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Odour Sample Diffusion Through Double Nalophan^{TM} Bags

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This paper describes the studies regarding ammonia losses through NalophanTM bags. 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 NalophanTM film was evaluated using the Fick's law, and it turned out to be equal to 2.38E-12 (m^2/s). The study also discusses the effect of the exchange surface on diffusion, by highlighting to which extent the surface-to-volume ratio affects the diffusion rate. 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 NalophanTM, the surface-to-volume ratio can be minimized by realizing bags with a slenderness ratio (h/D) equal to 1. Moreover, the effect of a double barrier on diffusion was studied by realizing "double bags". Double bags are concentric bags obtained starting from two different tubular films cut in different lengths. The experimental data show a reduction of ammonia losses due to the effect of the external multi barrier. The expedient of the double bag loaded both internally and externally with the same gas mixture allows to reduce the diffusion of ammonia into the internal bag. The diffusion through the internal bag is comparable to that obtained with a bag of triple thickness than the one used.

1. Introduction

The perception of odour from industrial sites is the cause of an increasing number of citizens complains.
It is nowadays universally accepted that the best way of measuring odours is to refer to the sensation caused by an odorous sample directly on a panel of human assessors (Capelli et al., 2010). This is the principle of sensorial techniques, such as dynamic olfactometry (EN13725, 2003), which are commonly applied for testing odours for environmental management purposes.
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 (Bokowa, 2008; Bourgeois et al., 2003; Capelli et al., 2010; Kim and Kim, 2012a; Laor et al., 2010).
The European Standard on dynamic olfactometry (EN13725, 2003) 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 a 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, TedlarTM) and polyethyleneterephthalate (PET, Nalophan™).

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

Many studies have been carried out on the materials performances listed in the European Norm (Akdezein et al., 2011; Beghi and Guillot, 2006, 2008; Cariou et al., 2006; Ghosh et al., 2011; Guillot and Beghi, 2008; Hansen et al., 2011; Kim, 2006; Kim et al., 2012b; Koziel et al., 2005; Mochalski et al., 2009; Parker et al., 2010; Trabue et al., 2006, van Harreveld, 2003; Wang et al., 2011) in the last years. The results of these studies proved polymeric materials not to be able to preserve the gas chemical composition unchanged for long periods (30 h) and highlighted that small or soluble molecules, such as ammonia (NH_3) and hydrogen sulphide (H_2S), diffuse through the sampling bag to a not negligible extent (Beghi and Guillot, 2006, 2008; Capelli et al., 2013; Guillot and Beghi, 2008; Sironi et al., 2014, in press).

The aim of this work is the evaluation of the ammonia losses through Nalophan^{TM} bags at the limit storage time imposed by the EN13725, which is 30h. Ammonia was chosen as target compound for the study of the influence both of the surface-to-volume ratio on the diffusion kinetics, and of the concentration gradient across the polymeric barrier.

2. Materials and Methods

2.1 Materials

The Nalophan^{TM} 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 Tillmanns S.p.A. .

A single bag was obtained starting from a tubular film with a diameter of 22.5 cm cut in different lengths to obtain different surfaces: 1900 cm^2, 2580 cm^2, 3520 cm^2. One end was equipped with a clamp closure while the other end is provided with a Teflon inlet tube for sample collection (Figure1 A). These bags were filled with the same amount (3000 cm^3) of gas, thus realizing bags with a different surface-to-volume ratio.

The double bags were obtained starting from two different tubular film cut in different lengths. The inner bag was obtained by a tubular film with diameter of 22.5 cm, the outer was obtained by a tubular film with diameter of 31 cm.

The double bag is a concentric bag composed (Figure 1B) by an inner bag with a capacity of 6000 cm^3 and surface equal to 2580 cm^2 and an outer bag with a capacity of 12000 cm^3 and surface equal to 5208 cm^2. The different volumes were realized to create an interspace between the two bags.

The double bag was made in the following way:

- One end of the inner bag was equipped with a clamp closure while the other end is provided with a Teflon inlet tube for sample collection.
- The outer bag is clamped on the Teflon inlet tube of the inner bag and on the other side it is provided with a Teflon inlet tube for sample collection.

Figure 1 Nalophan^{TM} bags:A) single bag B) double bags

The NH_3 decay over time was evaluated using gas-chromatography (GC) to quantify 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).

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

Tests were conducted by measuring the NH_3 concentration at the maximum storage time imposed by the EN13725, which is 30h. Each measurement involved the withdrawal of 300 µl of the test mixture by means of a syringe and the injection in the GC. The oven temperature of the GC 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 the 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 ppmV 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.

The NH_3 diffusion was evaluated both for the single bag and double bag.

The single bags studied were:

- 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
- Nalophan^{TM} bags having different surface in order to evaluate the role of the exchange surface (i.e., the bag surface area) on the NH_3 concentration decay inside the bag. The bags realized had different surface areas, i.e. 1900 cm^2, 2580 cm^2, 3520 cm^2, respectively. These bags had 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.

The NH_3 diffusion in the double bag was evaluated through a Nalophan^{TM} bags having respectively a capacity of about 6000 cm^3 and a surface equal to 2580 cm^2 for the inner bag and a capacity of about 12000 cm^3 and a surface equal to 5208 cm^2 for the outer bag. Both the bags were filled with 6000 cm^3 of the above defined test mixture. The double bag was studied in order to evaluate the role of the NH_3 concentration gradient across the polymeric membrane on the NH_3 concentration decay inside the both bags (i.e. inner bag and outer bag).

All the bags tested are stored at a constant temperature of 23°C and an external relative humidity of 60%. The external relative humidity was set equal to the internal one in order to avoid water diffusion during storage and its potential influence on NH_3 diffusion. The NH_3 concentrations were measured according to the above described test protocol.

3. Results and discussion

Table 1 shows the NH_3 concentration values measured at the initial storage time and after 30 h.

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 percent loss of NH_3 ($NH_{3\,loss\%}$). This parameter allows to highlight the differences obtained with different bag surfaces. Alike, the influence of the concentration gradient (ΔC) across the polymeric barrier for the double bag was evaluated in terms of percent loss of NH_3.

The percent NH_3 loss through the bag over time can be expressed as:

$$NH_{3\,loss\%} = 1 - \frac{C}{C_0} = 1 - e^{-\frac{S_n D}{V_n z_n}t}$$

The value for D is equal to 2.38 10^{-8} cm^2/s, as calculated by Sironi et al, (in press).

According to the above reported equation, the amount of ammonia losses through the bag depends on the surface-to-volume ratio (S_N/V_N), hereafter defined simply as S/V of the bag.

Table 1 shows the results of the tests performed varying the surface-to-volume ratio for the single bag (SB) and the concentration gradient using the double bag (DB). Table 1 reports the initial concentration (C_0, t=0), the ratio C/C_0 (where C is the concentration at t=30h) measured after 30 h, and the percent NH_3 loss ($NH_{3\,loss\%}$).

By comparing the different single bags (sample 1 to 4), it is possible to observe that the percent NH_3 loss for prolonged storage times (30h) depends on the surface-to-volume ratio and that the loss increases increasing the S/V ratio.

- The bag with a surface of 2580 cm^2 and a surface-to-volume ratio of 0.43 cm^{-1} gives a percent NH_3 loss equal to 42%.
- The bag with a surface of 1900 cm^2 and a surface-to-volume ratio of 0.63 cm^{-1} gives a percent NH_3 loss equal to 56%.
- The bag with a surface of 2580 cm^2 and a surface-to-volume ratio of 0.86 cm^{-1} gives a percent NH_3 loss equal to 67%.

- The bag with a surface of 3520 cm^2 and a surface-to-volume ratio of 1.17 cm^{-1} gives a percent NH_3 loss equal to 78%.

This clearly shows that that the diffusion of pollutants through the sampling bag is reduced by reducing the S/V ratio, as already observed in a recent study by Sironi et al. (in press).

The results show that, comparing sample #1 and #3, which have the same surface (2580 cm^2), but are filled with different volumes of test mixture, thus giving different S/V ratios, the NH_3 loss is reduced if the bag is filled to its maximum capacity (6000 cm^3), thus for its minimum S/V ratio.

This means that diffusion 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) tending to 1.

Table 1 Experimental data relevant to NH_3 diffusion over time in a Nalophan^{TM} bag

Sample	Bag	S/V [cm^{-1}]		Time [h] 0	30
			C_0 (ppm)	54714	31734
1	SB	2580/6000=0.43	C/C_0	1	0.58
			$NH_{3\ loss\ \%}$	0	42
			C_0 (ppm)	55000	24463
2	SB	1900/3000=0.63	C/C_0	1	0.44
			$NH_{3\ loss\ \%}$	0	56
			C_0 (ppm)	55000	18306
3	SB	2580/3000=0.86	C/C_0	1	0.33
			$NH_{3\ loss\ \%}$	0	67
			C_0 (ppm)	56553	12607
4	SB	3520/3000=1.17	C/C_0	1	0.22
			$NH_{3\ loss\ \%}$	0	78
			C_0 (ppm)	55000	40276
5	DBin	2580 /6000=0.43	C/C_0	1	0.73
			$NH_{3\ loss\ \%}$	0	27
			C_0 (ppm)	55000	23184
6	DB out	5280/6000=0.88	C/C_0	1	0.42
			$NH_{3\ loss\ \%}$	0	58

By comparing the double bags (sample #5 and #6) at prolonged storage times (30h), it is possible to observe the same behaviour as for the single bags: increasing the S/V ratio results in higher NH_3 losses.

- The inner bag with a surface of 2580 cm^2 and a surface-to-volume ratio of 0.43 cm^{-1} gives a percent NH_3 loss equal to 27%.
- The outer bag with a surface of 5280 cm^2 and a surface-to-volume ratio of 0.88 cm^{-1} gives a percent NH_3 loss equal to 58%.

Moreover, by comparing the bags having the same surface-to-volume ratio equal to 0.43 (sample #1 and #5), it is possible to observe that the percent NH_3 losses relevant to the two bags are different. This proves that the type of bag use, i.e. single bag or double bag, influences the ammonia diffusion. By comparing the trend of NH_3 losses over time it is possible to observe that the inner bag of the double bag (sample #5) gives more moderate losses than the inner bag with respect to a single bag having the same surface-to-volume ratio (sample #1). The reduction of the NH_3 concentration gradient through the polymeric film, obtained by the use of the double bag, reduces the loss of ammonia at 30 h changing from a loss of 42% (sample #1) to a loss of 26% (sample #5).

In order to evaluate the diffusion as a function of the surface-to-volume (S/V) ratio, it is possible not only to use the data described Table 1 by fixing the time equal to 30 h, and then comparing the different values of ΔC (i.e. the ppm that have crossed the film at time t), but also to evaluate the $\Delta C/t$ (i.e. the average speed at which the concentration changes inside the bag) obtained for the bags having different S/V ratios. In order to make the results of the test comparable (Table 1), the data have to be normalized with respect to C_0, thus representing $\Delta C/C_0$ or $\Delta C/t/C_0$.

Table 2 reports the experimental values of $\Delta C/C_0$ and $\Delta C/C_0/t$ after 30 hours for the different bags (having different S/V).

Table 2 Concentration and average permeation speed for specific S/V ratios

Sample	Bag	S [cm^2]	V [cm^3]	S/V [cm^{-1}]	$\Delta C/C_0$ exp (t=7h)	$\Delta C/C_0/t$ exp (t=7h)
1	SB	2580	6000	0.43	0.420	0.014
2	SB	1900	3000	0.63	0.560	0.019
3	SB	2580	3000	0.86	0.670	0.022
4	SB	3520	3000	1.17	0.780	0.026
5	DB_{in}	2580	6000	0.43	0.270	0.009
6	DB_{out}	5280	6000	0.88	0.580	0.019

The data reported in Table 2 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, as observed in the study by Sironi et al. (in press).

Moreover, from the data reported In Table 2 it is possible to observe that, for the same S/V ratio equal to 0.43, the inner bag of the double bag (sample #5) has a lower average diffusion speed in comparison with the single bag (sample #1). The observed reduction is of about 36%.

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 both the surface-to-volume ratio but also, for the same S/V ratio, the pollutant concentration gradient across the polymeric film. This can be achieved with the double bag expedient, which provides to add an outer bag filled with the same gas as the inner bag, in order to prevent the inner bag from diffusion phenomena.

4. Conclusion

NH_3 losses from the Nalophan^{TM} sampling bag always turned out to be significant. For instance, in the case of a bag with a surface of 2580 cm^2 filled with 6000 cm^3 of gas (i.e. a “test mixture” of NH_3 in air, at fixed temperature and relative humidity, S/V=0.43), the percent NH_3 loss after 30 h was 42%.

Results showed that bags with higher surface-to-volume ratios had higher NH_3 losses. Single bags with surface-to-volume equal to 0.43 cm^{-1} have a percent NH_3 loss after 30h of about 42%, while this loss is increased to about 78% for single bags with a surface-to-volume ratio equal to 1.17 cm^{-1}.

For a specific material, to which corresponds a specific diffusion coefficient D, one way to reduce diffusion over time is to reduce the surface-to-volume ratio. 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.

Moreover, the results obtained comparing bags with the same surface-to-volume ratio equal to 0.43 but different NH_3 concentration gradients across the polymeric film, showed different NH_3 losses over time. This proves that the type of bag used, i.e. single bag or double bag, can have a significant influence on the NH_3 diffusion. A reduction of the concentration gradient of the diffusing pollutant through the polymeric film, obtained with the expedient of the double bag, reduced the NH_3 losses after 30 h from a loss of 42% (single bag) to a loss of 26 % (double bag).

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