

Temperature Effect on H₂S Diffusion through Nalophan™

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The Hydrogen sulphide (H₂S) loss, an odorous molecule of small dimensions, through Nalophan™ bags has been studied.

The diffusion coefficient of H₂S through the Nalophan™ film was evaluated using the Fick's law, and it turned out to be equal to 7.55E-12 (m²/s) at a temperature of 23°C and a relative humidity of 60%. This D coefficient entails a reduction of 17% of H₂S into 30 hours of storage time. Moreover, the role of humidity on diffusion speed was evaluated by storing the Nalophan™ bags at relative humidity condition of 20% and temperature of 23°C. In this condition, the loss percentage of H₂S (%) after 30 h turns out to be equal to about 23%. The results show that the diffusion phenomena are affected by the relative humidity storage condition: by decreasing the relative humidity of storage condition it is observed a weak increase of H₂S (%) loss.

Also the sampling at high temperature (i.e 75°C or 130°C) was evaluated by heating the filled Nalophan™ bags for 5 minute respectively at 75°C and 130°C and then by storing the Nalophan™ bags at relative humidity condition of 20% or 60% and temperature of 23°C. The results show a loss percentage of H₂S after the heat treatment (i.e 75°C or 130°C) of the film not negligible in a range of 30-36%. This behaviour could be attributed to the proximity of the glass transition temperature of the Nalophan™.

1. Introduction

Odorous molecules with low odour threshold, easily perceived from people, often cause odour pollution and nuisance.

These odour molecules, emitted from different human activities as industry, (Sulyok et al., 2001) (Laor et al., 2010, Van Harreveld et al., 2003), agriculture (Trabue et al., 2013, Laor et al., 2010, Hansen et al., 2011, Parker et al., 2010), waste water treatment (Akdeniz et al., 2011) and waste treatment (Le et al., 2013) are considered a form of pollution.

Dynamic olfactometry is the only normed technique for the odour quantification (EN13725, 2003).

Olfactometric analyses on site provide to carry on a lab and the panel into the industrial pole or odorous site.

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 (Capelli et al., 2010; Laor et al., 2010; Kim and Kim, 2012). The European Standard on dynamic olfactometry (CEN, 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 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); polyvinylfluoride (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.

The norm under revision (EN13725, 2003) is considering problems linked with diffusion through sampling polymeric bags.

Some authors have been studying the characteristics of the materials listed in the EN 13725 (CEN, 2003) with the aim to verify their suitability for olfactometric measurements. Many studies have been conducted in order to assess the diffusion of odorous molecules through polymeric films (van Harreveld, 2003; Cariou., 2006; Guillot., 2008; Trabue et al., 2006; Mochalski et al., 2009; Parker et al., 2010; Hansen et al., 2011; Sironi et al., 2013, 2014a,b; Sulyok et al., 2001, 2002; Kim, 2006; Kim et al., 2006; Jo et al., 2012; Kim et al., 2012). 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.

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 (Crank, 1968; Sironi et al., 2014a).

Water can diffuse quickly through polymeric films because of its structure (Guillot and Beghi, 2008). Also other molecules having a dimension similar to water, such as ammonia (NH₃) and hydrogen sulphide (H₂S) (Beghi and Guillot, 2006, 2008; Guillot and Beghi, 2008, Sironi et al., 2014a, b), 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 (Crank, 1968). In this study, diffusion through polyethyleneterephthalate (PET, Nalophan™) is examined. Hydrogen sulphide has a very strong and bad odour which can be detected by human olfaction at very low concentration (in a range of ppb-few ppm) (Toombs et al., 2010). Moreover, although the American Conference of Governmental Industrial Hygienists (ACGIH) for an eight-hour time weighted average (TWA) recommends an exposure limit was a concentration of 10 parts per million, new recommendations for airborne H₂S (ACGIH 2010) lower TWA exposure for workers to 1 ppm. For general population the reference concentration (RfC, where a continuous inhalation exposure to the human population (including sensitive subgroups) is likely to be without an appreciable effects during a lifetime) is 0.002 mg/m³ (0.0013 ppm) (EPA 2003).

The gaseous emissions produced by the above-mentioned plants can therefore provoke diseases in the population living anywhere near, even for concentrations much lower than 10 ppm, causing also all stress-related diseases due to persistent bad smell, altering also psychophysical well-being and accurate determination are needed to describe the environmental quality.

More in detail, the experiments described in this paper have the aim to investigate the diffusion phenomena of H₂S 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. H₂S was chosen as target compound for the study, which involved an experimental part aiming to calculate the specific D coefficient through Nalophan™ and evaluate the influence of physical parameters (T, RH) on D coefficient. More in detail, the effect of the temperature was evaluated by storing the bag at high temperature for 5 minute, in order to simulate the sampling at the stack, respectively at 75°C and 130°C. After this period the bag was then stored in a climatic chamber at temperature of 23°C and humidity respectively of 60% and 20%.

2. Material and methods

2.1 Material

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

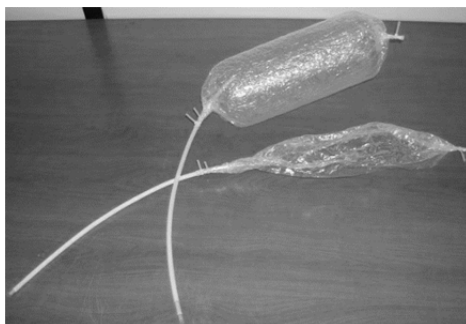


Figure 1. Nalophan™ bags

The bags were obtained starting from a tubular film. 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 hydrogen sulphide decay over time was evaluated using a high performance miniature sensor able to detect H₂S at the low ppbv level for the quantification of H₂S concentration inside the bag. The hydrogen sulphide concentration was measured using CairClip apparatus, developed by Cairpol, a French start-up (Alés Engineer School of Mines), that consist in an amperometric detection with dynamic air sampling system, a special filter and a high sensitive electronic circuit containing a data logger.

All the tested samples were realized by filling the Nalophan™ bags with a gaseous mixture of hydrogen sulphide with a concentration of 800 ppbV which will be defined as the “test mixture”. The test mixture was obtained using a certified H₂S gas cylinder (SAPIO technical gas, Milano, Italy). Hydrogen sulphide was withdrawn in bags with a volume of 6 liters and a surface of 2580 cm².

At the end of the period of storage, the final concentration of each sample was measured and compared to its initial concentration.

During storage, physical parameters like temperature and relative humidity were kept under control using a climatic chamber (Chamber GHUMY by Fratelli Galli, Milano, Italy). To simulate high temperature sampling a stove was used (High Performance Vacuum Oven 21GV by Fratelli Galli, Milano, Italy).

2.2 Methods

All tests were conducted by measuring the H₂S concentration at different time intervals after sample preparation from 0 to 30 h.

The diffusion of hydrogen sulphide was evaluated through a Nalophan™ bag having a capacity of about 6000 cm³ and a surface equal to 2580 cm².

This bag was filled with 6000 cm³ of the above defined test mixture and then stored at different conditions. The role of temperature on the H₂S concentration decay inside the bag was evaluate by storing bags at a temperature of 23°C. The role of humidity on the H₂S concentration decay inside the bag was evaluate by storing bags at different humidity respectively of 20% and 60%.

The effect of the temperature was evaluated by storing the bag at high temperature for 5 minute, in order to simulate the sampling at the stack respectively at 75°C and 130°C. The bag was then stored in a climatic chamber at condition above mentioned (i.e. temperature of 23°C and humidity respectively of 60% and 20%).

Based on the experimental data of residual H₂S concentration inside the bag and on the Fick's law, the diffusion coefficient D of hydrogen sulphide through Nalophan™ was calculated. The measurements were performed at different time and the diffusion coefficient D is averaged over the 30 hours.

The hydrogen sulphide concentrations over time were measured according to the above described test protocol.

3. Results and discussion

Table 1 shows the H₂S concentration values measured at different time intervals t_i at storage condition of temperature of 23°C and humidity respectively of 60% and 20%. Each concentration value reported in the table is the average of three replicate measurements.

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

$$D_{ti} = -\frac{V_B Z_B}{S_B t_i} \ln\left(\frac{C_{ti}}{C_{in}}\right) \quad (1)$$

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

The diffusion coefficient of H₂S through Nalophan™ is finally calculated as the average of the different values of D_{ti} weighted on the corresponding storage time t_i:

$$\bar{D} = \frac{\sum_i D_{ti} t_i}{\sum_i t_i} \quad (2)$$

The resulting value for \bar{D} is equal to 8.70 10⁻¹² m²/s with a standard deviation equal to 1.41 10⁻¹⁴ m²/s for the test performed at temperature of 23°C and humidity of 20%, while it is equal to 7.55 10⁻¹² m²/s with a standard deviation equal to 1.47 10⁻¹⁴ m²/s for the test performed at temperature of 23°C and humidity of 60%.

Moreover, the percent H₂S loss through the bag over time can be expressed as:

$$H_2S_{loss\%} = \left(1 - \frac{C_{ti}}{C_{in}}\right) * 100 = \left(1 - e^{-\frac{S_B \bar{D}}{V_B Z_B} t}\right) * 100 \quad (3)$$

The loss percentage of H₂S (%) after 30 h turns out to be equal to about 17% for the test performed at temperature of 23°C and humidity of 60%. The loss percentage of H₂S (%) after 30 h turns out to be equal to about 23% for the test performed at temperature of 23°C and humidity of 20%.

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. (2011) also dealing with H₂S losses through polymeric films (Tedlar and Flex Foil), reports losses of about 20% after 36 hours.

Table 1. Experimental data relevant to H₂S diffusion over time in a Nalophan™ bag stored at temperature of 23°C and humidity respectively of 60%, 20 %

Time (h)	T 23°C RH%20			T 23°C RH%60		
	C _{ti} /C ₀ (ppb)	% H ₂ S loss	D _{ti} (m ² /s)	C _{ti} /C ₀ (ppb)	% H ₂ S losses	D _{ti} (m ² /s)
3	0.95	5%	2.36E-12	0.98	2%	1.05E-12
24	0.87	13%	6.20E-12	0.84	16%	7.60E-12
30	0.77	23%	1.11E-11	0.83	17%	8.16E-12

Moreover, the data reported above shown almost the same trend of the diffusion phenomena decreasing the relative humidity storage condition with a weak increase of loss for the low relative humidity storage condition. Probably, this it is due to the humidity of the text mixture. In this study, a dry text mixture was used. So the driving force of the water as observed in Sironi et al (2014a, b) is attenuated.

Table 2 shows the H₂S concentration values measured at different time intervals t_i, after a thermic treatment of the bag. The storage condition, after the 5 minute at high storage temperature respectively at 75°C and 130°C, are: temperature of 23°C and humidity respectively of 60% and 20%.

The last column of each condition tested of table 2 reports the diffusion coefficient D_{ti} for each time interval t_i calculated according to the equation 1.

Table 2. Experimental data relevant to H₂S diffusion over time in a Nalophan™ bag after a thermic treatment respectively at 75°C and 130°C and stored at temperature of 23°C and humidity respectively of 20 and 60%.

Time (h)	5 minutes at 75°C						5 minutes at 130°C					
	T 23°C RH%20			T 23°C RH%60			T 23°C RH%20			T 23°C RH%60		
	C _{ti} /C ₀ (ppb)	% H ₂ S loss	D _{ti} (m ² /s)	C _{ti} /C ₀ (ppb)	% H ₂ S loss	D _{ti} (m ² /s)	C _{ti} /C ₀ (ppb)	% H ₂ S loss	D _{ti} (m ² /s)	C _{ti} /C ₀ (ppb)	% H ₂ S loss	D _{ti} (m ² /s)
3	0.89	11	4.30E-12	0.94	6	2.46E-12	0.89	11	5.20E-12	0.96	4	1.87E-12
24	0.70	30	1.94E-12	0.74	26	1.62E-12	0.69	31	2.04E-12	0.66	34	2.21E-12
30	0.70	30	1.54E-12	0.64	36	1.96E-12	0.69	31	1.59E-12	0.64	36	1.92E-12

The diffusion coefficient of hydrogen sulphide through Nalophan™ is finally calculated as the average of the different values of D_{ti} weighted on the corresponding storage time t_i as reported in equation 2.

The resulting value for \bar{D} , obtained after the heat treatment at 75 °C, is equal to 1.83 10⁻¹² m²/s, with a standard deviation equal to 6.02 10⁻¹⁵ m²/s for relative humidity of 20%. While, the \bar{D} value is equal to 1.84 10⁻¹² m²/s, with a standard deviation equal to 2.59 10⁻¹⁵ m²/s for relative humidity of 60%.

The resulting value for \bar{D} , obtained after the heat treatment at 130 °C, is equal to 1.97 10⁻¹² m²/s, with a standard deviation equal to 8.02 10⁻¹⁵ m²/s for relative humidity of 20%. While, the for \bar{D} value is equal to 2.04 10⁻¹² m²/s, with a standard deviation equal to 1.27 10⁻¹⁵ m²/s for relative humidity of 60%.

Analyzing results above mentioned it is possible to conclude that the \bar{D} values after thermal treatment at 75°C and 130 °C are comparable.

Instead, comparing the data obtained storing the bag for 30 hours with and without the heat treatment (i.e 75°C and 130°C), it is possible to observe an increase of the losses of H₂S:

- without the heat treatment the loss percentage average of H₂S (%) after 30 h turns out to be about 23% for relative humidity of 20% and about 17% for relative humidity of 60% (Table 1).
- with the heat treatment at temperature of 75°C the loss percentage average of H₂S (%) after 30 h turns out to be about 30% for relative humidity of 20% and about 36% for relative humidity of 60%.
- with the heat treatment at temperature of 130°C the loss percentage average of H₂S (%) after 30 h turns out to be about 31% for relative humidity of 20% and about 36% for relative humidity of 60%.

The loss percentage of H₂S with heat treatment (i.e 5 minute at a temperature respectively of 75°C and 130°C) is not negligible especially considering some sampling condition (i.e. emission from stack).

This behaviour could be attributed to the glass transition temperature of the Nalophan™ (T_g is 67 °C for amorphous PET (Demirel et al., 2011)) according to literature studies on permeability, diffusivity and solubility in polymers when temperature is varied across the T_g. Many studies (Eslami and Muller-Plathe, 2009; Li et al., 2008; Park, 2013; Minelli, 2014; Klopffer and Flaconnèche, 2001) show experimental data where the trend of \bar{D} coefficient is different below T_g (glassy polymer) or above T_g (rubbery polymer).

In order to evaluate the contribution of the accumulation term of H₂S in the Nalophan™ film, which was neglected for simplicity in the present paper, the tests for the determination of the H₂S decay were repeated by inserting inside the bag a polymer film having the same weight respect the membrane to be crossed (i.e. surface equal to 2658 cm², thickness equal to 20µm). This way, the different behaviour observed in the new tests is due to the H₂S amount absorbed on the inner film.

Table 3 shows the H₂S concentration values measured at different time intervals t_i for storage condition of temperature of 23°C and humidity of 60%.

The last column of table 3 reports the diffusion coefficient D_{ti} for each time interval t_i calculated according to the equation 1. The diffusion coefficient of hydrogen sulphide through Nalophan™ is calculated as reported in equation 2.

Table 3. Experimental data relevant to H₂S diffusion over time in a Nalophan™ bag with inside an empty bag stored at temperature of 23°C and humidity of 60%

Time (h)	C _{ti} /C ₀ (ppb)	% H ₂ S losses	D _{ti} (m ² /s)
3	0.90	10%	4.35E-12
24	0.36	64%	5.48E-12
30	0.28	72%	5.43E-12

The resulting value for \bar{D} is equal to 5.39 10⁻¹² m²/s, with a standard deviation equal to 2.30 10⁻¹⁵ m²/s.

The diffusion coefficient presents the same order of magnitude obtained for the bag with a volume of 6 liters and surface of 2580 cm² without polymeric film inside. However, the contribution of the absorption on the film is not entirely negligible.

4. Conclusions

This study allowed to evaluate and to quantify the phenomenon of hydrogen sulphide diffusion through Nalophan™ films at different storage conditions.

The experimental determinations allowed the calculation of the diffusion coefficient of H₂S through Nalophan™ according to the Fick's law, which turned out to be equal to 7.55 10⁻¹² m²/s at a temperature of 23°C and a relative humidity of 60%.

Instead, the diffusion coefficient of H₂S through Nalophan™ according to the Fick's law, which turned out to be equal to 8.70 10⁻¹² m²/s at a temperature of 23°C and a relative humidity of 20%.

The H₂S losses from the Nalophan™ sampling bag always turned out to be significant; for instance, in the case of storage condition of temperature equal to 23°C and humidity 60%, the percent hydrogen sulphide loss after 30 h was 17%; instead, in the case of storage condition of temperature equal to 23°C and humidity 20%, the percent hydrogen sulphide loss after 30 h was 23%. These results shown a weak acceleration of the diffusion phenomena decreasing the relative humidity storage condition. These values 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.

In order to simulate the sampling at the stack, the effect of the temperature was evaluated by storing the bag at high temperature for 5 minute, respectively at 75°C and 130°C. The bag was then stored in a climatic chamber at temperature of 23°C and humidity respectively of 60% and 20. The loss percentage of H₂S with heat treatment is not negligible and turns out to be in the range of 30-36%. This behaviour could be attributed to the glass transition temperature of the Nalophan™ (i.e. T_g is 67 °C for amorphous PET).

Thermal treatment of the polymeric film for 5 minutes caused a re-arrangement of polymeric chains.

The results shown that, under the test condition evaluated, the absorption phenomenon is not negligible.

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