

Ammonia diffusion through Nalophan™ bags

Selena Sironi, Lidia Eusebio, Licinia Dentoni, Laura Capelli
and Renato Del Rosso

Selena Sironi (corresponding author)

Lidia Eusebio

Licinia Dentoni

Laura Capelli

Renato Del Rosso

Department of Chemistry,

Materials and Chemical Engineering 'Giulio Natta', Politecnico di Milano,

Piazza Leonardo da Vinci 32,

20133 Milano,

Italy

E-mail: selena.sironi@polimi.it

First received 22 April 2013; accepted in revised form 7 October 2013. Available online 22 October 2013

INTRODUCTION

In recent years, growing urbanisation has raised environmental pollution problems associated with industrial odour emissions (Kim *et al.* 3102, 7002; Pal *et al.* 9002; Sironi *et al.* 7002, 6002, 5002; Capelli *et al.* 9002). Generally, odour emissions are not harmful to health, however they can cause physical and psychological stress (Capelli *et al.* 2102a, b). For this reason, during recent years, several studies concerning the control and monitoring of environmental odour emissions have been published (Nicell 9002; Capelli *et al.* 2102a, b).

Odour is defined as a mixture of compounds having less than 20 main atoms or molecular weight below 300 g/mol (Ohloff 16; Schiffman & Pearce 2004). Odorous substances can be either inorganic or organic compounds. For instance, inorganic odorous compounds include hydrogen sulphide (H₂S) and ammonia (NH₃). Volatile organic compounds are generally classified according to their functional groups (e.g., sulphur compounds, amines, oxygenated compounds, etc.) (Colomer *et al.* 2012).

For several years dynamic olfactometry has been consolidated as the most suitable technique to quantify the odour emissions (Capelli *et al.* 2010). Because of the difficulties associated with the conduction of olfactometric analyses on site, samples are generally collected and then stored in suitable containers for storage and transportation to the

laboratory for subsequent analysis (Bourgeois *et al.* 2003; Capelli *et al.* 2010).

Since the issuing of the European Standard for dynamic olfactometry (CEN 2003), precise rules were defined in order to make uniform the execution of olfactometric analyses, thereby improving their accuracy and repeatability (CEN 2003). Such rules also concern the definition of the allowed materials to be used for olfactometric sampling equipment (van Harrevelde *et al.* 1999; CEN 2003; Capelli *et al.* 2010).

In more detail, the European Standard defines the suitable materials for the making of sampling bags and their characteristics. They have to be chemically inert, avoiding leaks, diffusion and permeation, in order to preserve the sampled gas unchanged during storage. The following materials are allowed in the European Standard (EN):

- FEP (copolymer of tetrafluoroethylene-hexafluoropropylene);
- PVF (polyvinyl fluoride, Tedlar™);
- PET (polyethylene terephthalate, Nalophan™).

The EN also fixes a maximum storage time of 30 h in order to reduce the possibility of sample alteration during the time between collection and analysis.

Previous studies have shown that bags of FEP are quite inert but not very robust for use and rather expensive. Bags

in PVF are more robust but they have a background odour due to the solvents used during production. Bags in PET are relatively inexpensive, odourless and therefore most widely used (van Harreveld *et al.* 1999; van Harreveld 2003; Guillot & Beghi 2008; Ghosh *et al.* 2011).

In recent years, several studies have been conducted in order to assess the diffusion of odorous molecules through polymeric films (van Harreveld 2003; Koziel *et al.* 2005; Cariou & Guillot 2006; Trabue *et al.* 2006; Mochalski *et al.* 2009; Parker *et al.* 2010). Various analyses were performed to quantify the chemical losses over time and to compare the efficiency of different materials (van Harreveld 2003; Koziel *et al.* 2005; Cariou & Guillot 2006; Trabue *et al.* 2006; Kim *et al.* 2012).

Even though Nalophan™ is relatively inert and cheap, there is evidence of water permeation, as well as adsorption and desorption of some chemical species (Chandra 2006). Water can diffuse very quickly through polymeric films because of its structure. For this reason, permeability also towards other molecules having a dimension similar to water, such as NH₃ and H₂S (Beghi & Guillot 2006, 2008; Akdeniz *et al.* 2011) which are typically present in emissions from several operations such as wastewater treatment, livestock, composting and rendering, was observed.

Although many studies have been conducted on the materials used to design the sample bags, it is difficult to compare the results of such studies, because of the variability of the components considered (material typology, film thickness, and studied substances).

Table 1 reports an overview of some of the most significant studies conducted in this field.

Some factors affecting the diffusion processes in polymers are: chemical nature of the polymer, crystallinity and orientation of the polymer, free volume, molecular cohesion, relative humidity, temperature, hydrogen bonding, polarity, solubility, and solvent size and shape (Igwe *et al.* 2006; Mallia 2010; Piergiovanni & Limbo 2010).

Diffusion phenomena could be explained considering the characteristics of the material and of the gaseous mixture (Piergiovanni & Limbo 2010): the presence of dipole-dipole force increases the permeability to water.

The parameter describing this phenomenon is the water vapour transmission rate (WVTR), which represents the speed at which the water molecules move through the film when one side is wet and the other side is dry.

Indeed, the presence of water molecules interrupts the dipole-dipole interaction in the polymer barrier and, as a consequence, the packing of the polymer chains changes and the diffusion coefficient increases. For this reason,

when using a polymer membrane as material for the storage of odour samples, humidity shall be controlled in order to keep the sampled mixture unchanged. As a matter of fact, it is known from literature that it is possible to favour or to thwart the diffusion of small molecules through polymeric films by controlling the humidity conditions (Mallia 2010).

The aim of this work is to verify the diffusion rate of ammonia through the Nalophan polymeric film that constitutes the sampling bag. A further aim is to evaluate the diffusion reduction achievable by controlling the humidity during storage and by reducing the ammonia concentration gradient (ΔC).

METHODS

This study was designed to assess the ammonia (NH₃) concentration decay in sampling bags over time. The bags used consist in a one-layer foil of polyterephthalic ester copolymer (Nalophan™) with 20 μm thickness coming from a tubular film. All bags were used just once, i.e. they were not re-used for different tests.

Ammonia was used as test compound to study diffusion through the bags.

The NH₃ decay was evaluated using gas-chromatography (GC-TCD) for the quantification of NH₃ concentration inside the bag. The NH₃ concentration was measured using a HP Agilent 6890 gas chromatograph equipped with an Agilent HP-5MS fused silica capillary column (CP 7591-PoraPlot Amines, length 25 m, internal diameter 0.32 mm, film thickness 10 μm). The oven temperature follows a three step program: 100 °C for 12 min, from 100 to 200 °C with a rate of 8 °C/min, 200 °C for 5 min. The carrier gas was helium with a constant flow of 3 mL/min (pressure of 1.21 atm and mean velocity of 53 cm/s).

A calibration curve was built to relate the area of the GC peak with the NH₃ concentration (ppm). Instrument calibration was performed analysing different standard concentrations of NH₃ in air ranging from 10,000 to 60,000 ppm. Standards were obtained starting from different liquid mixtures of NH₃ in water and analysing the headspace obtained in a fixed volume of air where the liquid was placed.

The gaseous mixture inside the bags was analysed by GC at specific time intervals, in order to evaluate the variations of the NH₃ concentration (ppm) over time. In order to make tests run at different conditions (e.g., external

Table 1 | Studies conducted on different materials used to make the sample bags

Ref. article	Material	Thick.	Studied substances
Akdeniz <i>et al.</i> (2011)	Tedlar; FlexFoil	n.a. n.a.	Ammonia, Methane, Nitrogen oxide, Hydrogen sulfide
Beghi & Guillot (2006)	Tedlar, Teflon, FlexFoil	50 μm 50 μm 75 μm	Methanol, Ethanol, Acetone, n-Propanol, n-Hexane, Dichloroethane, Trichloroethane, Toluene, Butyl acetate
Beghi & Guillot (2008)	Nalophan, Tedlar	20 μm 50 μm	Acetone, n-propanol, Ethanol, n-Hexane, 1,2-Dichloroethane, Trichloroethylene, Methyl isobutyl ketone, Toluene, Butyl acetate, Ethyl benzene
Cariou & Guillot (2006)	Tedlar	50 μm	2-propanol, 2-butane, toluene
Ghosh <i>et al.</i> (2011)	Tedlar	n.a.	Phenol, Tetrahydrofuran, Benzene, Carbonyl sulfide, Dioxolane, Ethyl benzene, Isobutene, Methyl acetate, n-Dodecane, n-Octane, p-Xylene, o-Toluene
Guillot & Beghi (2008)	Nalophan, Tedlar Teflon, FlexFoil	20 μm 50 μm 75 μm	Hydrogen sulfide, Water vapour
Hansen <i>et al.</i> (2011)	Tedlar, Nalophan	50 μm 20 μm	Carboxylic acids, Phenols, Indoles, Skatole, Sulfur compounds
Kim <i>et al.</i> (2006)	Tedlar (PVF),	n.a.	Hydrogen sulfide, Sulfur compounds
Kim & Kim (2012)	Polyester, Aluminium bag	n.a.	Benzene, Toluene, Styrene, p-xylene, Methyl ethyl ketone, Methyl isobutyl ketone, Isobutyl alcohol, Butyl acetate, Acetaldehyde, Propionaldehyde, Butyraldehyde, Isovaleraldehyde, Valeraldehyde
Kim <i>et al.</i> (2012)	Polyester aluminium (PEA), Tedlar	50 μm 50 μm	Benzene, Toluene, p-xylene, Styrene, Methyl ethyl ketone, Methyl isobutyl ketone, Butyl acetate, Isobutyl alcohol
Koziel <i>et al.</i> (2005)	Nalophan, Tedlar FEP, FoilFilms, Tedlar, Canister	15 μm 50 μm 50 μm 125 μm 52 μm	Acetic acid, Propionic acid, Isobutyric acid, Butyric acid, Isovaleric acid, Valeric acid, Hexanoic acid, p-cresol, 2-Aminoacetophenone, Indole, 4-Ethylphenol
Mochalski <i>et al.</i> (2009)	Nalophan, Tedlar, Teflon FlexFoil	20 μm 50 μm 25 μm	Volatile Sulphur Compounds
Parker <i>et al.</i> (2010)	Tedlar	n.a.	p-cresol, Acetic acid, Propionic acid, Isobutyric acid, Butyric acid, Isovaleric acid, Valeric acid, Hexanoic acid
Trabue <i>et al.</i> (2006)	Tedlar	n.a.	Agricultural odorants
van Harreveld (2003)	Nalophan	20 μm 131 μm	Tobacco
Wang <i>et al.</i> (2011)	Nalophan, Treated Nalophan	0.40 μm 125 μm	Water Vapour

humidity, bag surface) comparable to each other, the concentration values obtained during each test were normalised referring to the test initial concentration value (NH_3 concentration at t_0):

$$\text{Relative NH}_3 \text{ concentration} = \frac{\text{NH}_3(t)}{\text{NH}_3(t_0)}$$

In this way, the loss of NH_3 is expressed as a deviation from the value 1.

All the tested samples were realised by filling the Nalophan™ bags with a test mixture of NH_3 in wet air (relative humidity, $\text{RH} = 100\%$). The test mixture was prepared by mixing 10.52 ml of liquid solution of NH_3 at a concentration of 30% w/w with 50 ml of distilled water, thus obtaining, by

equilibrium condition, samples with a final NH₃ concentration of about 40,000 ppm. The concentration in the bag was analysed at least twice.

During the storage time the physical parameters like temperature and relative humidity were kept under control using a climatic chamber (Chamber GHUMY by Fratelli Galli).

All tests provided NH₃ concentration to be evaluated at different time intervals after sample preparation. In more detail, NH₃ was analysed every hour from 0 to 7 h, and then again from 23 to 26 h. Each measurement involved the withdrawal of 300 µl of the test mixture by means of a syringe and injection into the GC.

The diffusion of NH₃ was first evaluated through a Nalophan™ single bag. The bag capacity was about 6 l (surface equal to 2,580 cm²). This bag was filled with 6 l of the test mixture and stored at a temperature (*T*) of 23 °C and an external RH of 60%.

In order to evaluate the influence of the physical parameters affecting diffusion, the bag surface area (*A*), the concentration gradients (ΔC of NH₃ and ΔC of water), and the temperature were changed separately.

In more detail, the role of the exchange surface, which is the bag surface area, was evaluated by designing bags having different surface areas, i.e. 1,900, 2,580 and 3,520 cm², respectively. These bags have different capacities (3, 6 and 9 l), but they were filled with the same amount (3 l) of the test mixture, thus designing bags with a different surface-to-volume ratio.

The role of the NH₃ concentration gradient was evaluated by fabricating so called ‘double bags’. The tested double bag consists of two concentric bags, whereby the interspace between inner and outer bag was filled with 3 l of the same test mixture (air and NH₃ at 40,000 ppm) contained in the inner bag. Both bags used have a capacity of about 6 l (and therefore a surface area of 2,580 cm²). The inner bag was only half-filled with 3 l of the test mixture.

All tested samples were kept at a storage *T* of 23 °C and RH of 60% for the whole duration of the test. The NH₃ concentrations over time were measured according to the above described test protocol.

The role of the humidity gradient between inside and outside the bag, both through the single and double bag, was evaluated by varying the external storage humidity by means of a climatic chamber ranging from low (20%) to high (90%) humidity values. The *T* during these tests was set at 23 °C.

Finally, in order to evaluate the role of the sole water ΔC on diffusion, the ‘double bags’, designed as described above, were tested in two different conditions. In both cases the inner bags were filled with 3 l of a gaseous mixture of NH₃ in air at 40,000 ppm. The interspaces between inner and outer bag were filled with 3 l of air saturated with water and dry air, respectively. The temperature was set at 23 °C.

Table 2 reports the scheme of the tests run and their descriptions.

Table 2 | Scheme of the tests

Code	Bag type	Test conditions <i>T</i> (°C) and RH(%)	Filling gas
SBcontrol	Single bag with 2,580 cm ² surface	<i>T</i> = 23 °C, RH% = 60	NH ₃
SB_A	Single bag with 1,900 cm ² surface	<i>T</i> = 23 °C, RH% = 60	NH ₃
SB_C	Single bag with 3,520 cm ² surface	<i>T</i> = 23 °C, RH% = 60	NH ₃
DB a_in	Inner bag of the double bag	<i>T</i> = 23 °C, RH% = 60	NH ₃
DB a_out	Outer bag of the double bag	<i>T</i> = 23 °C, RH% = 60	NH ₃
DB b_in	Inner bag of the double bag	<i>T</i> = 23 °C, RH% = 20	NH ₃
DB b_out	Outer bag of the double bag	<i>T</i> = 23 °C, RH% = 20	NH ₃
DB c_in	Inner bag of the double bag	<i>T</i> = 23 °C, RH% = 90	NH ₃
DB c_out	Outer bag of the double bag	<i>T</i> = 23 °C, RH% = 90	NH ₃
DB d_in	Inner bag of the double bag	<i>T</i> = 23 °C	NH ₃
DB d_out	Outer bag of the double bag	<i>T</i> = 23 °C	Saturated air
DB e_in	Inner bag of the double bag	<i>T</i> = 23 °C	NH ₃
DB e_out	Outer bag of the double bag	<i>T</i> = 23 °C	Dry air

The first column reports the codes of the bags (SB = single bag and DB = double bag). The second column reports details on the typology of the bag. Test conditions are reported in the third column. All the single bags were filled with 3 l of the test mixture of air and NH₃ at 40,000 ppm. As far as the tests with the double bags are concerned, the inner bags were always filled with 3 l of the test mixture. The contents of the outer bags was changed throughout the tests in order to study diffusion in different conditions; they were filled either with 3 l of the test mixture, or with the same amount of saturated or dry air.

RESULTS AND DISCUSSION

Figure 1 shows the NH₃ diffusion trend over time for the single bag. The error bars account for the instrumental error and the variability due to manual injection. A significant decrease of the NH₃ concentration over time can be observed.

In more detail, the NH₃ concentration decay follows a first-order kinetics that may be expressed by means of an exponential law.

The exponential law describing the NH₃ concentration trend over time can be derived from the theory of diffusion explained by the Fick law.

According to it, the specific molar flow is defined as:

$$j = -D \frac{\partial C}{\partial x}$$

whose integration, in this case, gives:

$$\ln\left(\frac{C}{C_0}\right) = -\frac{AD}{Vz}t$$

where j is the specific molar flow [mol/m²s]; C is the concentration of the diffusing compound at a generic time t [mol/m³]; C_0 is the initial concentration in the bag, x is the differential thickness of the film, thus $\int_0^z dx = z$, where z is the film thickness [m]; D is the diffusion coefficient of the compound through the film [m²/s].

The influence of the bag surface on diffusion was studied by comparing the NH₃ concentration decay in three different bags having the same volumes but increasing surfaces (Figure 2).

As expected from the theory, an increase of the NH₃ diffusion rate with the increase of the surface/volume ratio is observed.

Moreover, it is possible to observe that the bag having the lowest surface, i.e. SB_A with about 1,900 cm², does not present a significant diffusion of NH₃ up to 7 h. The bags having higher surfaces/volume (high S/V values), i.e. SBcontrol with 2,580 cm² and SB_C with 3,520 cm², respectively, limit NH₃ diffusion only for the first 4 h.

Figure 3 shows the diffusion of NH₃ over time both in the double bag (DB a_in e DB a_out) and the single bag (SBcontrol).

The outer bags of the double bags present a diffusive behaviour towards NH₃ comparable with the one of the single bag.

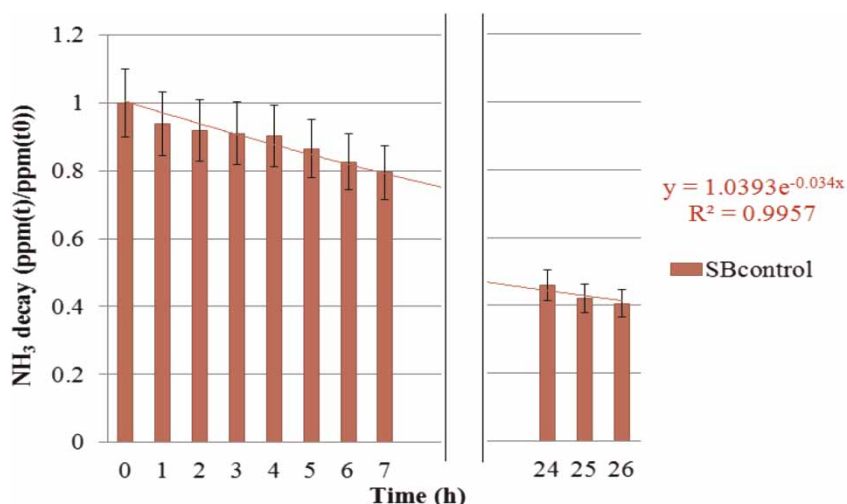


Figure 1 | NH₃ diffusion rate in the single Nalophan bag.

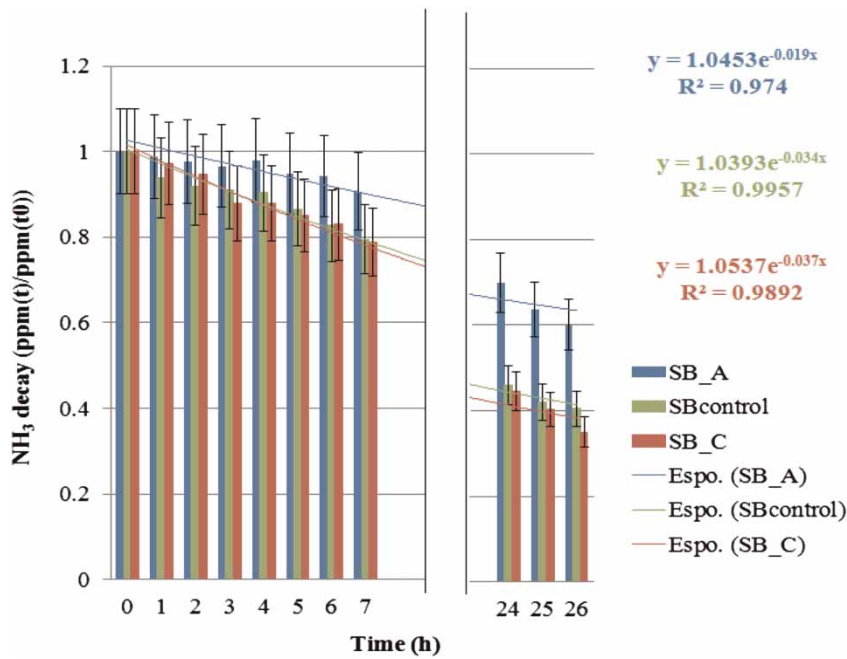


Figure 2 | NH₃ diffusion rate as a function of the bags surface.

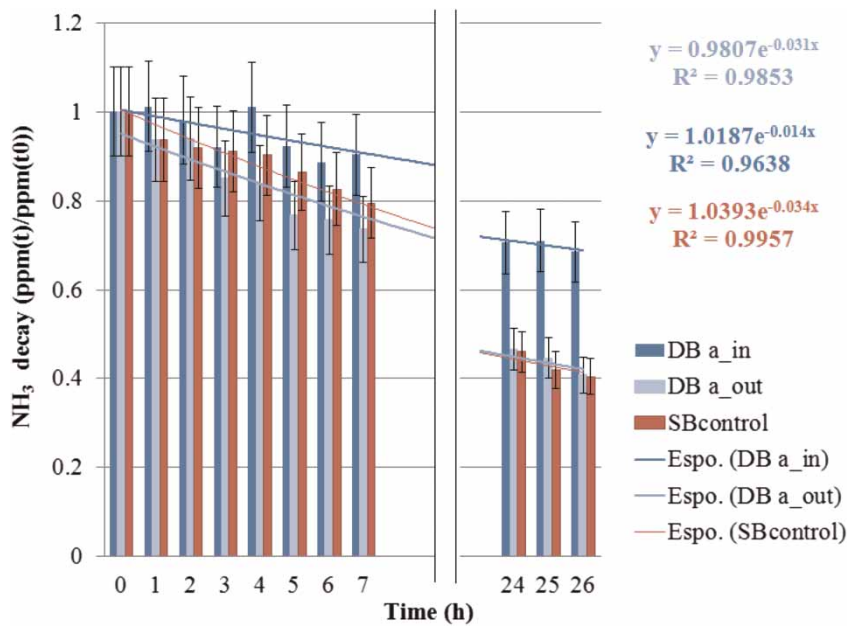


Figure 3 | Diffusion of NH₃ over time both in the double bag and the single bag.

The use of double Nalophan bags, with both (inner and outer) bags loaded with the same test mixture (air and NH₃ at 40,000 ppm), seems to be effective in order to reduce the loss of the NH₃ stored, by slowing down the diffusion in the inner bag. As shown in Figure 3, with the double bag, NH₃ concentration inside the inner bag (DB a_in) remains almost the same for about 7 h, whereas in the external bag

(DB a_out) a decrease of NH₃ concentration is observed after 4 h.

The external humidity, which was controlled during the experiment by means of a climatic chamber, does affect the NH₃ diffusion during the storage time.

Table 3 shows the NH₃ diffusion rates obtained by varying the sample storage humidity inside the climatic chamber

Table 3 | NH₃ diffusion in the double bags with varying humidity

Code	External RH (%)	ΔNH ₃ after 4 h (%)	ΔNH ₃ after 26 h (%)
DB b_in	20	4	31
DB b_out		16	58
DB a_in	60	2	30
DB a_out		11	56
DB c_in	90	1	28
DB c_out		6	57

from 20 to 90%, while the inner and outer bag were both filled with 3 l of the same test mixture.

The results prove that the increase of the water concentration gradient, i.e. the decrease of the storage humidity, cause an acceleration of the NH₃ diffusion, especially in the first 4 h. Actually, the results relevant to the bags stored at high humidity (RH 90%) indicate a moderate NH₃ decay both in the inner and outer bag, whereas the low humidity seems to accelerate the NH₃ diffusion during the first hours, especially in the outer bag.

Finally, the sole effect of the water gradient was evaluated.

Figure 4 shows the NH₃ diffusion in the inner bag filled with the test mixture, while the outer bag was filled with saturated air (DB d) and dry air (DB e), respectively. The results relevant to the inner bag with the outer bag filled

with the solution of NH₃ (40,000 ppm) in saturated air (DB a) are reported as well.

The comparison between the NH₃ diffusion in the bags DB a and DB d (outer bag filled either with the test mixture or saturated air, respectively) shows that the NH₃ diffusion trends are similar in both cases. Thus, both the NH₃ and the water gradients through the polymer interface play an important role in the diffusion phenomena: a reduction of those gradients causes a reduction of the NH₃ diffusion.

Table 4 shows the NH₃ gradient ΔNH₃% in the inner bag filled with the test mixture, when the outer bag was filled with the test mixture (DB a), saturated air (DB d) and dry air (DB e) respectively. The data reported in Table 4 show that in the first 8 h the reduction of the NH₃ ΔC has the main effect in the reduction of the NH₃ diffusion. Nonetheless, also the reduction of the sole water ΔC prevents the diffusion phenomenon.

Based on the discussed results, the double bags turn out to be a simple expedient that may be adopted in order to prevent the diffusion of the sampled gas through the Nalophan™ during storage. In more detail, the NH₃ losses can be slowed down by reducing one of the ‘engines’ of diffusion: either the Δc of the NH₃ or the ΔC of the sole water.

During sampling, this may be easily achieved by filling the outer bag of the double bag either with the same gas contained in the inner bag (thereby reducing the NH₃ ΔC) or with water (thereby reducing the sole water ΔC).

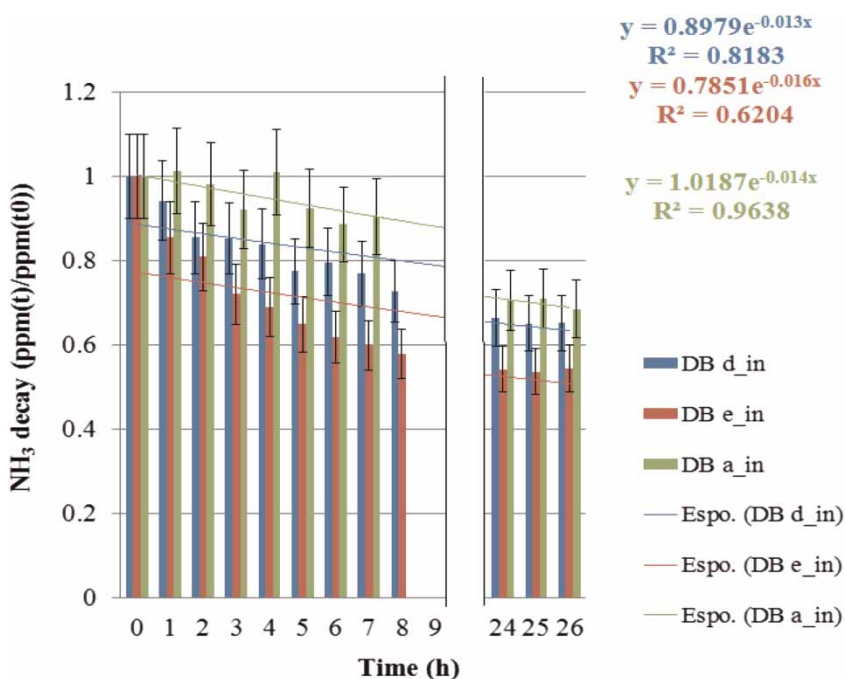


Figure 4 | NH₃ diffusion in double bags, where the outer bag is filled with saturated air (DB d), dry air (DB e), and with the solution of NH₃ in saturated air (DB a), respectively.

Table 4 | Averaged NH₃ concentration values relevant to different time intervals (1–8 h and 24–26 h)

Code	Filling gas in the outer bag	Δ NH ₃ % (1–8 h)	Δ NH ₃ % (24–26 h)
DB a_in	NH ₃ (40,000 ppm) in sat. air	5	30
DB d_in	Saturated air	18	34
DB e_in	Dry air	31	25

CONCLUSIONS

The NH₃ diffusion through a single layer of Nalophan™ film (single bag, $T = 23$ °C, RH = 60%) causes a decrease of the NH₃ concentration of about 60% after 26 h. This value is not negligible, especially if considering that the European Standard on dynamic olfactometry allows a maximum storage time of 30 h.

The NH₃ diffusion rate is affected by the bag surface: the higher the bag surface, the higher the NH₃ diffusion rate through the polymeric film.

One of the main engines of diffusion has been proven to be the gradient of the NH₃ concentration at the Nalophan interface. This is demonstrated by the use of a ‘double bag’, whereby the NH₃ diffusion in the inner bag is significantly reduced by filling the outer bag with the same mixture of NH₃ in air contained in the inner bag, thereby reducing the NH₃ Δc through the polymeric film.

A similar result, i.e., a moderate reduction of the NH₃ diffusion, was obtained by solely reducing the water concentration gradient at the Nalophan interface.

These results are very interesting, pointing out the possibility of using such double bags as a simple and effective solution for reducing NH₃ (or generally odorants) losses from odour samples during storage.

REFERENCES

- Akdeniz, N., Janni, K. A., Jacobson, L. D. & Hetchler, B. P. 2011 Comparison of gas sampling bags to temporarily store hydrogen sulfide, ammonia, and greenhouse gases. *Transactions of the ASABE* **54** (2), 653–661.
- Beghi, S. & Guillot, J.-M. 2006 Sample water removal method in volatile organic compound analysis based on diffusion through poly(vinyl fluoride) film. *Journal of Chromatography A* **1127** (1–2), 1–5.
- Beghi, S. & Guillot, J.-M. 2008 Use of poly(ethylene terephthalate) film bag to sample and remove humidity from atmosphere containing volatile organic compounds. *Journal of Chromatography A* **1183** (1–2), 1–5.
- Bourgeois, W., Romain, A. C., Nicolas, J. & Stuetz, R. M. 2003 The use of sensor arrays for environmental monitoring: interests and limitations. *Journal of Environmental Monitoring* **5**, 852–860.
- Capelli, L., Sironi, S., Del Rosso, R. & Céntola, P. 2009 Predicting odour emissions from wastewater treatment plants by means of odour emission factors. *Water Research* **43** (7), 1977–1985.
- Capelli, L., Sironi, S., Del Rosso, R., Centola, P. & Bonati, S. 2010 Improvement of olfactometric measurement accuracy and repeatability by optimization of panel selection procedures. *Water Science and Technology* **61** (5), 1267–1278.
- Capelli, L., Sironi, S. & Del Rosso, R. 2012a Odor sampling: techniques and strategies for the estimation of odor emission rates from different source types. *Sensors* **13** (1), 938–955.
- Capelli, L., Sironi, S., Del Rosso, R., Bianchi, G. & Davoli, E. 2012b Olfactory and toxic impact of industrial odour emissions. *Water Science and Technology* **66** (7), 1399–1406.
- Cariou, S. & Guillot, J. M. 2006 Double-layer Tedlar bags: a means to limit humidity evolution of air samples and to dry humid air samples. *Analytical and Bioanalytical Chemistry* **384** (2), 468–474.
- Chandra, P. 2006 Multi-component Transport of Gases and Vapors in Poly(ethylene Terephthalate). PhD Thesis, Georgia Institute of Technology.
- CEN 2003 *EN13725 Air Quality—Determination of Odour Concentration by Dynamic Olfactometry*. Comité Européen de Normalisation (CEN), Brussels, Belgium.
- Colomer, F. L., Espinós-Morató, H., Iglesias, E. M., Pérez, T. G., Campos-Candel, A. & Coll Lozano, C. 2012 Characterization of the olfactory impact around a wastewater treatment plant: optimization and validation of a hydrogen sulfide determination procedure based on passive diffusion sampling. *Journal of the Air and Waste Management Association* **62** (8), 863–872.
- Ghosh, S., Kim, K.-H. & Sohn, J. R. 2011 Some insights into analytical bias involved in the application of grab sampling for volatile organic compounds: a case study against used Tedlar bags. *The Scientific World Journal* **11**, 2160–2177.
- Guillot, J.-M. & Beghi, S. 2008 Permeability to water vapour and hydrogen sulphide of some sampling bags recommended by EN 13725. *Chemical Engineering Transactions* **15**, 79–86.
- Hansen, M. J., Adamsen, A. P. S., Feilberg, A. & Jonassen, K. E. N. 2011 Stability of odorants from pig production in sampling bags for olfactometry. *Journal of Environmental Quality* **40** (4), 1096–1102.
- Igwe, I. O., Ewulonu, C. M. & Igboanugo, I. 2006 Studies on the diffusion characteristics of some aromatic solvents into polypropylene film. *Journal of Applied Polymer Science* **102** (2), 1985–1989.
- Kim, Y.-H. & Kim, K.-H. 2012 Experimental approach to assess sorptive loss properties of volatile organic compounds in the sampling bag system. *Journal of Separation Science* **35** (21), 2914–2921.
- Kim, K.-H., Choi, G.-H., Choi, Y.-J., Song, H.-N., Yang, H. S. & Oh, J. M. 2006 The effects of sampling materials selection in

- the collection of reduced sulfur compounds in air. *Talanta* **68** (5), 1713–1719.
- Kim, K. H., Jeon, E. C., Koo, Y. S., Im, M. S. & Youn, Y. H. 2007 An on-line analysis of reduced sulfur gases in the ambient air surrounding a large industrial complex. *Atmospheric Environment* **41** (18), 3829–3840.
- Kim, K.-H., Jo, S.-H., Song, H.-C., Pandey, S. K., Song, H.-N., Oh, J.-M., Sunwoo, Y. & Choi, K. C. 2013 Diagnostic analysis of offensive odorants in a large municipal waste treatment plant in an urban area. *International Journal of Environmental Science and Technology* **10** (2), 261–274.
- Kim, Y. H., Kim, K. H., Jo, S. H., Jeon, E. C., Sohn, J. R. & Parker, D. B. 2012 Comparison of storage stability of odorous VOCs in polyester aluminum and polyvinyl fluoride Tedlar (R) bags. *Analytica Chimica Acta* **712**, 162–167.
- Koziel, J. A., Spinhirne, J. P., Lloyd, J. D., Parker, D. B., Wright, D. W. & Kuhrt, F. W. 2005 Evaluation of sample recovery of malodorous livestock gases from air sampling bags, solid-phase microextraction fibers, Tenax TA sorbent tubes, and sampling canisters. *Journal of the Air & Waste Management Association* **55** (8), 1147–1157.
- Mallia, I. 2010 *Sviluppo di una nuova metodologia per la misura della permeabilità di film plastici ad uso alimentare*. Dipartimento di Ingegneria Agraria - Sezione Meccanica, Università degli studi di Catania, Catania.
- Mochalski, P., Wzorek, B., Sliwka, I. & Amann, A. 2009 Suitability of different polymer bags for storage of volatile sulphur compounds relevant to breath analysis. *Journal of Chromatography B-Analytical Technologies in the Biomedical and Life Sciences* **877** (3), 189–196.
- Nicell, J. A. 2009 Assessment and regulation of odour impacts. *Atmospheric Environment* **43** (1), 196–206.
- Ohloff, G. 1986 Chemistry of odor stimuli. *Experientia* **42** (3), 271–279.
- Parker, D. B., Perschbacher-Buser, Z. L., Cole, N. A. & Koziel, J. A. 2010 Recovery of agricultural odors and odorous compounds from polyvinyl fluoride film bags. *Sensors* **10** (9), 8536–8552.
- Pal, R., Kim, K. H., Jeon, E. C., Song, S. K., Shon, Z. H., Park, S. Y., Lee, K. H., Hwang, S. J., Oh, J. M. & Koo, Y. S. 2009 Reduced sulfur compounds in ambient air surrounding an industrial region in Korea. *Environmental Monitoring and Assessment* **148** (1), 109–125.
- Piergiovanni, L. & Limbo, S. 2010 Proprietà chimiche dei materiali di packaging. In: *Food Packaging*, Springer-Verlag Italia, Milan, pp. 11–20.
- Schiffman, S. S. & Pearce, T. C. 2004 Introduction to olfaction: perception, anatomy, physiology, and molecular biology. In: *Handbook of Machine Olfaction* (T. C. Pearce, S. S. Schiffman, H. T. Nagle & J. W. Garder, eds). Wiley-VCH Verlag GmbH & Co. KGaA, pp. 1–31.
- Sironi, S., Capelli, L., Centola, P., Del Rosso, R. & Grande, M. I. 2005 Odour emission factors for assessment and prediction of Italian MSW landfills odour impact. *Atmospheric Environment* **39** (29), 5387–5394.
- Sironi, S., Capelli, L., Centola, P., Del Rosso, R. & Il Grande, M. 2006 Odour emission factors for the prediction of odour emissions from plants for the mechanical and biological treatment of MSW. *Atmospheric Environment* **40** (39), 7632–7643.
- Sironi, S., Capelli, L., Centola, P., Del Rosso, R. & Il Grande, M. 2007 Odour emission factors for assessment and prediction of Italian rendering plants odour impact. *Chemical Engineering Journal* **131** (1–3), 225–231.
- Trabue, S. L., Anhalt, J. C. & Zahn, J. A. 2006 Bias of Tedlar bags in the measurement of agricultural odorants. *Journal of Environmental Quality* **35** (5), 1668–1677.
- van Harreveld, A. P. 2003 Odor concentration decay and stability in gas sampling bags. *Journal of the Air & Waste Management Association* **53** (1), 51–60.
- van Harreveld, A. P., Heeres, P. & Harssema, H. 1999 A review of 20 years of standardization of odor concentration measurement by dynamic olfactometry in Europe. *Journal of the Air & Waste Management Association* **49** (6), 705–715.
- Wang, C., Lai, P.-C., Syu, S. H. & Leu, J. 2011 Effects of CF₄ plasma treatment on the moisture uptake, diffusion, and WVTR of poly(ethylene terephthalate) flexible films. *Surface and Coatings Technology* **206** (2–3), 318–324.