H$_2$S DIFFUSION THROUGH NALOPHAN^{TM} BAGS

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ABSTRACT

The Hydrogen sulphide (H$_2$S) loss through Nalophan^{TM} bags has been studied. H$_2$S 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 and hydro-soluble molecules may be significantly underestimated if samples are not analyzed immediately after sampling.

The diffusion coefficient of H$_2$S through the Nalophan^{TM} film was evaluated using the Fick's law, and it turned out to be equal to 1.49E-12 (m^2/s) at a temperature of 23°C and a relative humidity of 60%. This D coefficient gives a reduction of 30% of H$_2$S into 30 hours of storage time not negligible for odour determination.

Moreover, the role of humidity and temperature on diffusion speed was evaluated by storing the Nalophan^{TM} bags at relative humidity condition of 20%, 60% and temperature of 23°C, 75°C. The results show a dependence of D coefficient with the amount of water present in the gas across the membrane.

Moreover, the early loss (3h) percentage of H$_2$S at high temperature (75°C) is not negligible about 17% and 14% respectively for relative humidity of 20% and 60%. This behavior could be attributed to the proximity of the glass transition temperature of the Nalophan^{TM}.

KEYWORDS: Diffusion; H$_2$S; Nalophan^{TM}; odour sampling; sampling bag.

INTRODUCTION

Even though environmental odours are generally not harmful to health (Capelli et al., 2011), 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. The way to measure odours is a sensorial techniques, such as dynamic olfactometry (EN13725, 2003), which are commonly applied for testing odours for environmental management purposes (Schultz, 1996). This technique is based to the sensation caused by an odorous sample directly on a panel of human assessors (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 until they are analysed in an olfactometric laboratory (Bourgeois et al., 2003; Capelli et al., 2010; Laor et al., 2010; 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); polyvinylfuoride (PVF, Tedlar[TM]) 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 (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; Wang et al., 2011; Sulyok et al., 2001, 2002; Kim, 2006; Kim et al., 2006; Saìz et al., 2011; 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[TM] 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, 2008). Also other molecules having a dimension similar to water, such as ammonia (NH_3) and hydrogen sulphide (H_2S) (Beghi, 2006, 2008; Guillot, 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 (Igwe et al., 2006; Piergiovanni, 2010).

The experiments described in this paper have the aim to investigate the diffusion phenomena of H_2S through Nalophan[TM], 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. H_2S was chosen as target compound for the study, which involved an experimental part aiming to calculate the specific D coefficient through Nalophan[TM] and evaluate the influence of physical parameters (T, RH) on D coefficient. Hydrogen sulphide has a very strong and bad odour which can be detected by human olfaction at very low concentration – about 10-50 ppb (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 H_2S (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/m^3 (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.

MATERIAL AND METHODS

Material

The Nalophan[TM] used to prepare 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. One end was equipped with a clamp closure while the other end is provided with a Teflon inlet tube for sample collection (Figure 1).
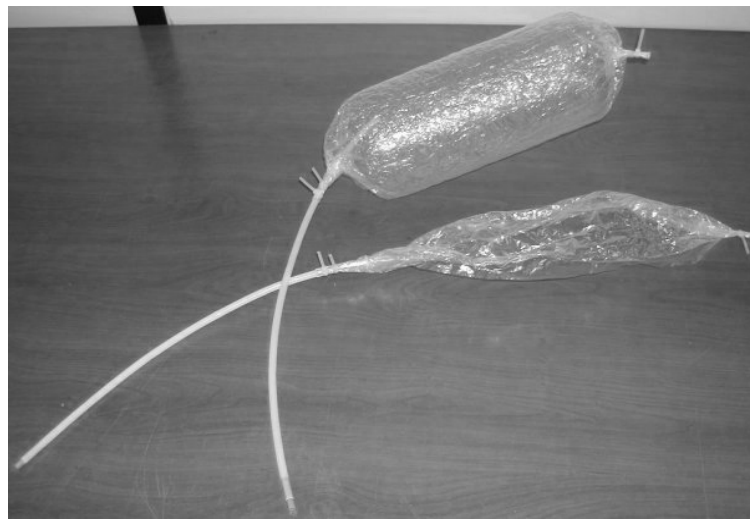
Figure 1. Nalophan[TM] bags

The hydrogen sulphide decay over time was evaluated using a high performance miniature sensor able to detect H_2S at the low ppbv level for the quantification of H_2S 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[TM] bags with a gaseous mixture of hydrogen sulphide with a concentration of 500 ppb_V and a relative humidity of 40%, which will be defined as the "test mixture". The test mixture was obtained using a certified H_2S gas cylinder (SAPIO technical gas, Milano, Italy). Hydrogen sulphide was withdrawn in bags with a volume of 6 liters and a surface of 2580 cm^2.
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).

Methods

All tests were conducted by measuring the H_2S concentration at different time intervals after sample preparation from 0 to 30 h.

The diffusion of hydrogen sulphide was evaluated through a Nalophan[TM] 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 respectively of 23°C and 75°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 conditions of the experimental tests are reported in Table 1.

Table 1. Experimental tests conditions

T (°C)	RH%	Partial pressure (mmHg)
23	20	4
23	60	13
75	20	58
75	60	173

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[TM] 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.

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:

$$j = -D \frac{\partial C}{\partial x} \qquad (1)$$

where:
- j is the specific molar flow (mol/m²/s)
- D is the diffusion coefficient of the compound through the film (m²/s)
- C is the concentration of the diffusing compound (mol/m³)
- x is the differential thickness of the film.

The film thickness can therefore be expressed as:

$$\int_0^z dx = z \qquad (2)$$

where z is the film thickness (m);
Referring to Figure 2, which schematizes the diffusion phenomenon through the thin film which constitutes the sampling bag, we can define:
- S_B is the surface of the polymeric film of the bag (m²)
- Z_B is the thickness of the film (m)
- C_B is the concentration in the inside volume (mol/m³)
- C_O is the concentration outside the film (mol/m³), for a single bag it is generally considered negligible ($C_O=0$),
- j is the specific molar flow through the film (mol/m²/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 is constant along the film (x).
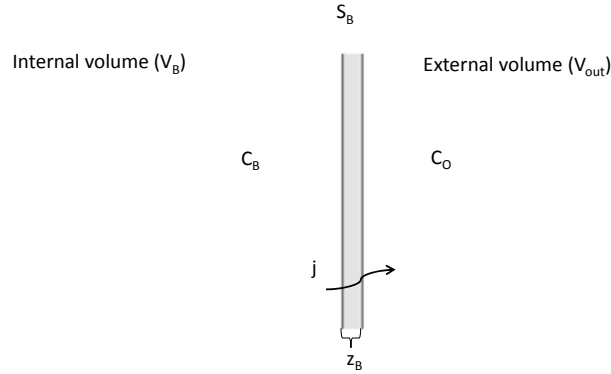
Figure 2. Schematization of diffusion through the thin film of the bag

By integrating equation (1) in dx between 0 and z_B, the specific molar flow j can be expressed as:

$$j = -D \frac{C_0 - C_B}{z_B} \quad (3)$$

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

Assuming that the internal molar concentration C_B is constant inside the whole internal volume V_B and also the external concentration C_O is constant inside the external volume, then the global flow J through the exchange surface S_B can be calculated by integrating as follows:

$$J = \int_0^{S_B} j \, dS \quad (4)$$

$$J = S_B j \quad (5)$$

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

$$\frac{\partial M_B}{\partial t} = -\frac{\partial C_B V_B}{\partial t} = -\frac{S_B D}{z_B}(C_B - C_0) \quad (6)$$

If the external concentration C_0 is assumed to be equal to zero ($C_O=0$), and if the external volume is taken equal to infinity, which is the case if the bag is placed in a neutral environment (where the presence of H_2S may be considered negligible), then equation (6) can be rewritten as:

$$-\frac{\partial C_B V_B}{\partial t} = -\frac{S_B D}{z_B} C_B \quad (7)$$

According to this model, the concentration decay over time turns out to be a function of the surface area (S_B), the volume of the sampled gas V_B, the film thickness (z_B), 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:

$$C_B = C \text{ for } t = t^* \quad (8)$$

$$C_B = C_{in} \text{ for } t = 0 \quad (9)$$

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

$$\ln\left(\frac{C}{C_{in}}\right) = -\frac{S_B D}{V_B z_B} t \quad (10)$$

$$\frac{C}{C_{in}} = e^{-\frac{S_B D}{V_B z_B} t} \quad (11)$$

RESULTS AND DISCUSSION

Table 2 shows the H_2S concentration values measured at different time intervals t_i at storage condition of temperature of 23°C and humidity of 60%. Each concentration value reported in the table is the average of three replicate measurements.

The last column of table 2 reports the diffusion coefficient D_{ti} for each time interval t_i calculated according to the following equation:

$$D_{ti} = -\frac{V_B \, z_B}{S_B t_i} \ln\left(\frac{C_{ti}}{C_{in}}\right) \qquad (12)$$

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

The diffusion coefficient of H_2S through Nalophan^{TM} is finally calculated as the average of the different values of D_{ti} weighted on the corresponding storage time t_i:

$$\overline{D} = \frac{\sum_i D_{ti} \, t_i}{\sum_i t_i} \qquad (13)$$

The resulting value for $\overline{D}$ is equal to $1.49 \cdot 10^{-12}$ cm^2/s, with a standard deviation equal to $1.94 \cdot 10^{-15}$ cm^2/s.

Table 2. *Experimental data relevant to H2S diffusion over time in a NalophanTM bag stored at temperature of 23°C and humidity of 60%*

Time (h)	C_{ti} (ppb)	C_{ti}/C_0 (ppb)	% H_2S losses	D_{ti} (m^2/s)
3	476	0.95	5%	2.1E-12
6	450	0.90	10%	2.28E-12
9	431	0.86	14%	2.26E-12
17	419	0.84	16%	1.39E-12
20	414	0.83	17%	1.22E-12
22	396	0.79	21%	1.36E-12
24	395	0.79	21%	1.27E-12
30	350	0.70	30%	1.53E-12

Moreover, the percent H_2S loss through the bag over time can be expressed as:

$$H_2S_{loss\%} = \left(1 - \frac{C_{ti}}{C_{in}}\right) * 100 = \left(1 - e^{-\frac{S_B \overline{D}}{V_B z_B}t}\right) * 100 \qquad (14)$$

The loss percentage of H_2S (%) after 30 h turns out to be equal to about 30%.

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 H_2S losses through polymeric films (Tedlar and Flex Foil), reports losses of about 20% after 36 hours.

Table 3 shows the H_2S concentration values measured at different time intervals t_i for storage condition of temperature of 23°C and humidity of 20%. Each concentration value reported in the table is the average of three replicate measurements.

The last column of table 3 reports the diffusion coefficient D_{ti} for each time interval t_i calculated according to the equation 12.

The diffusion coefficient of hydrogen sulphide through Nalophan^{TM} 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 13.

The resulting value for $\bar{D}$ is equal to 3.22 10^{-12} cm^2/s, with a standard deviation equal to 1.22 10^{-15} cm^2/s.

Table 3. *Experimental data relevant to H$_2$S diffusion over time in a Nalophan^{TM} bag stored at temperature of 23°C and humidity of 20%*

Time (h)	C_{ti} (ppb)	C_{ti}/C_0 (ppb)	% H$_2$S losses	D_{ti} (m^2/s)
3	461	0.92	8%	3.49E-12
6	424	0.85	15%	3.57E-12
24	293	0.59	41%	2.88E-12
30	227	0.45	55%	3.40E-12

The data reported above shown an acceleration of the diffusion phenomena decreasing the relative humidity storage condition.
The loss percentage of H$_2$S (%) after 30 h turns out to be equal to about 55%.
Table 4 shows the H$_2$S concentration values measured at different time intervals t_i for storage condition of temperature of 75°C and humidity respectively of 20% and 60%.
The fifth and last column of table 4 reports the diffusion coefficient D_{ti} for each time interval t_i calculated according to the equation 12.

Table 4. *Experimental data relevant to H$_2$S diffusion over time in a Nalophan^{TM} bag with inside an empty bag stored at temperature of 75°C and humidity of 60%*

	T 75°C RH%20				T 75°C RH%60			
Time [h]	C_{ti} [ppb]	C_{ti}/C_0 [ppb]	% H$_2$S losses	D_{ti} [m^2/s]	C_{ti} [ppb]	C_{ti}/C_0 [ppb]	% H$_2$S losses	D_{ti} [m^2/s]
3	410	0.82	18%	8.53E-12	417	0.83	17%	7.79E-12
3	410	0.82	18%	8.53E-12	440	0.88	12%	5.47E-12
3	431	0.86	14%	6.38E-12	430	0.86	14%	6.45E-12
24	353	0.71	29%	1.88E-12	358	0.72	28%	1.8E-12
24	368	0.74	26%	1.66E-12	334	0.67	33%	2.16E-12
24	347	0.69	31%	1.97E-12	334	0.67	33%	2.16E-12
30	341	0.68	32%	1.64E-12	332	0.66	34%	1.76E-12
30	354	0.71	29%	1.49E-12	329	0.66	34%	1.8E-12
30	335	0.67	33%	1.72E-12	326	0.65	35%	1.85E-12

The diffusion coefficient of hydrogen sulphide through Nalophan^{TM} 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 13.
The resulting value for $\bar{D}$ at storage time of 3 hours is equal to 7.81 10^{-12} cm^2/s, with a standard deviation equal to 9.73 10^{-15} cm^2/s for relative humidity of 20%. While, the $\bar{D}$ value is equal to 6.57 10^{-12} cm^2/s, with a standard deviation equal to 9.18 10^{-15} cm^2/s for relative humidity of 60%. Also in this case the data reported above shown a light acceleration of the diffusion phenomena decreasing the relative humidity storage condition.
Comparing the data obtained storing the bag for 3 hours at different temperature respectively at 23°C and 75°C, it is possible to observe an increase of the losses of H$_2$S:
- At temperature of 23°C the loss percentage average of H$_2$S (%) after 3 h turns out to be about 8% for relative humidity of 20% and about 5% for relative humidity of 60%.

- At temperature of 75°C the loss percentage average of H_2S (%) after 3 h turns out to be about 17% for relative humidity of 20% and about 14% for relative humidity of 60%.

The early loss percentage of H_2S at high temperature (75°C) is not negligible especially considering some sampling condition (i.e. emission from stack). This behavior could be attributed to the glass transition temperature of the Nalophan^{TM} (Tg is 67 °C for amorphous PET (Demirel et al., 2011)).

The resulting value for $\bar{D}$ at storage time 24-30 hours is equal to 1.71 10^{-12} cm^2/s, with a standard deviation equal to 1.95 10^{-14} cm^2/s for relative humidity of 20%, instead the $\bar{D}$ value is equal to 1.91 10^{-12} cm^2/s, with a standard deviation equal to 1.49 10^{-14} cm^2/s for relative humidity of 60%. Both the value are comparable to the $\bar{D}$ value obtained at temperature of 23°C and relative humidity of 60% (i.e. 1.49 10^{-12} cm^2/s). This result is due to the amount of water present across the material (i.e. humidity driving force) in the tested condition. An increase of water amount in the external gas of the Nalophan^{TM} film lead to a decrease of diffusion phenomena.

It is important to underline that D coefficient is influenced by the water amount differences across the material (i.e. Nalophan^{TM} film). A relative humidity of 20% or 60% correspond to a certain amount of water depending on the temperature (i.e. 23°C, 75°C). At the same value of relative humidity as temperature increases the amount of water in the gas increases as well (i.e. absolute humidity with RH% 60 at 23°C is much lower than absolute humidity with RH% 60 at 75°C (cfr. Table 1 column partial vapor pressure)).

The loss percentage of H_2S (%) after 30 h turns out to be equal to about 33% and 35% respectively for relative humidity of 20% and 60%.

In order to evaluate the contribution of the accumulation term of H2S in the NalophanTM 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 behavior observed in the new tests is due to the H2S amount absorbed on the inner film.

Table 5 shows the H_2S 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 5 reports the diffusion coefficient D_{ti} for each time interval t_i calculated according to the equation 12. The diffusion coefficient of hydrogen sulphide through Nalophan^{TM} is calculated as reported in equation 13.

Table 5. *Experimental data relevant to H_2S diffusion over time in a Nalophan^{TM} bag with inside an empty bag stored at temperature of 23°C and humidity of 60%*

Time (h)	C_{ti} (ppb)	C_{ti}/C_0 (ppb)	% H_2S losses	D_{ti} (m^2/s)
3	452	0.90	10%	4.35E-12
24	181	0.36	64%	5.48E-12
30	142	0.28	72%	5.43E-12

The resulting value for $\bar{D}$ is equal to 5.39 10^{-12} cm^2/s, with a standard deviation equal to 2.30 10^{-15} cm^2/s.

The diffusion coefficient presents the same order of magnitude obtained for the bag with a volume of 6 liters and surface of 2580 cm^2 without polymeric film inside. However, the contribution of the absorption on the film is not entirely negligible.

CONCLUSIONS

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

The experimental determinations allowed the calculation of the diffusion coefficient of H_2S through Nalophan^{TM} according to the Fick's law, which turned out to be equal to $1.49 \ 10^{-12}$ cm^2/s at a temperature of 23°C and a relative humidity of 60%.

Instead, the diffusion coefficient of H_2S through Nalophan^{TM} according to the Fick's law, which turned out to be equal to $3.22 \ 10^{-12}$ cm^2/s at a temperature of 23°C and a relative humidity of 20%. These results shown an acceleration of the diffusion phenomena decreasing the relative humidity storage condition. The H_2S losses from the Nalophan^{TM} 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 30%; 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 55%. 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. At a temperature of 75°C, the diffusion coefficient of H_2S through Nalophan^{TM} according to the Fick's law at storage time 24-30 hours is equal to $1.71 \ 10^{-12}$ cm^2/s and equal to $1.91 \ 10^{-12}$ cm^2/s respectively at relative humidity of 20% and 60%.

Both the value are comparable to the D value obtained at temperature of 23°C and relative humidity of 60% ($1.49 \ 10^{-12}$ cm^2/s). It is important to underline that D coefficient is influenced by the water amount differences across the material (i.e. Nalophan^{TM} film). A relative humidity of 20% or 60% correspond to a certain amount of water depending on the temperature (i.e. 23°C, 75°C). At the same value of relative humidity as temperature increases the amount of water in the gas increases as well. Moreover, the absorption role was evaluated. The results shown that, under the test condition evaluated, the absorption phenomenon is not negligible. Further test have to be performed in order to investigate the absorption role better.

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