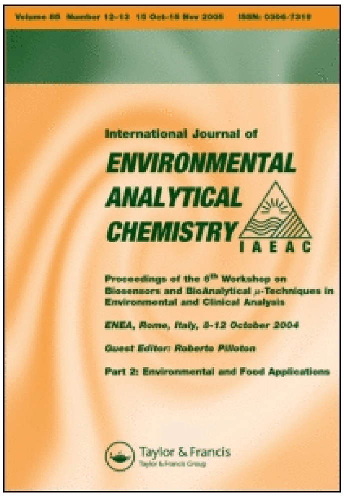

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A clever strategy for permeability studies of methyl bromide and some organic compounds through high-barrier plastic films

Cristina Nerín[a]; Elena Canellas[a]; Joaquín Romero[a]; Ángel Rodriguez[a]
[a] Grupo GUIA-Instituto de Investigación de Ingeniería en Aragón (I3A), 50018 Zaragoza, Spain

To cite this Article Nerín, Cristina , Canellas, Elena , Romero, Joaquín and Rodriguez, Ángel(2007) 'A clever strategy for permeability studies of methyl bromide and some organic compounds through high-barrier plastic films', International Journal of Environmental Analytical Chemistry, 87: 12, 863 — 874

To link to this Article: DOI: 10.1080/03067310701297787

URL: http://dx.doi.org/10.1080/03067310701297787

Intern. J. Environ. Anal. Chem.
Vol. 87, No. 12, 15 October 2007, 863–874

A clever strategy for permeability studies of methyl bromide and some organic compounds through high-barrier plastic films

CRISTINA NERÍN*, ELENA CANELLAS, JOAQUÍN ROMERO and
ÁNGEL RODRIGUEZ

Grupo GUIA-Instituto de Investigación de Ingeniería en Aragón (I3A), Centro Superior de Ingenieros (CPS), María de Luna 350018 Zaragoza, Spain

(*Received 13 December 2006; in final form 21 February 2007*)

An analytical strategy has been proposed and optimized to study the permeability of several flexible plastic materials, some of them with high-barrier properties, *versus* naphthalene, methyl bromide, toluene, ethylbenzene, and *ortho*- and *para*-xylenes. The strategy involves using a system of concentric plastic bags made from the materials to be tested polyethylene (PE) and used as permeable plastics to facilitate the homogeneous distribution of a solid compound, such as naphthalene, in vapour phase. After the permeation test, the vapour phase containing the pollutants that cross the plastic barrier is trapped in a 12% ethanol–water solution and further analysed by SPME in headspace mode. Several experimental conditions as well as different samples were tested. The results obtained are shown and discussed.

Keywords: Permeation; Methyl bromide; Naphthalene; Toluene; Ethylbenzene; Xylene high-barrier plastics; Packaging materials; SPME analysis; Wine transport

1. Introduction

Methyl bromide is used as pesticide in agricultural activities and structural fumigation. As it is a gaseous compound, it is usually injected into the soil through which it permeates, reaching the roots and the plants. It was the most widely used fumigant for soil disinfestations due to its broad spectrum activity and high penetration ability [1–4]. Its high ozone depletion potential led to an international agreement under the Montreal protocol to restrict sales and consumption of methyl bromide uses within developed countries, reaching 100% reduction in 2005 [5].

In plasticulture, the plants are covered by plastic small tunnels, and then the methyl bromide is concentrated in the trapped atmosphere under the plastic, and acts as an

---

*Corresponding author. Fax: +34-976762388. Email: cnerin@unizar.es

International Journal of Environmental and Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online
DOI: 10.1080/03067310701297787

efficient pesticide. Although some characteristics of MeBr such as mass transfer coefficient from the plastic layer have been previously measured, the permeation of methyl bromide through the agricultural plastic has not been studied to any great extent [6], and then the applied amount of this pesticide has to be overdosed to balance the losses caused by the permeation of the compound through the plastic layer.

As the efficiency of methyl bromide as pesticide has been demonstrated, this compound is also used as a disinfectant in cargo containers used for food-exportation purposes between continents. Then, food containers usually covered and protected by high-barrier polymers can be exposed to this pesticide. If the permeability properties to the specific compound are not tested, the food being carried could be contaminated by methyl bromide. Other organics commonly used as solvents, such as toluene, xylenes, or ethylbenzene, could permeate as well.

Surprisingly, high-barrier materials and plastic layers are tested for permeability to permanent gases, such as O_2 or CO_2, even water vapour or specific aromas, but organic contaminants have been rarely studied. In fact, high-barrier polymers are defined on the basis of their permeability properties *versus* oxygen, but this does not imply that they are non-permeable to organic compounds such as those mentioned above [7, 8].

The diffusion of an organic compound through a polymer layer depends on the polymer structure, area, concentration gradient, temperature, pressure gradient, and crystallinity of the material, as well as the size, shape, and polarity of the compound that diffuses [7–9]. For this reason, predicting the behaviour of specific compounds through polymeric matrices is very difficult, and experimental work is required to obtain permeability data.

The permeability study for any organic compound through a plastic layer is not an easy task. The careful design of the study, as well as very sensitive and accurate analytical procedures, are required. Also, a robust system to trap the compounds under study is necessary to guarantee that the behaviour of the set organic-compound high-barrier polymer-trapping system is stable enough over time.

Several methods for measuring permeability have been used, such as permeability cell methods, glass sorption apparatus or flow-through flux-chamber-based methods [10–17]. However, these methods require special laboratory conditions and large, complex, and expensive equipment. Consequently, a large amount of time is necessary to prepare and optimize the experimental equipment. In nearly all cases, the permeant gas is introduced directly into the measuring system. The sensitivity required for pollutants analysis is very high as the presence of pollutants, even at very low levels in goods and especially in food samples, can ruin foodstuffs and render them unsuitable for human consumption.

The direct headspace (HS) technique is not appropriate for permeation studies, since the concentration of compounds to be analysed can be very low, especially when the polymer specimen being tested is very small, such as that required for using automatic HS devices. Manual HS could be applied to larger test samples, but in this case the reproducibility and robustness of the procedure are not sufficient to guarantee the analytical requirements. Among the sensitive analytical procedures, SPME coupled to GC has been shown to be a powerful technique, which is very convenient for this type of study. This is a rapid, selective, easily automated, and solvent-free technique that simplifies the analysis of compounds in different matrices such as soil, air, or water [18–20]. Using headspace or total immersion modes, SPME has been found to be a good alternative for measuring methyl bromide, naphthalene, xylenes, toluene, ethylbenzene, and other pollutants [21–25].

Methyl bromide can be analysed using gas chromatography-electron capture detector and gas chromatography-flame ionization detector or chromatography-mass detector are appropriate for xylenes, naphthalene, ethylbenzene, toluene and related compounds.

This article shows the design of the permeability study carried out for these permeability tests, and the main objectives are:

1. To establish a robust and reliable strategy for permeability studies of high-barrier polymers or any kind of flexible material, including multilayer materials.
2. To study in depth the permeability process of methyl bromide, xylenes, toluene, styrene, and naphthalene as representative of aromatic pollutants throughout several high-barrier polymers.
3. To study the permeation properties of several plastic materials *versus* a series of organic compounds, using a 12% ethanol–water solution to trap them.
4. To study the period required for a 12% ethanol–water solution used as a wine simulant, to eliminate the pollutants after contamination through the permeation process from the barrier material.

The results obtained are shown and discussed.

2. Experimental

2.1 *Materials*

A 2-L cylinder containing methyl bromide of 99% purity from Sigma-Aldrich (Barcelona) equipped with a special valve connected to the outlet and a flexible tube connected to a needle were used as the methyl bromide source.

Toluene, *p*-xylene, *o*-xylene, ethylbenzene, styrene, naphthalene, 98% methanol, and 98% ethanol were purchased from Sigma-Aldrich. A standard solution of $200\,\mu g\,mL^{-1}$ methyl bromide was prepared in methanol.

Several polymeric materials such as polyethylene (PE) and several high-barrier materials, some made from poly-5-methylcaprolactam (polyamide) combined with other materials such as additivated PE, were used for testing their permeability to methyl bromide, toluene, *p*-xylene, *o*-xylene, ethylbenzene, styrene, and naphthalene.

Divinylbenzene/Carboxen/PDMS (DVB/CAR/PDMS) (50 µm) and polydimethylsiloxane (PDMS) (100 µm) SPME fibres were purchased from Supelco.

2.2 *Apparatus*

Thermo Trace-GC equipped with FID detector was used for naphthalene and toluene, *p*-xylene, *o*-xylene, ethylbenzene, and styrene analyses. A GC-ECD Hewlett-Packard 5890 series 2 was used for the analysis of methyl bromide.

2.3 *Permeation tests*

2.3.1 First attempt. The first attempt involved a series of concentric bags made from the plastic materials to be tested, and PE used as permeable material. The plastic bags were thermosealed in all cases. Figure 1(a) shows the first design used.

For the naphthalene assay, the internal bag was made from PE with and without holes, and this bag, containing 0.5 g of naphthalene, was placed into a high-barrier material bag. This high-barrier material bag was placed into a 0.002 dm^3 closed glass chamber. A special cap with septum was installed in the glass chamber to allow the vapour sampling. From the internal PE bag (total surface of 0.04 dm^2), the vapour of naphthalene permeates into the atmosphere named A, which is separated from atmosphere B by the high-barrier material. Then, the compounds under study are sampled in B. The volume of B, i.e. 0.002 dm^3, was measured by gravimetry after filling the space with water. Special care was taken to place the plastic bag upright in the chamber so that any reduction in plastic bag surface area exposed to permeation

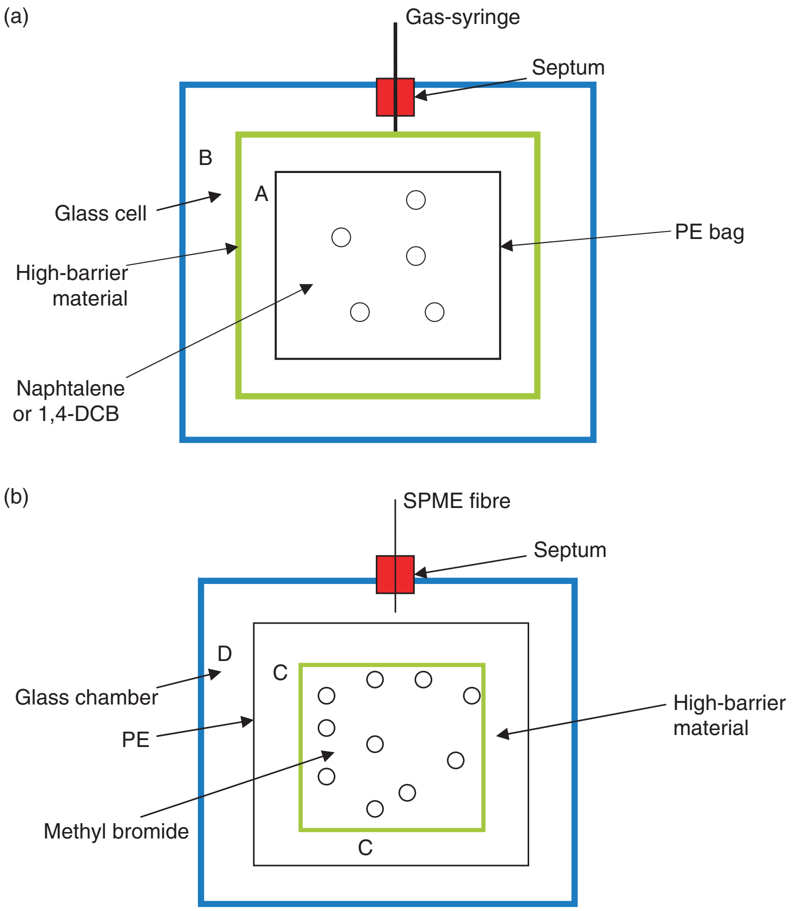

Figure 1. (a) First design used for permeability studies. (b) Second design used for permeability studies.

was negligible. The whole chamber was kept at a constant temperature of 65°C for 24 h to allow the equipment to reach equilibrium.

For the methyl bromide assay, the internal volume of the 0.02 dm^3 high-barrier polymer bag was filled with this gas and weighed to determine the initial concentration of MeBr. The high-barrier material was made of a double layer of poly-5-methylcaprolactam and additivated PE. Then, this filled bag was placed into another bag of PE. In this way, the MeBr vapour that crossed the high-barrier layer would be theoretically more protected by a second PE layer. MeBr was only sampled in D. The total set of concentric bags was placed upright in a closed glass chamber, and the volume of the external space D measured with water by gravimetry as described above was 0.4 dm^3. No direct contact between the plastic bags occurred. The whole assembling system was kept at 30°C for 24 h to allow it to reach equilibrium. Figure 1(b) shows the second design used.

Three independent cells were prepared and tested in all cases. The remaining naphthalene or MeBr in the first plastic bag was not analysed. Only the atmospheres specifically mentioned in the description and pointed out in the figures were analysed.

2.3.2 Second attempt. The second attempt involved a series of concentric bags made from high-barrier materials to be tested and PE used as permeable material. For the methyl bromide test, the internal volume of the 0.02 dm^3 high-barrier polymer bag was filled with this gas and then weighted to determine the exact amount of MeBr inside the bag. Then, this filled bag (with a total surface area of 0.3 dm^2) was placed into another plastic bag of the same material with a surface area of 0.5 dm^2. The remaining space between the two high-barrier plastic bags was filled with 100 mL of a 12% ethanol–water solution, used here as a wine simulant. No direct contact between the different plastic bags existed. Figure 2 shows the third design used. This solution, labelled as E in the figure, was sampled and analysed. For toluene, *p*-xylene, *o*-xylene, ethylbenzene, styrene, and naphthalene test the internal volume of the high-barrier polymer bag was 0.0015 dm^3. Once the high-barrier bag was ready, an adhesive septum was stuck on the external surface of the bag, and 10 μL of a solution of these compounds containing 1400 mg dm^{-3} was introduced into the bag with a syringe through the septum Then, this filled bag was placed into another PE plastic bag, and this second bag was placed into a third bag, this time of a high-barrier material. The space remaining between the second and the third bag, named G in the figure, was filled with 100 mL of a 12%

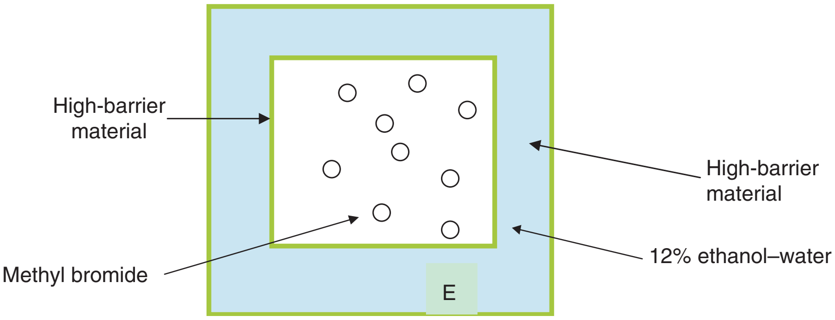

Figure 2. Third design used for permeability studies.

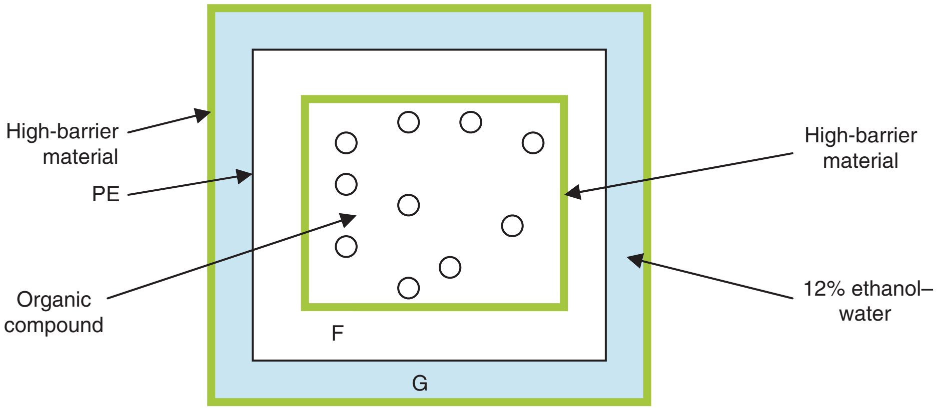

Figure 3. Fourth design used for permeability studies.

ethanol–water solution, used here as a wine simulant. No direct contact between the plastic layers was observed. Figure 3 shows the fourth design used. The whole assembly system was kept at 40°C. In all cases, three independent cells were prepared and tested. The ethanol solution was then analysed to control the increase in concentration of the permeants with time.

In a second step, 7 mL fractions of the ethanol–water solution from the bags were taken and placed into another plastic bag made of the same plastic material. The ethanol solution was then analysed over time. In this way, the permeability of the high-barrier material was obtained, as the decrease in the concentration of the volatile compounds was caused by the permeation process. The whole assembly system was kept at 40°C.

2.4 *Extraction and analysis*

In the first test prepared with naphthalene, a sample of 400 µL was taken in B (see figure 1a) with a gas syringe to perform a manual headspace analysis. Analysis was carried out by GC-FID; the injection mode was splitless; the split time was 1 min; the column type was BPX5 10 m × 0.1 mm × 0.1 µm; and the oven temperature was 40°C, held for 1 min, 30°C min^{-1} to 150°C and held for 1 min.

Methyl bromide, toluene, *p*-xylene, *o*-xylene, ethylbenzene, styrene, and naphthalene were sampled in the other tests using solid-phase microextraction (SPME).

Divinylbenzene/Carboxen/PDMS (DVB/CAR/PDMS) (50 µm) fibre was used for methyl bromide sampling and polydimethylsiloxane (PDMS) (100 µm) fibre was used for toluene, *o*-xylene, *p*-xylene, styrene, naphthalene, and ethylbenzene.

Methyl bromide was also directly sampled with SPME in the D atmosphere (figure 1(b)) inside the glass chamber, with an extraction time of 10 min.

In the third and fourth tests prepared, all the compounds were sampled by SPME in headspace mode at 40°C in a 2.5-mL fraction of the 12% ethanol–water solution, and the extraction time was 10 min.

Methyl bromide was analysed by GC-ECD; the desorption time was 10 min; the injection mode was splitless; the split flux was 30 mL min^{-1}; the split time was 2 min; the column type was ZB-624 30 m × 32 mm × 1.8 µm; and the oven temperature was held at 70°C for 2 min, 20°C min^{-1}, and held at 200°C for 4 min.

Toluene, *p*-xylene, *o*-xylene, ethylbenzene, styrene, and naphthalene analysis was carried out in a GC-FID; the injection mode was splitless; the split time was 0.55 min; the column type was DB5 MS 30 m × 25 mm × 250 µm; and the oven temperature was held at 30°C for 1 min, 10°C min^{-1} held at 80°C for 10 min, and 25°C min^{-1} to 200° C.

In all cases, calibration plots were prepared, extracted, and analysed following the same procedure.

3. Results and discussion

3.1 *First attempt*

The vapour contained in the glass cell was manually sampled with a syringe, as described above, and analysed by GC-FID. The first problem found was the sampling temperature. Naphthalene permeated more than expected and saturated the atmosphere inside the glass chamber. Then, microcrystals were observed on the external surface of the plastic material as well as on the glass surface of the chamber and even on the septum, indicating that the concentration in all the cell zones was approaching equilibrium, that is vapour pressure at saturation of the compound, Sampling at high temperature, 70°C, avoided this problem, but stabilized septa were required in the cap of the glass chamber to avoid bleeding, which could interfere with the analysis. Another key point was the reproducibility of the system. As the permeant concentration had to be measured in the vapour phase, a very strong dependence on the air volume inside the chamber was found. Small differences in the size of the plastic bags caused high differences in the concentration of naphthalene in the atmosphere as a consequence of the variation of the free air volume in the cell. A series of experiments were then carefully prepared and measured over time. Although reproducibility was considerably improved when the size of the plastic bags and consequently the free air volume were under control, another problem was observed. Depending on the concentration gradient between the internal and external atmosphere, i.e. on both sides of the plastic layer, the permeation values found were different. It is assumed that once equilibrium is reached, the concentration remains constant, but in this case the data obtained suggest that equilibrium is not reached. Thus, the higher the naphthalene amount on one side of the plastic layer, the higher the permeability of the material. To confirm these data, another series of experiments were carried out in which the internal PE bag containing the naphthalene had several holes, made to facilitate the transference of naphthalene vapour towards the high-barrier material. Theoretically, PE is permeable to organic vapours, and because of this, it was used to create a vapour enriched in naphthalene at one side of the high-barrier material.

In this case, the concentration of naphthalene in the PE bag and in zone A would be in equilibrium at all times. The main difference with respect to the first attempt is the time at which zone A is in equilibrium with the atmosphere inside the PE bag.

Comparing the results of both series of experiments, with and without holes, the conclusion obtained was that the concentration gradient affects the permeation results,

Table 1. Permeability of naphthalene through several plastic materials.

Material	Mode	Permeation (mg dm^{-2} h)
Material A naphthalene	(i) Without holes	0.0057 ± 0.0019
	(ii) With holes	0.0063 ± 0.0015
Material B naphthalene	(i) Without holes	0.0023 ± 0.0006
	(ii) With holes	0.0081 ± 0.0002
Material C naphthalene	(i) Without holes	0.0007 ± 0.0001
	(ii) With holes	0.0035 ± 0.0001
Material D naphthalene	(i) Without holes	0.0049 ± 0.0007
	(ii) With holes	0.0092 ± 0.0021

as the concentration of naphthalene from the plastic with holes was much higher than that obtained without them, as can be seen in table 1.

Special attention had to be paid to avoid the naphthalene condensation on the plastic surface, which could change the permeation process into a migration process from the plastic material. The permeation process is the result of the mass transference in which a substance is sorbed in the surface of the film, diffuses through the polymer matrix, and is released by the other side of the film. This process in fact corresponds to a sorption–migration process. Both processes can take place, but the selection of each depends on the concentration of the permeant. High concentration values allow the system to behave in a sorption–migration manner, while a low concentration of permeants in the vapour phase allows it to behave in a pure permeability manner. The later is the real situation in establishing the permeability properties of one plastic material and consequently in predicting the risk of pollution of goods when plastic layers are used as packaging materials. No other differences were observed in the behaviour of the materials under test that could justify their change in properties such as plasticity and thus explain the behaviour with the concentration gradient. Thus, a PE bag without holes is recommended for use as a permeable layer to supply a known small amount of the organic compound in the vapour phase for permeability studies following the assembly proposed here.

3.2 *Second attempt*

However, when the permeability is to be measured over time, an additional problem appears. Each analysis implies that 400 µL of gas is taken out, and the volume of gas inside the glass cell is modified along with the kinetic study. This is another variable that contributes to the whole permeation technique and requires an additional supplier of clean gas to substitute that taken out by analytical sampling. Thus, the whole system is rather complex, and a careful design is necessary to guarantee analytical control.

SPME was a good alternative to avoid this problem, and it was used to study the permeation of methyl bromide in the conditions described above, i.e. by direct sampling with SPME in the vapour phase. No analytical results were obtained in this case, as the theoretical high-barrier material was not good enough, and the ECD detector was saturated by the high concentration of methyl bromide. Therefore, another system would be required for this study.

To overcome the problems described above, the system was modified by substituting the external atmosphere in which the permeants were sampled by a liquid phase in

Table 2. Analytical features of the whole system.

	Methyl bromide	Toluene	*p*-Xylene	*o*-Xylene	Styrene	Naphthalene	Ethyl benzene
Linear range ($\mu g\,g^{-1}$)	1–60	1–150	1–150	1–150	1–150	1–150	1–150
Detection limit ($\mu g\,g^{-1}$)	0.043	0.036	0.069	0.092	0.008	0.157	0.006
Quantification limit ($\mu g\,g^{-1}$)	0.143	0.120	0.231	0.305	0.034	0.026	0.021
Repeatability (RSD%)	19.5	6.0	4.5	5.4	4.5	4.6	3.0

which the permeants were soluble. Then, sampling the liquid phase was easier than the vapour phase, and the addition of the same amount of liquid to balance the total amount in the cell was very easy.

A solution of 12% ethanol in water was chosen as the liquid phase for several reasons. First, the solubility of the compounds under study was higher than in water, and this solution did not affect the behaviour of the plastic itself. In fact, the solubility values were approximately 1.5 g/100 mL for methyl bromide and 0.003–0.05 g/100 mL for the rest of the compounds. Second, one of the widely used systems for wine transport in cargo carriers is the large bag containing high-barrier plastic layers. Consequently, this solution would be an appropriate wine simulant.

Methyl bromide, toluene, *o*-xylene, *p*-xylene, styrene, naphthalene, and ethylbenzene were used as permeants. The glass chamber in this case was also substituted by another plastic bag made from the high-barrier material under study. The likely loose of compounds by permeation through this external layer was considered as negligible. In these conditions, different sizes of plastic layers could be studied.

A kinetic study was designed in this case to confirm the availability and robustness of the new technique. It involved taking a fraction of 2.5 mL of the ethanol–water solution after each fixed time and analysing this by SPME. After the analysis, this amount of 12% ethanol–water solution was added back to the bag to keep the volume of the liquid phase constant.

To study the time required for releasing MeBr from the ethanol solution throughout the high-barrier material, fractions of 7 mL were taken and placed into another plastic bag made of the same plastic material, and the analysis of compounds over time was carried out.

SPME in headspace mode was applied in this case. The optimization of the SPME procedure for these pollutants was previously developed and optimized [20–25]. Divinylbenzene/carboxen/PDMS (DVB/CAR/PDMS) (50 μm) was used for methyl bromide sampling and polydimethylsiloxane (PDMS) (100 μm) was used for toluene, *o*-xylene, *p*-xylene, styrene, naphthalene, and ethylbenzene sampling in the experimental conditions above described. The analytical features are shown in table 2. As can be seen, with the exception of MeBr, the RSD values are lower than 6%, which is acceptable, taking into account that these values represent the reproducibility of the whole system: permeation + sampling + SPME analysis.

Figure 4 shows the concentration of permeants in the wine simulant over time. As can be seen, the plots in figure 4 present the same profile as that for a standard permeation experiment following the quasi-isostatic procedure [26]. Therefore, the strategy designed appears to be valid. From the slope of the central linear part of the curve, the permeability can be determined. Only one high-barrier material is shown here, since the

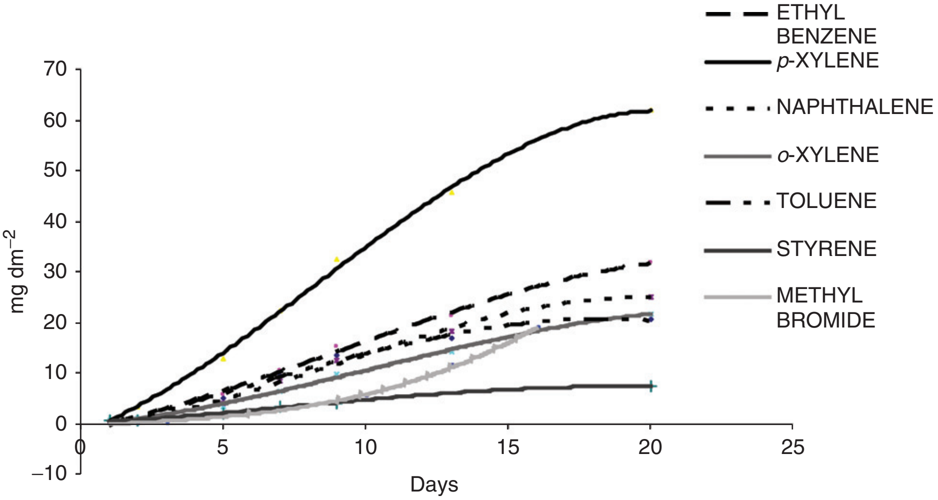

Figure 4. First step. Evolution of the concentration of permeants over time from the gas phase through the high-barrier material to the ethanol–water solution.

purpose is to study the performance of the designed system, instead of the individual permeability values of one specific polymer. As can be seen, the permeability properties depend on the chemical compound, and even those having a very similar chemical structure, such as *ortho*- and *para*-xylenes, behave differently. Methyl bromide showed very little permeation during the first 6 days, but after this period the permeation value showed an exponential increase. This is quite surprising, as MeBr is a quite small size, and its permeation through the pores of the plastic barrier would be expected to be rapid and constant over time. As MeBr is liposoluble, it could be trapped in the plastic layer and likely diffuse towards the outer side of the plastic, thus increasing the concentration of this compound in the ethanol–water solution. This behaviour was not observed for any of the other compounds studied.

Among the compounds studied, styrene had the lowest permeation properties which could be attributed to its stereochemical characteristics with a planar aromatic ring and a polar and three-dimensional vinyl group. It is well known that styrene diffusion permeation and migration from a wide variety of plastics are very low [27]. None of the compounds reached the saturation level in the wine simulant. This means that if goods with a high-barrier plastic as packaging material are in contact with a polluted environment, they could be seriously affected. Nevertheless, the permeation process involves the transference of gases through the plastic layer. Consequently, it is interesting to determine the time required for the ethanol–water solution to remove the pollutant through the plastic layer once the source of MeBr has been removed.

Figure 5 shows the concentration profile of the compounds in the wine simulant as a result of the permeation process from the solution towards the external atmosphere throughout the plastic material. It is clear that in all cases, once the compounds reach the wine simulant, a period of at least 5 days is required to remove the pollutants from the solution when it is still contained in the high-barrier material. Also, in this case, methyl bromide behaves differently to the other compounds, and its concentration remains almost constant in the wine simulant, even after 12 days.

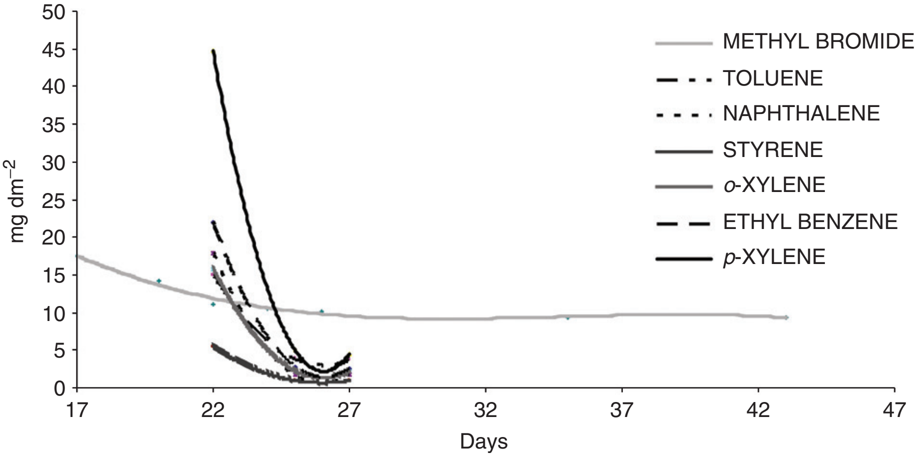

Figure 5. Second step. Evolution of the concentration of permeants over time from the ethanol–water solution through the high-barrier material to the atmosphere.

4. Conclusions

Following the technique of using concentric bags and using a wine simulant to trap permeants, which are then analysed by SPME in headspace mode, the permeability results for naphthalene, styrene, toluene, ethylbenzene, and *ortho*- and *para*-xylenes are robust and reliable. In this way, the potential contamination of goods protected by high-barrier plastics can be studied, and the permeability studies of organic compounds, in any kind of plastic material, can be carried out. The proposed technique does not require complex apparatus or hyphenated techniques, as the experimental device is very cheap, easy to prepare and use, and available for any laboratory carrying out such permeability studies. The proposed procedure provides a similar permeability profile but using an easier and cheaper experimental approach than the quasi-isosthatic method proposed by Crank [26]. The method is also similar to that proposed by Chitwood *et al.* [28] to measure the mass transference coefficient of MeBr.

Acknowledgements

This work has been financed by Gobierno de Aragón, Consolidated Research Group GUIA, reference T-10, 2006.

References

[1] A. GamLiel, A. Grinstein, L. Klein, Y. Cohen, J. Katan. *Crop. Prot.*, **17**, 241 (1998).
[2] A. Minuto, G. Gilardi, M.L. Gullino, A. Garibaldi. *Crop. Prot.*, **18**, 365 (1999).
[3] S. Klose, V. Acosta-Martínez, H.A. Ajwa. *Soil. Biol. Biochem.*, **38**, 1243 (2006).
[4] B.M. Santos, J.P. Gilreath, T.N. Motis, J.W. Noling, J.P. Jones, J.A. Norton. *Crop. Prot.*, **25**, 690 (2006).
[5] Y. Yokouchi, D. Toom-Sauntry, K. Yazawa, T. Inagaki, T. Tamaru. *Atmos. Environ.*, **36**, 4985 (2002).

[6] M. Austerweil, B. Steiner, A. GamLiel. *Phytopathology*, **24**, 491 (2006).
[7] K. Galic, N. Cikovic. *Polymer Test*., **20**, 599 (2001).
[8] D. Wang, S.R. Yates, J. Gan, J.A. Knuteson. *Atmos. Environ*., **33**, 401 (1999).
[9] J. Gajdos, K. Galic, Z. Kurtanjek, N. Cikovic. *Polymer Test*., **20**, 49 (2001).
[10] S.K. Papiernik, S.R. Yates, J. Gan. *Environ. Sci. Technol*., **35**, 1240 (2001).
[11] S.K. Papiernik, F.F. Ernst, S.R. Yates. *J. Environ. Qual*., **31**, 358 (2002).
[12] K. Chao, J. Lai, H. Lin, Y. Hsu. *Polymer Test*., **25**, 975 (2006).
[13] M. Pino, R.A. Duckett, I.M. Ward. *Polymer Test*., **46**, 4882 (2005).
[14] K. Friess, M. Šípek, V. Hynek, P. Sysel, K. Bohatá, P. Izák. *J. Membr. Sci*., **240**, 179 (2004).
[15] H. Lin, B.D. Freeman. *J. Membr. Sci*., **239**, 105 (2004).
[16] R. Gavara, R. Catalá, P. Hernández-Muñoz. *Addit. Contam*., **14**, 609 (1997).
[17] P. Hernandez-Muñoz, R. Catalá, R. Gavara. *Food Addit. Contam*., **18**, 673 (2001).
[18] C. Nerín, C. Rubio, J. Salafranca, R. Batlle. *Rev. Anal. Chem*., **19**, 435 (2000).
[19] R. Batlle, C. Sánchez, C. Nerín. *Anal. Chem*., **71**, 2417 (1999).
[20] X. Liu, J. Pawliszyn. *J. Membr. Sci*., **268**, 65 (2006).
[21] O. Ezquerro, G. Ortiz, B. Pons, M.T. Tena. *J. Chromatogr. A*, **1035**, 17 (2004).
[22] J. Salafranca, C. Domeño, C. Fernández, C. Nerín. *Anal. Chim. Acta*, **477**, 257 (2003).
[23] J.C. Flórez Menéndez, M.L. Fernández Sánchez, J.E. Sánchez Uría, E. Fernández Martínez, A. Sanz-Medel. *Anal. Chim. Acta*, **415**, 9 (2000).
[24] B.C. Blount, R.J. Kobelski, D.O. McElprang, D.L. Ashley, J.C. Morrow, D.M. Chambers, F.L. Cardinali. *J. Chromatogr. B*, **832**, 292 (2006).
[25] C. Domeño, Fca. Martínez-García, L. Campo, C. Nerín. *Anal. Chim. Acta*, **524**, 51 (2004).
[26] J. Crank. *The Mathematics of Diffusion*, 2nd Edn, Clarendon Press, Oxford (1975).
[27] C. Nerín, C. Rubio, J. Cacho, J. Salafranca. *Food Addit. Contam*., **15**, 346 (1998).
[28] D. Chitwood, M.A. Deshusses. *Environ. Sci. Technol*., **35**, 636 (2001).