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Abstract

The ammonia loss through Nalophan™ bags has been studied. Ammonia was chosen as target compound in order to be representative of odorous molecules of small dimensions. The losses observed for storage conditions and times as allowed by the reference standard for dynamic olfactometry (EN 13725:2003) indicate that odour concentration values due to the presence of small molecules may be significantly underestimated if samples are not analysed immediately after sampling. The diffusion coefficient of ammonia through the Nalophan™ film was evaluated using the Fick's law, and it turned out to be equal to 2.38E−12 (m²/s). The results and their theoretical interpretation indicate that concentration losses due to ammonia diffusion through the Nalophan™ film can be decreased by using large bags and filling them up to their maximum capacity.

Keywords

1. Introduction

Even though environmental odours are generally not harmful to health [1], in the last 30 years odour pollution has become a serious environmental concern because it may be the cause of physiological stress to the population. For this reason, during the last years, several studies have been undertaken to assess how to control and

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monitor odour emissions [2]. For many years, researchers have tried to characterize odour using chemical and physical techniques like GC and GC-MS. Although dozens, sometimes hundreds of odorants can be identified, such identification mostly fails to predict odour as it is perceived by human nose [3] [4]. This is the reason why sensorial odour measurement using human observers has become the main tool to quantify odours. Dynamic olfactometry has therefore been consolidated as the best analysis method to quantify odour emissions in terms of odour concentration or odour emission rate [5].

Because of the difficulties associated with the conduction of olfactometric analyses on site, samples are generally collected and then stored in suitable containers until they are analysed in an olfactometric laboratory [5]-[9]. The European Standard on dynamic olfactometry [10] fixes the general requirements relevant to the materials used for the realization of sampling equipment. According to the European Standard, the materials used for olfactometry shall be odourless, they shall be selected to minimize the physical or chemical interaction between sample components and sampling materials, have low permeability in order to minimize sample losses caused by diffusion and smooth surface.

The materials allowed for realizing sample containers (bags) and listed in point 6.3.1 of the actual standard are: tetrafluoroethylene hexafluoropropylene copolymer (FEP); polyvinylfuoride (PVF, Tedlar™) and polyethyleneterephthalate (PET, Nalophan™).

According to the European Standard these materials shall be tested for suitability, by verifying they can hold a mixture of odourants with minimal changes for periods of storage of 30 hours, which is the maximum storage time allowed by the European Standard.

Some authors have been studying the characteristics of the materials listed in the EN 13725 [10] with the aim to verify their suitability for olfactometric measurements. Previous studies have shown that FEP bags are quite inert but not very robust and rather expensive [11]. PVF bags are more robust but they have a background odour caused by the use of solvents during production [12]. These disadvantages are the reason why PET, which is relatively cheap and odourless, is actually the most widely used material for the realization of sample bags [11] [13]-[16].

Many studies have been conducted in order to assess the diffusion of odorous molecules through polymeric films [11] [17]-[23]. In these studies, chemical analyses have been performed to quantify the losses of specific compounds over time and to compare the recovery efficiency of different materials [11] [17]-[19] [24]-[30].

Despite of its inertia and cost effectiveness Nalophan™ has been proved to allow the diffusion of specific molecules, such as water, and its permeability has been studied.

Both the nature of the polymer and nature of the diffusing molecule affect the diffusion rate through the material that is expressed by the diffusion coefficient D [31].

Water can diffuse quickly through polymeric films because of its structure [14]. Also other molecules having a dimension similar to water, such as ammonia (NH_3) and hydrogen sulphide (H_2S) [14] [32] [33], which are typically found in emissions from several operations such as solid waste and waste water treatment, can diffuse easily.

The characteristics of the polymer itself affecting the diffusion processes are: the chemical nature of the polymer, its crystalline structure and orientation, the free volume, the molecular cohesion, the relative humidity, temperature, hydrogen bonding, polarity, solubility parameter, solvent size and shape [34]-[36].

The experiments described in this paper have the aim to investigate the diffusion phenomena through Nalophan™, which is one of the most widespread materials used for the realization of sampling bags (EN 13725:2003), thereby calculating the diffusion coefficient relevant to this material. Ammonia was chosen as target compound for the study, which involved both an experimental part aiming to calculate the specific D coefficient through Nalophan™ as well as to evaluate the influence of the surface/volume ratio on the diffusion kinetics. The described approach is important in order to increase knowledge in this field, suggesting possible technical expedients to reduce diffusion, and possibly improve regulatory issue.

2. Materials and Methods

2.1. Materials

The Nalophan™ used to fabricate the bags employed for the experimental tests consists in a one-layer foil of polyterephtalic ester copolymer with 20-µm thickness supplied by Tilmmanns S.p.A.

The bags were obtained starting from a tubular film cut in different lengths.

One end was equipped with a clamp closure while the other end is provided with a Teflon inlet tube for sample collection (**Figure 1**).

The NH_3 decay over time was evaluated using gas-chromatography (GC) for the quantification of NH_3 concentration inside the bag. The ammonia 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 steps program: 100˚C for 12 minutes, from 100˚C to 200˚C with a rate of 8˚C/min, 200˚C for 5 minutes. 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). The gaseous mixture inside the bags was analysed by a GC, equipped with a TCD detector, at specific time intervals, in order to evaluate the variations of NH_3 concentration (ppm) over time.

A calibration curve was built to relate the area of the GC peak with the NH_3 concentration (ppm). Instrument calibration was performed analysing different standard concentrations of NH_3 in air ranging from 10,000 to 60,000 ppm. Standards were obtained starting from different liquid mixtures of NH_3 in water and analysing the headspace obtained in a fixed volume of air where the liquid was inserted and then kept at a controlled temperature.

All the tested samples were realized by filling the Nalophan^{TM} bags with a gaseous mixture of ammonia in wet air, with an ammonia concentration of about 55,000 ppm_V and a relative humidity of 60%, which will be defined as the "test mixture". The test mixture was prepared using the headspace technique. The liquid phase was realized at room temperature mixing 10.5 ml of a liquid solution of NH_3 at a concentration of 30% w/w and 50 ml of distilled water.

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

2.2. Methods

All tests were conducted by measuring the NH_3 concentration at different time intervals after sample preparation. More in detail, NH_3 was analysed, every hour, from 0 to 26 h. Each measurement involved the withdrawal of 300 μl of the test mixture by means of a syringe and the injection in the GC.

The diffusion of ammonia was first evaluated through a Nalophan^{TM} bag having a capacity of about 6000 cm^3 and a surface equal to 2580 cm^2. This bag was filled with 6000 cm^3 of the above defined test mixture and then stored at a constant temperature of 23˚C and an external relative humidity of 60%. The external relative humidity was set equal the internal relative humidity in order to avoid water diffusion during storage and its potential influence on ammonia diffusion. Based on the experimental data of residual NH_3 concentration inside the bag and on the Fick's law, the diffusion coefficient D of ammonia through Nalophan^{TM} was calculated. The measurements were repeated three times each and the diffusion coefficient D is averaged over the 26 hours.

The role of the exchange surface (*i.e.*, the bag surface area) on the NH_3 concentration decay inside the bag was evaluated by realizing bags having different surface areas, *i.e.* 1900 cm^2, 2580 cm^2, 3520 cm^2, respectively. These bags have different capacities (3000, 6000 and 9000 cm^3), but they were filled with the same amount (3000 cm^3) of the test mixture, thus realizing bags with a different surface-to-volume ratio.
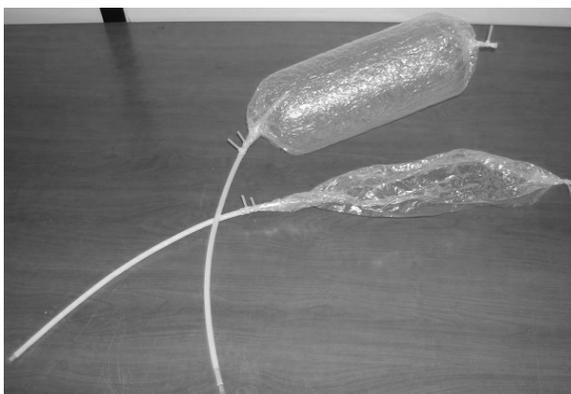

Figure 1. Nalophan^{TM} bags.

Also in this case, all tested samples were stored at a T of 23°C and RH of 60% for the whole duration of the test. The ammonia concentrations over time were measured according to the above described test protocol.

3. Calculations

The diffusion phenomena through a polymeric film are described by the Fick's law. According to it, the specific molar flow is defined as:

$$j = -D\frac{\partial C}{\partial x} \tag{1}$$

where:
- j is the specific molar flow (mol/m^2/s)
- D is the diffusion coefficient of the compound through the film (m^2/s)
- C is the concentration of the diffusing compound (mol/m^3)
- x is the differential thickness of the film.

The film thickness can therefore be expressed as:

$$\int_0^z dx = z \tag{2}$$

where z is the film thickness (m);

Referring to **Figure 2**, which schematizes the diffusion phenomenon through thethin filmwhich constitutes the sampling bag, we can define:
- S_N is the surface of the polymeric film (m^2)
- z_N is the thickness of the film (m)
- C_N is the concentration in the inside volume (mol/m^3)
- C_{N+1} is the concentration outside the film (mol/m^3), for a single bag it is generally considered negligible ($C_{N+1} = 0$),
- j_N is the specific molar flow through the film (mol/m^2/s).

If the film thickness can be considered as negligible, then the accumulation term inside the material is negligible, as well.

With this assumption j_N is constant along the film (x).

By integrating Equation (1) in dx between 0 and Z_N, the specific molar flow j_N can be expressed as:

$$j_N = -D\frac{C_{N+1} - C_N}{z_N} \tag{3}$$

j_N is relevant to an infinitesimal portion of the exchange surface dS.

Assuming that the internal molar concentration C_N is constant inside the whole internal volume V_N and also the external concentration C_{N+1} is constant inside the external volume V_{N+1}, then the global flow J through the exchange surface S_N can be calculated by integrating as follows:
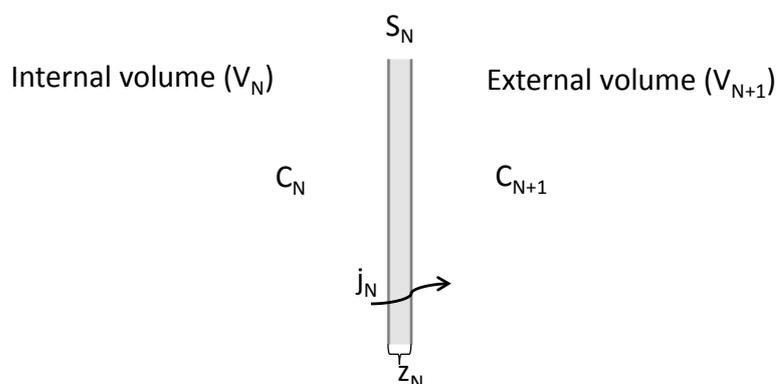
Figure 2. Schematization of diffusion through the thin film of the bag.

$$J = \int_0^{S_N} j_N \, dS \tag{4}$$

$$J = S_N j_N \tag{5}$$

Combining Equation (3) with Equation (5), the molar flow through the surface is expressed as:

$$\frac{\partial M_N}{\partial t} = -\frac{\partial C_N V_N}{\partial t} = -\frac{S_N D}{z_N}(C_N - C_{N+1}) \tag{6}$$

If the external concentration C_{N+1} is assumed to be equal to zero ($C_{N+1} = 0$), and if the volume V_{N+1} is taken equal to infinity ($V_{N+1} = \infty$), which is the case if the bag is placed in a neutral environment (where the presence of NH_3 may be considered negligible), then Equation (6) can be rewritten as:

$$-\frac{\partial C_N V_N}{\partial t} = -\frac{S_N D}{z_N} C_N \tag{7}$$

According to this model, the concentration decay over time turns out to be a function of the surface area (S_N), the volume of the sampled gas V_N, the film thickness (z_N), the time (t), the diffusion coefficient (D) that depends on the characteristics of the material, and the concentration gradient through the polymeric barrier (ΔC).

The boundary conditions considered for the integration of Equation (7) are:

$$C_N = C \text{ for } t = t^* \tag{8}$$

$$C_N = C_0 \text{ for } t = 0 \tag{9}$$

The integration of Equation (7) allows the calculation of the concentration trend over time:

$$\ln\left(\frac{C}{C_0}\right) = -\frac{S_N D}{V_N z_N} t \tag{10}$$

$$\frac{C}{C_0} = e^{-\frac{S_N D}{V_N z_N} t} \tag{11}$$

4. Results and Discussion

Table 1 shows the NH_3 concentration values measured at different time intervals t_i. Each concentration value reported in the table is the average of three replicate measurements.

The last column of Table 1 reports the diffusion coefficient D_{ti} for each time interval t_i calculated according to the following equation:

$$D_{ti} = -\frac{V_N z_N}{S_N t_i} \ln\left(\frac{C_{ti}}{C_0}\right) \tag{12}$$

where t_i is the time interval and C_{ti} is the concentration measured after t_i.

In order to give a better representation of the diffusion phenomena through the polymeric film, as well as to make it possible to compare results obtained with different bag filling volumes (V_N), it was decided to make all further considerations about the bag contents considering the number of moles (n) instead of the concentrations.

For this reason, the third column of Table 1 reports the number of millimoles (mmol) contained in the bag, and the fourth column represents the number of moles divided by the bag surface (n/S). This parameter allows highlighting the differences obtained with different bag surfaces.

The fifth column reports Δn, which is the difference between the number of moles at $t_0 = 0$ h and the number of moles at time t (n_0-n) and therefore represents the number of moles that have crossed the film.

$\Delta n/t$ represents the number of moles passed through the film during the whole time interval t, thus representing the direction coefficient of the line connecting n_0 and n, *i.e.* the average speed at which the moles have crossed the film.

The diffusion coefficient of ammonia through Nalophan[TM] is finally calculated as the average of the different values of D_{ti} weighted on the corresponding storage time t_i:

Table 1. Experimental data relevant to NH_3 diffusion over time in a Nalophan^{TM} bag with $V_N = 6000$ cm^3 and $S_N = 2580$ cm^2.

Time [h]	C_{ti} [ppm]	n [mmol]	n/S [mmol/cm^2]	Δn [mmol]	$\Delta n/t$ [mmol/h]	D_{ti} [cm^2/s]
0	54714	13.51	5.24E−03			
1	54698	13.50	5.23E−03	0.00	0.004	1.30E−08
2	54652	13.49	5.23E−03	0.02	0.008	2.37E−08
3	51625	12.75	4.94E−03	0.76	0.254	3.10E−08
4	50334	12.43	4.82E−03	1.08	0.270	2.56E−08
5	48393	11.95	4.63E−03	1.56	0.312	4.29E−08
6	45778	11.30	4.38E−03	2.21	0.368	3.19E−08
7	49613	12.25	4.75E−03	1.26	0.180	2.15E−08
…	…	…	…	…	…	…
23	36034	8.90	3.45E−03	4.61		2.21E−08
24	34878	8.61	3.34E−03	4.90	0.204	2.32E−08
25	36033	8.90	3.45E−03	4.61	0.184	2.19E−08
26	34248	8.46	3.28E−03	5.05	0.194	2.20E−08

$$\overline{D} = \frac{\sum_i D_{ti} t_i}{\sum_i t_i} \tag{13}$$

The resulting value for $\overline{D}$ is equal to 2.38 10^{-8} cm^2/s, with a standard deviation equal to 3.70 10^{-11} cm^2/s. The percent NH_3 loss through the bag over time can be expressed as:

$$NH_{3loss\%} = \left(1 - \frac{n}{n_0}\right) \times 100 = \left(1 - e^{-\frac{S_N \overline{D}}{V_N z_N} t}\right) \times 100 \tag{14}$$

Figure 3 shows the experimental NH_3 losses over time during the test period of 26 h. These results were obtained using a bag with a surface of 2580 cm^2 filled with 6000 cm^3 of the test mixture (surface-to-volume ratio equal to 0.430 cm^{-1}). The frequency of the measurements of the ammonia losses was focused on the first hours of the storage time (1 - 7 h) in order to investigate the initial concentration decrease trend, and close to the limit storage time (23 - 26 h) imposed by the European norm, which is 30 h, in order to evaluate the cumulative losses.

The loss percentage of NH_3 (%) after 26 h turns out to be equal to about 37%.

This trend is coherent with other data reported in scientific literature dealing with the same subject. As an example, a study by Akdezin *et al*. [37] also dealing with NH_3 losses through polymeric films, reports losses of about 25% after 48 h. This value is lower compared to the 37% found in this study and reported in **Figure 3**. This may be due to the fact that the starting NH_3 concentration is much lower (ppb) than in our case (thousands of ppm), thus resulting in a lower concentration gradient, which is the driving force of the diffusion phenomenon.

A similar trend was observed in other studies by Beghi and Guillot [14] [33], which investigate H_2S diffusion through different Nalophan^{TM} film having a different thickness. Also in this case, the reported H_2S losses through a 20 µm thick Nalophan^{TM} film are lower, presumably due to the lower starting concentration.

Figure 4 represents the experimental data relevant to the number of NH_3 moles over time (third column of **Table 1**). The experimental data show a good correspondence with the theoretical trend derived from Equation (11), which can be alternatively expressed as:

$$n = n_0 e^{-\frac{S_N \overline{D}}{V_N z_N} t} \tag{15}$$

The theoretical trend is shown in **Figure 4** as a continuous line. This trend was obtained by inserting, in Equation (15), the averaged diffusion coefficient calculated as described above (Equations (12) and (13)).
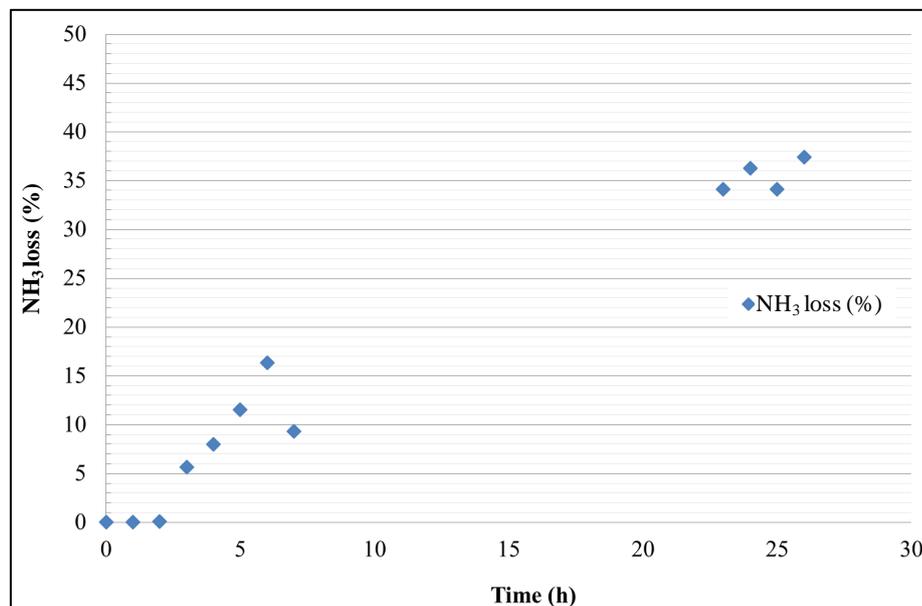
Figure 3. NH_3 loss (%) over time from the Nalophan^{TM} bag with $V_N = 6000$ cm^3 and $S_N = 2580$ cm^2.
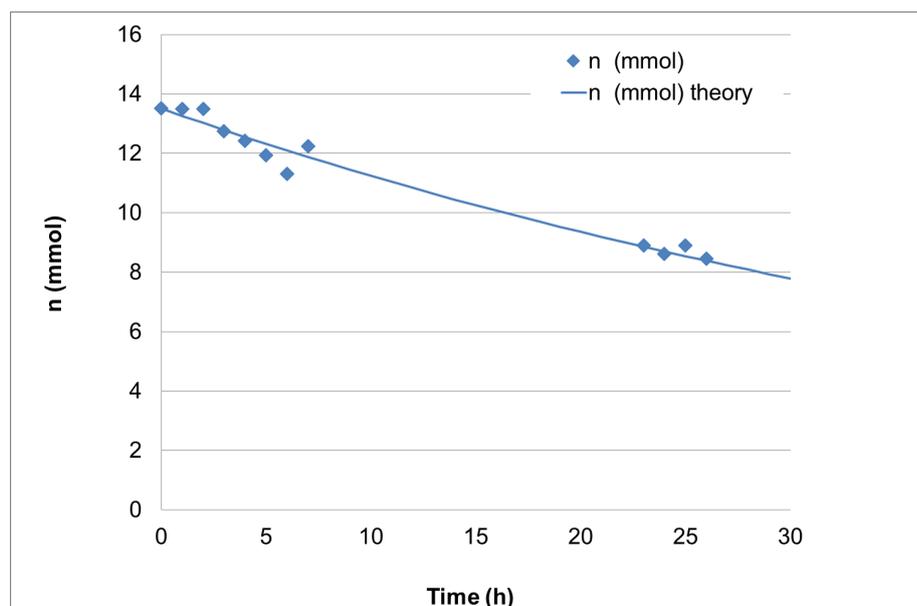
Figure 4. Number of NH_3 moles over time: experimental data (dots) vs. theoretical trend (continuous line) in a Nalophan^{TM} bag with $V_N = 6000$ cm^3 and $S_N = 2580$ cm^2.

As described by Equation (15), the variation of moles inside the bag depends on the surface-to-volume ratio (S_N/V_N, hereafter defined simply as S/V) of the bag.

In order to quantify this effect, different tests were performed using bags having different surface-to-volume ratios. This was realized by fabricating bags having different surface areas (*i.e.* $S = 1900$ cm^2, 2580 cm^2, 3520 cm^2, respectively) and therefore different capacities, and then filling them with the same amount ($V = 3000$ cm^3) of the test mixture. Thus the surface-to-volume ratio was changed: the surface area S_N was varied while the gas volume V was kept constant.

Table 2 reports the number of NH_3 moles (n) and their percent variation over time ($\Delta n\%$) for the three bags having different surface-to-volume ratios, as described above. It is possible to observe that the percent variation

of ammonia in the considered 26 h interval increases with the bag exchange surface S, passing from 51% for the bag with the smaller surface ($S = 1900$ cm^2) to 72% for the bag with the larger surface ($S = 3520$ cm^2).

Table 2 also reports the ratio between NH$_3$ moles and the bag surface (n/S): this ratio allows better discriminating the experimental data relevant to the bags having different surface-to-volume ratios, which are shown in Figure 5. Figure 5 also illustrates the theoretical trends, calculated based on Equation (15), thereby the surface S for each bag, and the average diffusion coefficient obtained from the experimental data (2.38 10^{-8} cm^2/s).

A good correspondence is observed between experimental and theoretical trends.

Figure 6 illustrates the ammonia loss percentage over time for bags filled with the same amount ($V = 3000$ cm^3) of the test mixture, but with different surfaces. As already mentioned, diffusion is accentuated in the bags with a larger exchange surface.

Table 2. Molar variation in function of Nalophan^{TM} bag surface.

Time [h]	S/V = 0.63; S = 1900 cm²			S/V = 0.86; S = 2580 cm²			S/V = 1.17; S = 3520 cm³		
	n [mmol]	n/S [mmol/cm²]	Δn [%]	n [mmol]	n/S [mmol/cm²]	Δn [%]	n [mmol]	n/S [mmol/cm²]	Δn [%]
0	6.790	3.57E−03	0	6.790	2.63E−03	0	6.981	1.98E−03	0
1	6.471	3.41E−03	5	6.205	2.41E−03	9	6.754	1.92E−03	3
2	6.312	3.32E−03	7	5.913	2.29E−03	13	6.527	1.85E−03	7
3	6.152	3.24E−03	9	5.620	2.18E−03	17	6.072	1.73E−03	13
4	6.106	3.21E−03	10	5.521	2.14E−03	19	5.589	1.59E−03	20
5	6.059	3.19E−03	11	5.422	2.10E−03	20	5.106	1.45E−03	27
6	5.727	3.01E−03	16	5.336	2.07E−03	21	4.897	1.39E−03	30
7	5.395	2.84E−03	21	5.249	2.03E−03	23	4.689	1.33E−03	33
…	…	…	…	…	…	…	…	…	…
23	3.505	1.84E−03	48	2.839	1.10E−03	58	2.070	5.88E−04	70
24	3.300	1.74E−03	51	2.653	1.03E−03	61	1.925	5.47E−04	72
25	3.095	1.63E−03	54	2.468	9.57E−04	64	1.779	5.05E−04	75
26	3.300	1.74E−03	51	2.653	1.03E−03	61	1.925	5.47E−04	72
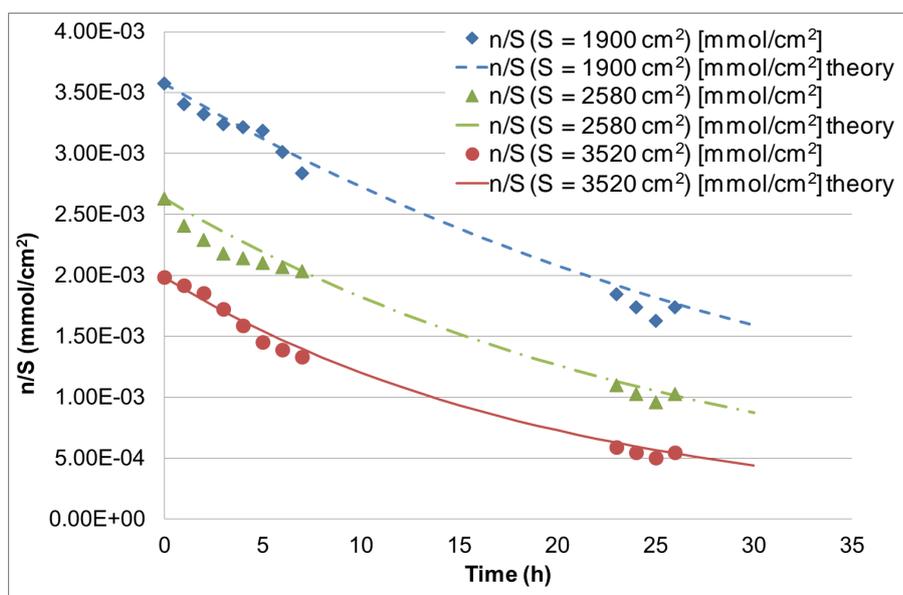
Figure 5. n/S trends for the three bags having different surfaces (1900 cm^2, 2580 cm^2 and 3520 cm^2, respectively) and different S/V ratios (0.63 cm^{-1}, 0.86 cm^{-1} and 1.17 cm^{-1}, respectively).
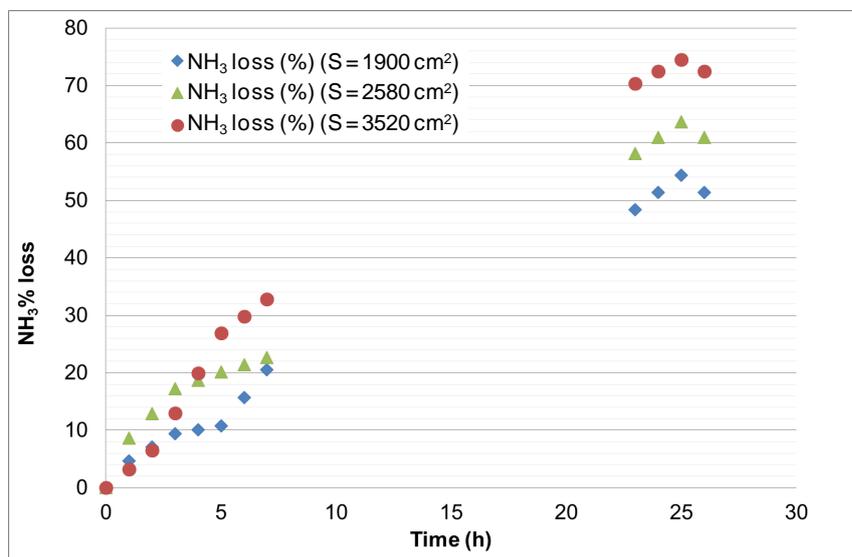
Figure 6. NH$_3$ loss (%) over time from the three bags having different surfaces (1900 cm^2, 2580 cm^2 and 3520 cm^2, respectively) and different S/V ratios (0.63 cm^{-1}, 0.86 cm^{-1} and 1.17 cm^{-1}, respectively).

The bag with a surface of 1900 cm^2 and a surface-to-volume ratio of 0.633 cm^{-1} gives a NH$_3$ loss percentage for prolonged storage times (26 h) of about 50%. This loss increases to about 60% for the bag with a surface of 2580 cm^2 and a surface-to-volume ratio of 0.860 cm^{-1}, and to about 70% for the bag with a surface of 3520 cm^2 and a surface-to-volume ratio of 1.17 cm^{-1}. The experimental data are in agreement with the theoretical trend expressed by Equation (15), which indicates that, at a given time t, n/n_0 is lower, *i.e.* the NH$_3$ loss percentage is higher, for higher surface-to-volume ratios S_N/V_N. The same assumption is discussed in Sironi *et al.* [23].

In order to evaluate the diffusion as a function of the surface-to-volume (S/V) ratio, it is possible to use the data relevant to the different tests described in this section (see **Table 1** and **Table 2**) by fixing the time t, and then comparing the different values of Δn (*i.e.* the total number of moles that have crossed the film at time t) or Δn/t (*i.e.* the average speed at which the moles have crossed the film) obtained for the bags having different S/V ratios. In order to make the results of the first test (**Table 1**) comparable with those of the other tests (**Table 2**), given the different number of initial moles n_0, the data have to be normalized with respect to n_0, thus representing Δn/n_0 or Δn/t/n_0. As an example, **Table 3** reports the experimental values of Δn/n_0 and Δn/t/n_0 measured after 7 hours for the different bags (having different S/V). The last columns of **Table 3** report the theoretical data, as calculated based on Equation (15).

The values of Δn/t/n_0, *i.e.* the average permeation speed in the first 7 hours of storage normalized with respect to n_0, both measured experimentally and calculated with Equation (15), are also represented in **Figure 7**.

The data reported in **Table 3** and **Figure 7** further prove how the surface-to-volume ratio affects diffusion: the average diffusion speed increases with the S/V ratio, thus resulting in higher percent losses after a given storage time t.

This means that, for a given material, to which corresponds a given diffusion coefficient D, one way to reduce diffusion over time is trying to reduce the surface-to-volume ratio.

For bags of given dimensions, *i.e.*, same surface and same maximum capacity, the only way to minimize S/V is to fill the bags to their maximum capacity. Bags filled only partially will have a higher S/V and therefore higher losses over time.

Another way to reduce S/V is to realize bigger bags. As an example, if cylindrical bags having a slenderness ratio (*i.e.*, h/D) equal to 2 are considered, the bag surface will be:

$$S = \frac{5}{2}\pi d^2 \propto d^2$$

where *d* is the diameter of the bag. If the bag is filled completely with the sample gas, then gas volume *V* is equal to the bag volume:

Table 3. Number of moles and average permeation speed for different S/V ratios.

Test	S [cm²]	V [cm³]	S/V [cm⁻¹]	$\Delta n/n_0$ exp (t = 7 h)	$\Delta n/n_0/t$ exp (t = 7 h)	$\Delta n/n_0$ th (t = 7 h)	$\Delta n/n_0/t$ th (t = 7 h)
1	2580	6000	0.43	0.093	0.013	0.121	0.017
2	1900	3000	0.63	0.205	0.029	0.171	0.024
3	2580	3000	0.86	0.227	0.032	0.226	0.032
4	3520	3000	1.17	0.328	0.047	0.295	0.042
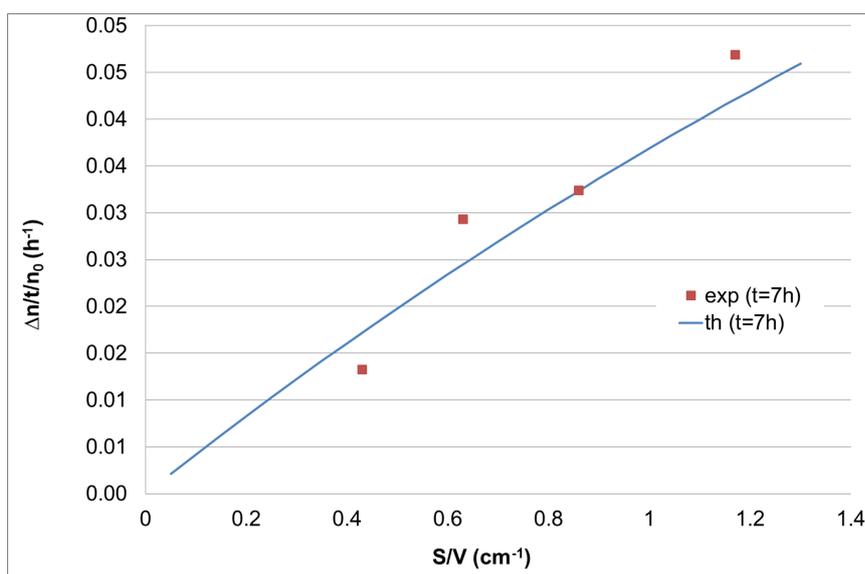
Figure 7. Average permeation speed (t = 7 h) normalized with respect to n_0 for different values of S/V.

$$V = \frac{\pi}{2}d^3 \propto d^3$$

The surface-to-volume ratio in this case depends on the diameter:

$$\frac{S}{V} = \frac{\frac{5}{2}\pi d^2}{\frac{\pi}{2}d^3} \propto \frac{1}{d}$$

And will therefore be proportional to the inverse of the diameter, *i.e.* decrease with the bag capacity.

Moreover, for a given d, S/V may be reduced by reducing the slenderness ratio, giving that the lowest S/V ratio is obtained for a slenderness ratio equal to 1, *i.e.* $h = D$.

Similar considerations can be made considering other bag shapes, always giving that diffusion phenomena can be reduced by using bigger bags, filled to their maximum capacity.

5. Conclusions

This study allowed to evaluate and to quantify the phenomenon of ammonia diffusion through Nalophan™ films.

The experimental determinations allowed the calculation of the diffusion coefficient of ammonia through Nalophan™ according to the Fick's law, which turned out to be equal to 2.38×10^{-8} cm²/s at a temperature of 23˚C and a relative humidity of 60%.

The ammonia losses from the Nalophan™ sampling bag always turned out to be significant; for instance, in the case of a bag with a surface of 2580 cm² filled with 6000 cm³ of gas (*i.e.* a "test mixture" of ammonia in air,

at fixed temperature and relative humidity), the percent ammonia loss after 26 h was 37%. This value is not negligible especially considering that the European Norm EN 13725:2003 allows a maximum storage time of 30 hours, thus assuming that the sampled mixture remains almost unaltered for 30 hours.

This study discusses the effect of the exchange surface on diffusion, by highlighting to which extent the surface-to-volume ratio affects the diffusion rate.

Diffusion was tested in bags with different S/V giving that the bag with a surface-to-volume ratio of 0.633 cm^{-1} has a NH_3 loss percentage after 26h of about 50%, while this loss increases to about 70% for the bag with a surface-to-volume ratio of 1.17 cm^{-1}. The experimental data are in agreement with the theoretical trend derived from the Fick's law, which indicates that, at a given time t, n/n_0 is lower, *i.e.* the percent NH_3 loss is higher, for higher surface-to-volume ratios S_N/V_N. Of course, the percentages of losses obtained during the presented experiments corresponds to a range of ammonia concentration. These losses can present different values if ammonia concentrations are in other ranges (higher or lower).

This means that, for a given material, to which corresponds a given diffusion coefficient D, one way to reduce diffusion over time is trying to reduce the surface-to-volume ratio. As a consequence, diffusion phenomena can be reduced by using bigger bags, filled to their maximum capacity. For cylindrical bags obtained from tubular Nalophan^{TM}, S/V can be minimized by realizing bags with a slenderness ratio (h/D) equal to 1.

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