CHEMICAL ENGINEERING TRANSACTIONS, Volume 15, 2008
Edited by Renato Del Rosso

Permeability to water vapour and hydrogen sulphide of some sampling bags recommended by EN 13725

Jean-Michel GUILLOT, Sandra BEGHI
Ecole des Mines Alès, 6 av. de Clavières, 30319 Alès cedex, France
jean-michel.guillot@ema.fr ; sandrabeg@yahoo.fr

A sample preparation method developed and called SWR for Sample Water Removal use the water vapour permeability of bag films. Such behaviour can be used as pre-treatment of sample. Water elimination is very useful for some physical-chemical analyses that are not compatible with high humidity level in the air sample. Because H_2O can diffuse very quickly through films, it is necessary to verify if Hydrogen sulphide (H_2S) can diffuse also easily. The present study shows the water diffusion through different films and hydrogen sulphide diffusion through Tedlar and Nalophan films. These films are used to make sample bags for odour sampling before olfactometric measurements.
The concentration level of H_2S in bags was followed by GC-PFPD. The initial levels were around 10 mg/m3. At 24±1°C, 7% and 15% are respectively lost by Tedlar and Nalophan bags over a period of 48 hours. This decrease can be attributed mainly at a diffusion process through the film. If the analysis is carried out in a short delay after sampling (less than 20 h), the decrease is still lower than 5% and can be considered as negligible on odour concentration impact for olfactometric measurement. This fact confirms the necessity to quantify odour quickly after sampling but the study clearly shows that water diffusion must be verified. Because a sample in bag can be easily dried or humidified by the influence of the external atmosphere, the sample inside can evaluate. A dried sampled atmosphere can become quickly humid (5-7 hours) during transportation for example and if some compounds are easily hydrolysable, the sample will change in terms of chemical composition and probably in odour level. Sampling bags can be still used but a better control of temperature and humidity conditions during short-time storage is necessary.

1. Introduction

Sampling of odorous and/or VOC contaminated atmospheres is often carried out using sampling bags. Such a sampling technique is easy to handle, cheap and well adapted on odour measurement by connecting bags with air samples to the olfactometer. A standard norm (CEN, 1999) indicates that best materials for bags are Tedlar, Teflon and Nalophan. If Tedlar bags has been used for 20 years, Nalophan bags are more recent and cheaper and Teflon bags are expensive. Van Harreveld (2003) had shown that odour is stable in Nalophan bags for a period of 4 to 12 hours. Another study (Koziel et al., 2005) had shown that Nalophan bags give the best recovery for 11 odorous compounds comparatively to Tedlar and Flex Foil films.
In the present work, the water diffusion through a poly(vinylfluoride) or a poly(ethylene-terephtalate) PET films respectively named Tedlar and Nalophan has been studied. A sample preparation method based on this diffusion has been developed and called SWR for Sample Water Removal (Beghi et Guillot 2006 et 2008). This pre-

treatment is different from classical approaches based on water trapping on Nafion membrane (Foulger and Simmonds, 1979) or on drying agents (Guillot et al., 2000). It is also a different way comparatively to dry purge to eliminate water on sorbent, dry dilution to decrease gas humidity or warm trap to limit water trapping on a solid sorbent. In all cases, losses of other compounds can be observed.
With the SWR method, it has been shown that kinetic aspects of water diffusion and organic diffusion were different. With a high differential gradient of humidity (between inside and outside the bag), a humid atmosphere in a bag can be dried in a few hours when organic compound diffusion is not significant over a same period and needs a few days to give important concentration decrease. Hydrogen sulphide H_2S seems similar to H_2O in terms of geometry although sulphur is a bigger atom than oxygen. Because H_2S is very often present in odorous atmospheres, specific tests were carried out with this compound. In the case of sulphur compound analysis (especially with reduced compounds), sample protocol must be tested because interactions between sampling device materials and compounds can be observed (Kim et al., 2006a and 2006b).

2. Materials and methods

2.1 Experiments of water diffusion through sampling bag films

Firstly, a Tedlar bag was compared to equal volume bags made with other films: Flex foil and Teflon. The Teflon and Tedlar films used had a 50 µm thickness while the Flex foil bag was made of different layers, its global thickness was 75 µm. For this first comparison, sample bags had a 3 L volume and the same stainless-steel valves (bags were all purchased from SKC-Arelco A.R.C., Fontenay sous bois, France). Sample bags of each film (2 bags for each film) were filled with humid air at around 55 % relative humidity at 24°C. Such humidity level corresponds to 25 mg of water for 3 L of air at this temperature according to the Mollier diagram. The bags were placed simultaneously in a Plexiglas chamber shown in figure 1 (dimensions: 0.675 m x 0.685 m x 0.332 m; volume 153.5 L) flushed by a dry air stream (rH < 5 %) at 5 L/min flow. Relative humidity was measured with HD 100 Kimo hygrometer (Montpon, France). The procedure for humidity measurement was as follows: For one bag of each film, the internal relative humidity of the sample bags was measured by pumping the sample at around 250 mL/min during 45 sec every 1 or 2 hours. For the second bag, the relative humidity was only measured at the end of the experiment to verify that the samples taken from the first bag did not significantly affect the rate of water diffusion.

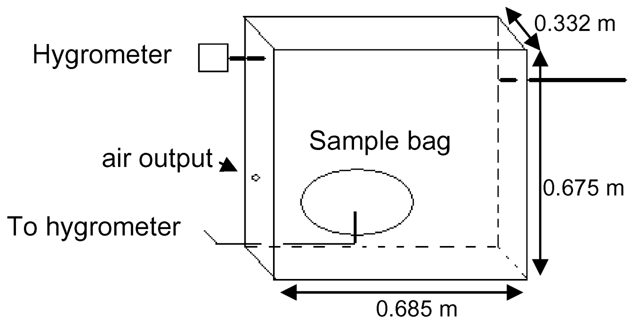

Fig. 1. Chamber flushed with a dry air stream

Secondly, water vapour diffusion through Nalophan bag walls was compared to water vapour diffusion through Tedlar bag walls. Characteristics of sample bags are given in table 1. Both sample bags were filled with humid air at around 80 % relative humidity at 20 °C which corresponds to 14 mg of water vapour per litre of air according to the Mollier diagram. The bags were placed simultaneously in the Plexiglas chamber flushed by a dry air stream (RH < 5 %), at a 10 L/min flow. For both bags, the internal relative humidity was measured with the procedure described previously.

Table 1: Characteristics of Nalophan and Tedlar bags

Film	Bag volume (L)	Ratio surface/volume (cm²/L)	Film thickness (µm)	Type of valve	Supplier
Nalophan	10	356	20	Teflon	Olfatec, Germany
Tedlar	10	273	50	Stainless steel	SKC, Arelco, France

2.2 Experiments of hydrogen sulphide diffusion through sampling bag films

For tests with hydrogen sulphide, bags were filled with air at 10 mg/m^3 of H_2S. Such concentration was obtained by dilution of standard gas at 1 g/m^3 (Messer, Asnières, France). The concentration level of H_2S in bags was measured by a CP-3800 Varian gas chromatograph equipped with a gas valve for injection of air sample and a PFPD detector. For these experiments, the bags were left, at room temperature and room humidity for four days. Because tests of diffusion are based on the great difference between internal and external concentration, bags with H_2S are kept in the laboratory during the experiment. It was not necessary to maintain a great difference as previously with humidity because ambient air does not contain H_2S comparatively to H_2O.

3. Results and discussion

3.1 Water diffusion through sampling bag films

For the first comparison of films, Tedlar bags were tested simultaneously with Teflon and FlexFoil bags of three litres each. These results are shown on figure 2 and demonstrate that water diffusion is important with Tedlar film comparatively to others. In the Tedlar bag, the amount of water decreases from 22.5 mg to less than 3.5 mg (r.H < 10%) in less than 6 hours. Over the same period, the amount of water in Teflon bag is three times less important. It needs one day to reach 2.9 mg (r.H < 20%). For FlexFoil film, no significant water diffusion can be observed over a short period and over several days.

For the second comparison, Tedlar and Nalophan bags of 10 L were used. The air contained in the Nalophan bag lost more than 10 mg of water per litre of air in 2 hours which correspond to 100 mg of water vapour for the whole bag. During those 2 hours, the air contained in the Tedlar bag lost less than 6 mg of water per litre of air (60 mg for the bag). The Nalophan bag sample humidity dropped from 80 % to 20 % relative humidity at 20 °C in 2 hours, the Tedlar bag in 4.5 hours. Finally, the sample water removal (SWR) method was faster with Nalophan bags than with Tedlar bag.

Both sample bags do not have the same surface/volume ratio, film thickness and type of valve as mentioned in table 1. For these reasons, this experiment the whole water vapour diffusion through the bags compared but not both film permeability to humidity.

Indeed the thickness of the PET film can be the reasons why the diffusion of water is faster through Nalophan bag walls than in the Tedlar bag, figure 3.
When this experiment was run, it was not possible to find any commercial Nalophan bags which have the same characteristics (valves and film thickness) as the Tedlar bags ones.

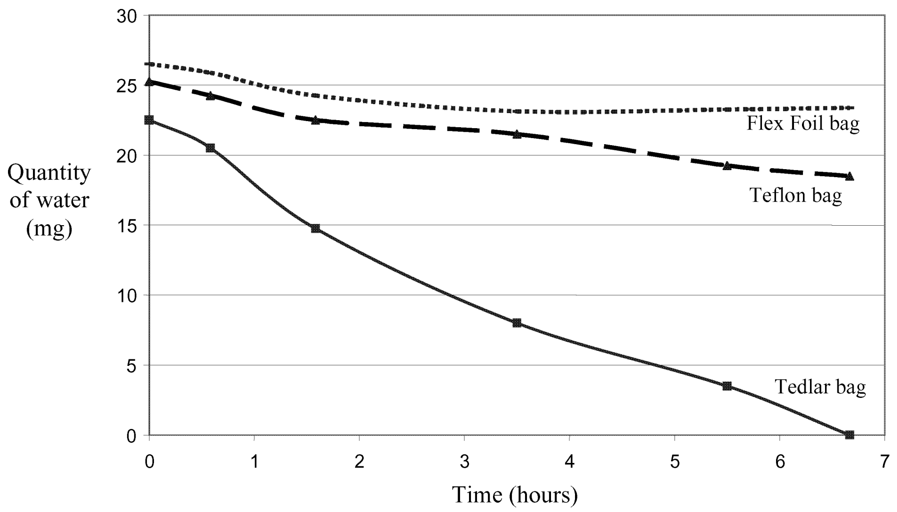

Figure 2: Water diffusion through 3 L sample bags (Teflon, Flex Foil and Tedlar)

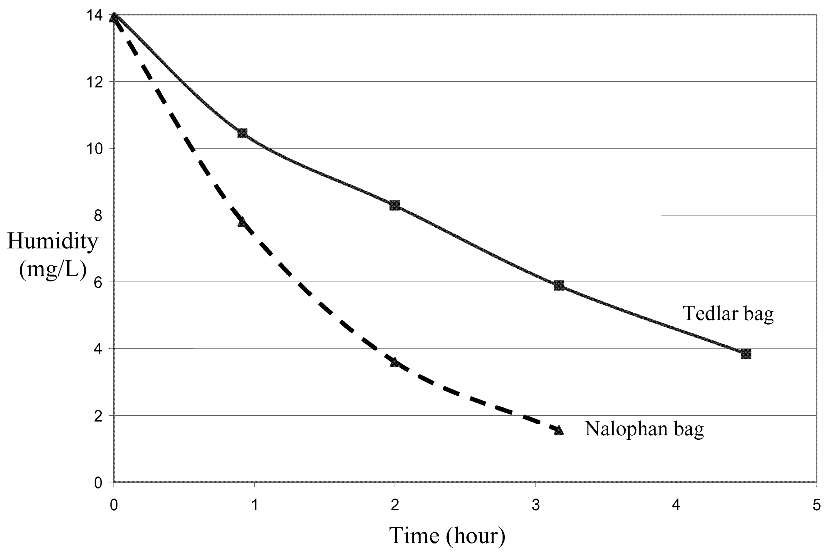

Figure 3: Water diffusion through Nalophan and Tedlar bags

3.2 Hydrogen sulphide diffusion through sampling bag films

At 24±1°C, 10% and 20% were respectively lost by Tedlar (figure 4) and Nalophan (figure 5) bags over a period of 70 hours. This decrease can be attributed mainly at a diffusion process through the film. Some variations can be also correlated with moderate variation of the temperature.

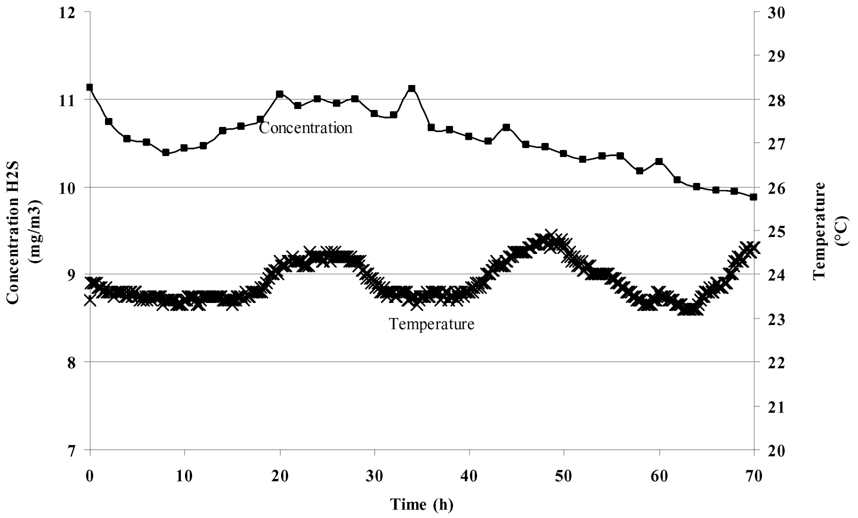

Figure 4: Evolution of H2S concentration in Tedlar bag

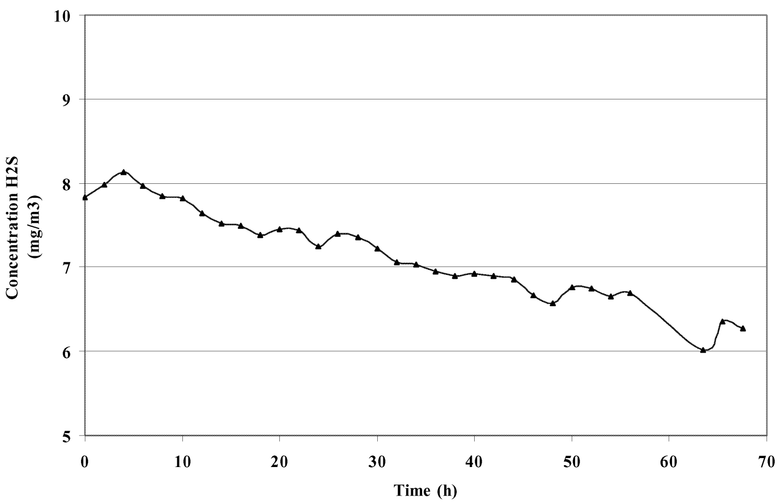

Figure 5: Evolution of H2S concentration in Nalophan bag

Considering the first two days and average concentration around values obtained each 6 hours, the results between the two films can be compared (see figure 6). These results clearly indicate that the decrease is quicker in Nalophan than in Tedlar. This difference was previously observed for water and can be also explained, of course by the difference of film but also by the thickness. In 2 days, H_2S losses are around 5-6 % and 15% for Tedlar and Nalophan bags respectively.

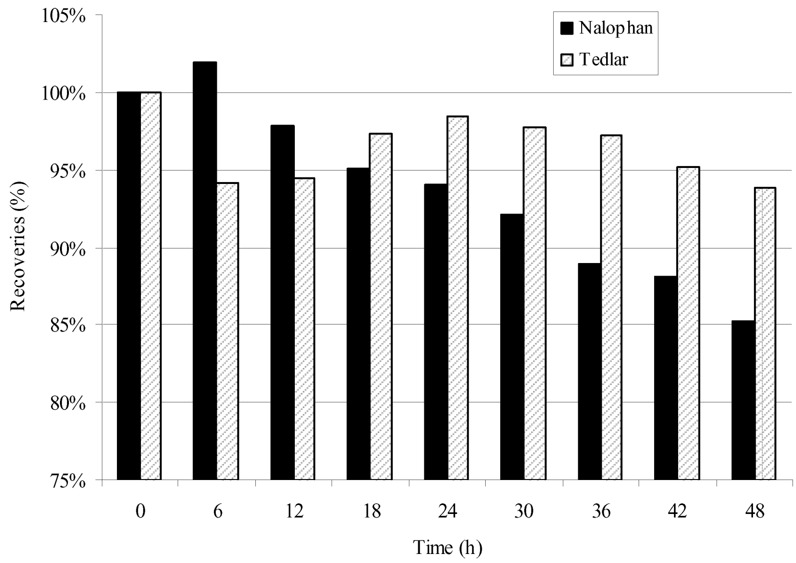

Figure 6: Comparison of H2S evolution in bags during 48 hours

If the analysis is carried out in a short delay after sampling (less than 20 h), the decrease is still lower than 5% and can be considered as negligible on odour concentration impact for olfactometric measurement for both bags. This fact confirms the necessity to quantify odour quickly after sampling but the study clearly shows that water diffusion must be verified. Because a sample in bag can be easily dried or humidified by the influence of the external atmosphere, the sample inside can react. A dried sampled atmosphere can become quickly humid (5-7 hours) during transportation for example and if some compounds are easily hydrolysable, the sample will change in terms of chemical composition and probably in odour level. Sampling bags can be still used but a better control of temperature and humidity conditions (and eventually oxidative gas composition) during short-time storage is necessary.

4. Conclusion

Sample Water Removal (SWR) method had shown that Tedlar and Nalophan films present higher water diffusion rates than Teflon or Flex Foil films. This implies that samples can be dried by this method, in short time (4-6 hours), while other compounds are stable. If water can diffuse quickly, hydrogen sulphide is globally kept in bags. With the necessity to minimise time storage between sampling and olfactometric measurement, Tedlar and Nalophan bags are efficient enough for short term stability

and then are logically mentioned as sampling materials by European standard EN 13725. If water can be easily removed, by SWR method, it decreases the probability of sampled compounds to react with water by hydrolysis mechanism. But water can diffuse through the films in both directions (from inside to outside or the contrary depending on the gradient) and this study shows that bags must be kept in dry conditions during transport and storage. Such dry conditions limit the accumulation of water into the bag and therefore the potential evolution of sample with water.
Once more, these results had shown that sampling procedures must be well controlled for environmental measurements and especially for both chemical and sensory analysis.

5. References

Beghi S., J.M. Guillot, 2006, J. Chromatogr. A, 1127, 1.

Beghi S., J.M. Guillot, 2008, J. Chromatogr. A, 1183, 1.

CEN, 1999, EN 13725, Air quality-determination of odor concentration by Dynamic Olfactometry, Comité Européen de Normalisation, Brussels.

Foulger B.E., P.G. Simmonds, 1979, Anal. Chem., 51, 1089.

Guillot J.M., B. Fernandez, P.L. Cloirec, 2000, Analusis, 28, 180.

Kim K.H., G.H. Choi, Y.J. Choi, H.N. Song, H.S. Yang, J.M. Oh, 2006a, Talanta, 68, 1713.

Kim K.H., J.W. Ahn, J.J. Choi, H.T. Nguyen, 2006b, J. Chromatogr. A, 1132, 228.

Koziel J., J. Spinhirne, J. Lloyd, D. Parker, D. Wright, F. Kuhrt, 2005, , J. Air Waste Manage Assoc., 55, 1147.

Van Harreveld A., 2003, J. Air Waste Manage Assoc., 53, 51.