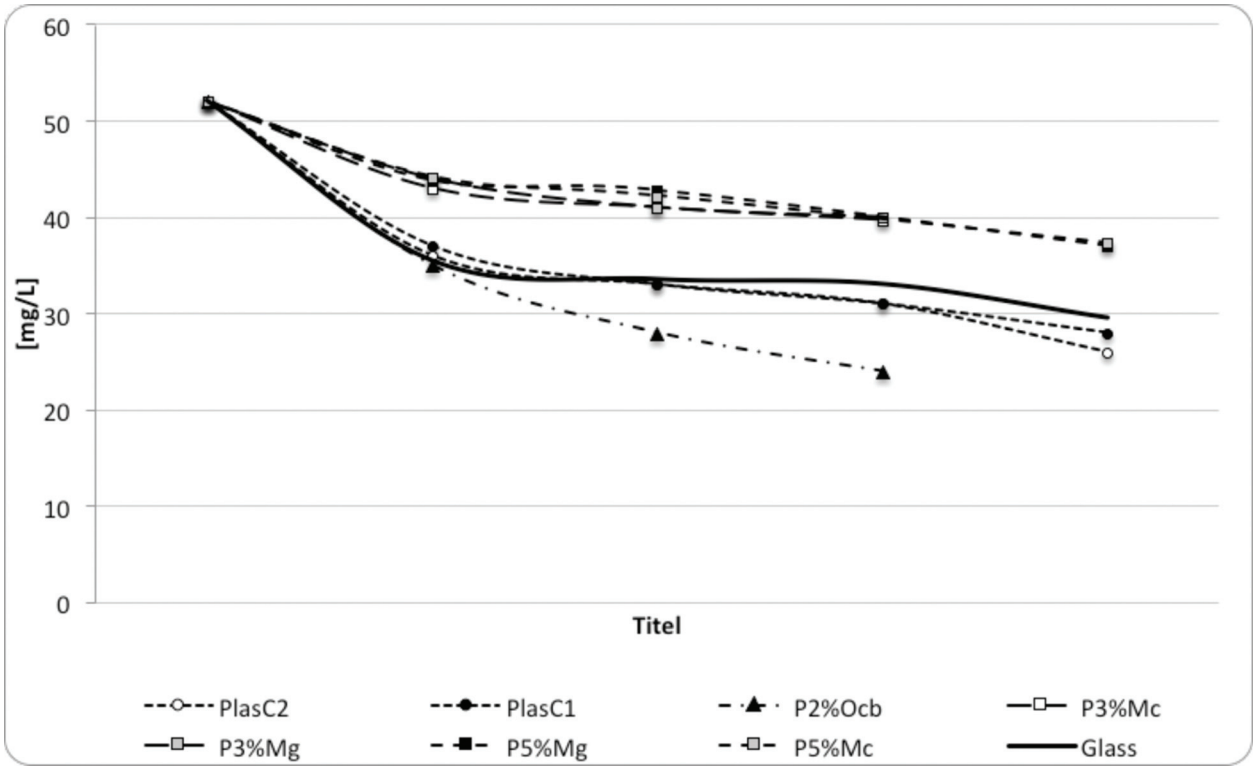

Fig. 7: Contents of free sulfur dioxide in 'Pinot blanc' (2007) in PET-bottles of different types vs. glass bottles during ageing for 24 months at 15 °C, average from n = 10

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