

Background odour from sampling bags. Influence in the analysis of the odour concentration

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The sampling of odours and volatile organic compounds by means of sample bags for later analysis is a simple and economic method which can, however, generate problems of lack of representativity in samples with odour concentrations between 30 and 100 OU_E/m^3 due to the compounds transferred from the bags themselves. This study, which is based on the material known as Nalophan[®], has evaluated the odour concentration that these transferred compounds give to odour-free air, as well as the manner in which they can influence the odour concentration of odorous samples. Furthermore, it describes a method developed to eliminate the background odour that the bags might generate before their being used. By means of this method, the background odour from a Nalophan[®] bag has been reduced down to 5 OU_E/m^3 after 30 hours of odour-free air storage.

1. Introduction

The use of sampling bags, for their simplicity and low cost (Camel and Caude, 1995; McClenny et al. 1999), has been, and is, a very common practice for sample taking of gaseous contaminants in the field, for both odours and volatile organic compounds (VOCs) (Sueng-Woon et al., 1997; Davoli et al., 2003; Dincer et al., 2006; Kleeberg et al., 2005). In the specific case of measuring odour concentrations by Dynamic Olfactometry, sample bags should comply with the following requirements: be odour free, be inert with respect to the compounds under study, be impermeable (to avoid loss by diffusion), and have a smooth surface. The procedures for the measurement of odour concentration by dynamic olfactometry are to be found in the European Standard EN-13725, in which the following materials to make sampling bags are recommended: FEP (a copolymer of tetrafluoroethylene hexafluoropropylene), PVP (Polyvinyl fluoride, Tedlar[®]) and PET (polyethylene terephthalate, Nalophan[®]). Of all these materials, the most widely used (for their low cost and useful chemical properties), are Tedlar[®] and Nalophan[®]. The latter being the most economical, and the best for storage of volatile chlorinated compounds (Jae-Hwan et al., 2002; Görgényi et al., 2000). However, despite their interesting chemical properties, these materials display an important drawback when it comes to measuring odours, as a consequence of the release of certain volatile organic compounds from the polymer itself. These compounds produce a certain odour threshold, by generating a residual, or background odour contamination (Begui and Guillot, 2008; Trabue et al., 2006). Taking into account the fact that, depending the conditions, this background odour could have a value from 5 up to to as high as 100 OU_E/m^3 , this effect could be really important in environmental

samples of low odour concentration. It is evident that this background odour will directly influence the quantification limits of this technique. However, it is worth asking if this background odour might also either augment, or mask the odour in certain environmental samples. In which case the problem is further aggravated.

This present study has therefore been designed to evaluate the variation of the background odour of the material Nalophan® under different conditions of storage typically found in laboratories. At the same time, a simple protocol has been optimised for the treatment of Nalophan® by means of a heat treatment which allows a considerable reduction of the background odour. And finally, a comparison is made of the low concentration odour samples stored in conventional bags, against samples stored in bags which have been subjected to the newly developed treatment.

2. Experimental

2.1 Preparation of Nalophan bags.

The Nalophan® bags were prepared from a commercially available roll of 1000 metres length, 28 cm width and 20 µm film thickness (Kalle GmbH, Germany). The bags were made from equal pieces (28 x 83 cm) taken from the roll. The bags were sealed using 10 cm plastic pull tight seals. The treatment at room temperature was done by placing the pieces of Nalophan® in a clean room (according to the specifications of the regulation EN-13725) and subjecting them to a forced air flow with extraction for a minimum of 24 hours and a maximum of 54 hours. The heat treatment of the Nalophan® (Fig. 1) was done using an oven type DIGITHEAT of 80 litres capacity (J.P. Selecta, Spain). Three temperatures were tested, 40, 50 and 60°C using an purified air flow of 1 l/min during 24 hours. Temperatures higher than 60°C were not considered as there becomes apparent a slight deterioration of the polymer at around 70°C, producing a contraction of the material with the formation of wrinkles in the film. The pieces of Nalophan®, once ventilated, were used to make bags with a surface area/volume ratio of 0.3.

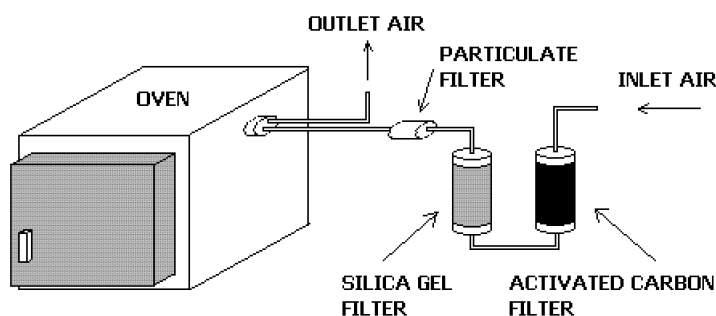


Figure 1: Scheme of the system for heating treatment

2.2 Evaluation of the changes in the background odour with respect to storage time.

The residual volatile organic compounds present in the commercial Nalophan® product are progressively freed by vaporization. Bearing in mind the fact that the commercially available product comes in 1000 metre rolls, it is reasonable to suppose that the more external layers of the roll, which are exposed to the environment, will liberate these VOCs at a much faster rate than the internal layers of the same roll. Furthermore, the concentration of VOCs in the interior of the bags will increase over time, from the moment of manufacture in the laboratory, and especially from the moment of filling with the sample (as the formation of a concentration gradient will enhance the transfer of the VOCs from the polymer to the air inside) up to the time of its olfactometric analysis. The object of this study is to observe the evolution of the odour concentration with respect to the storage time before the olfactometric analysis.

To evaluate the effect on the internal and external layers from a roll, 4 series of bags were prepared (S1 to S4), two of which (S1 and S2) were made from the deepest layers of a commercially available roll of Nalophan®, while the other two (S3 and S4) came from the external part. For each series, 5 replicas were prepared and subject to room temperature ventilation (as per section 2.1). Each of the replicas were filled with synthetic air (99.9995% purity, Liquid Air) and were stored for various lengths of time (0, 1.5, 7, 23 and 30 hours) before being analysed by dynamic olfactometry. Each of the samples were analysed by a panel which consisted of 4 panelists in accordance with EN-13725. The olfactometric analysis was done using an olfactometer model TO8 (ECOMA GmbH, Alemania) programming the following parameters (Table 1).

Table 1: Olfatometric analysis parameters

Type of analysis	Measurement of odour threshold yes/no
Rounds	3
Breathing time (ms)	2200
Blank (%)	20
Flushing time between rounds (s)	5
Flushing time after sample (s)	20
Room temperature during analysis	<25°C
Temperature oscillations during analysis	< ±3°C
Dilution factor	2
Factor A (accuracy)	0.195
Repeatability	0.2882
K factor (95% confidence)	2
Calculation method	Dravnieks ¹

¹ In order to make clear the trends observed on the olfactometric analysis at low concentrations, the odour concentration values have been calculated considering as 1 OU_E/m³ those results

2.3 Evaluation of the reduction of background odour with respect to temperature.

To evaluate the effect of the heat treatment, 3 series of samples (T1 to T3) were prepared from pieces of Nalophan® taken from the interior of a commercially available roll, and were subjected to a 24 hour heat treatment at 40, 50 and 60°C respectively (Fig.1). Once the treatment was completed, the bags were made up and filled with synthetic air (Air Liquide, France) and stored during different lengths of time (30, 23, 7, 1.5 and 0 hours) before their olfactometric analysis.

2.4 Effect of background odour of the Nalophan® bags on the odour concentration of the samples.

Six sample types were made up in the laboratory with odour concentrations between 30-100 OU_E/m^3 . The first four samples were made from certified gas samples: one sample of n-butanol, two samples of H_2S at two different concentration levels, and a fourth sample with a mixture of amines (made up from propyl amine and butyl amine). The fifth and sixth samples were prepared by bubbling synthetic air at a rate of 20 mL/min, through 50 mL of untreated waste water in an impinger. Each one of these samples was used to fill 6 bags made from Nalophan®. Three of these had been subjected to room temperature pretreatment, and the other three had been subjected to thermal treatment at 60°C. The bags were then stored for 7 hours before their dynamic olfactometric analysis.

3. Results and discussion

3.1 Evaluation of the changes in background odour concentration with respect to storage time.

As can be seen in Fig. 2, the series of bags which were made from the interior of the commercially available roll showed, for each and every time interval tested, an odour concentration notably higher than those shown by the series of bags made from the exterior of the roll. It can also be seen that the odour concentration increases with the storage time, with the maximums reached at 30 hours (being the maximum permitted storage time according to EN-13725) of 15 to 25 OU_E/m^3 for the bags made from the exterior of the roll, and 136-456 OU_E/m^3 for those made from the deepest part of the roll. So, according to these results, we can deduce that the background odour detected must come from certain compounds (perhaps added during the manufacturing process of the Nalophan® film, such as plasticizers, solvents, etc.) that are released over a period of time. This liberation of volatile substances is more noticeable as much polymeric film is exposed. For this reason, the Nalophan® situated in the deepest part of the roll, as it is not so much exposed, shows a greater amount of volatile compounds, and as a result, a higher odour concentration. The commercially available rolls of 1000 metres have a roll thickness of about 20 cm. The samples from the interior correspond to the innermost turns on the roll (which made it necessary to completely unwind the roll). This experiment went on to confirm this fact, which meant that the work was done under very awkward conditions. In the conditions normally encountered in normally laboratory work, it would be unusual to find such extreme situations, where the

obtained as 0 OU_E/m^3 for each panellist. In these cases has not been considered the geometric mean of the last two positive values.

background levels after 30 hours would be greater than $100 \text{ OU}_E/\text{m}^3$. However, background levels in the region of 15 to $25 \text{ OU}_E/\text{m}^3$ would be systematically found in samples stored for 30 hours.

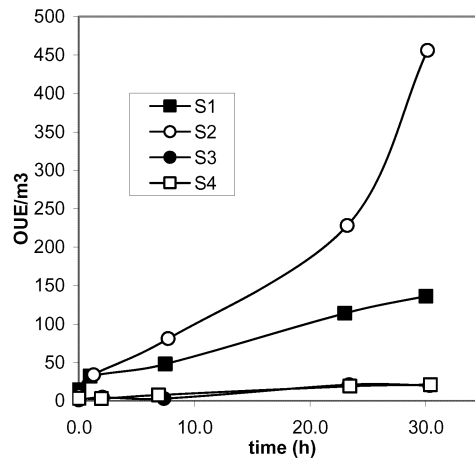


Figure 2: Changes in background odour concentration with respect to storage time.

3.2 Evaluation of the elimination of background odour with heated ventilation.

The results obtained of the concentration of odour by dynamic olfactometry at different temperatures and lengths of storage time (Fig 3), demonstrate a similar trend as that observed in the experiments using room temperature ventilation. Additionally, it is shown that, as the temperature of treatment increases, the background odour concentration decreases. Maximum values obtained with treatment at 60°C , and 30 hours of storage were all below $5 \text{ OU}_E/\text{m}^3$. This fact can be explained by the increased kinetics of release of the volatile compounds responsible for the background odour, with the increase in the treatment temperature. Values reached for background odour concentration using the heat treatment (T3 series) were below the values obtained from prolonged exposure (weeks) of Nalophan® at room temperature (S4 series). The treatment at a temperature of 60°C gives a notable lowering of the odour threshold for Nalophan® bags (Fig. 4), without affecting their integrity, which allows for a considerable improvement in the detection limits using dynamic olfactometry.

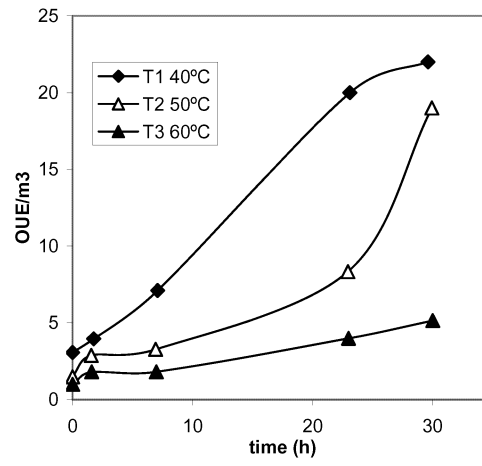


Figure 3: Changes in the concentration of background odour with respect to temperature.

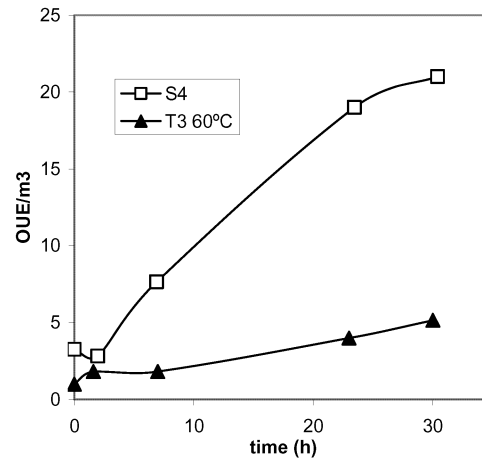


Figure 4: Elimination of background odour by thermal treatment compared with room temperature ventilation.

Table 2: Concentration of odours (OU_E/m^3) in analysed samples taken from treated and untreated Nalophan bags.

	Deodorised bags (treated at 60°C)	Not deodorised bags (treated at room temperature)
Sample 1 (buthanol)	45	76
Sample 2 (H_2S)	60	38
Sample 3 (H_2S)	483	176
Sample 4 (amines)	32	31
Sample 5 (waste water)	28	25
Sample 6 (waste water)	406	203

3.3 Influence of background odour in Nalophan® bags on the evaluation of odour concentrations in diluted samples.

This part of the study evaluated the effect on the calculation of odour concentration in a series of laboratory prepared samples (with odour concentrations ranging mainly between 30-100 OU_E/m^3), of the background odour from Nalophan® bags. Samples of Nalophan® were taken from the interior of the roll, and the odour samples were stored for 7 hours. Under these conditions, the background odour of the bags which had not been treated thermically was in the range 50-80 OU_E/m^3 (Fig. 2). For each odour type, six bags were prepared (three subjected to room temperature ventilation, and three subjected to 60°C heat treatment ventilation. See section 2.1) and each was filled with the same odour sample mixture. After 7 hours, the triple analysis was performed, giving the results which can be seen in Table 2. As can be observed on the Table, almost in all cases, there is a notable difference between the results given by treated bags and non-treated bags. In all samples it can be seen (in more or less extent) a masking phenomena caused by the background odour produced by non-trated bags, since in any case, the odour contracion of non-treated bags is not the sum of the odour concentration of the treated bags and the background odour concentration. In some cases such as samples 2, 3 and 6, seem to be an important masking effect, in which the odour concentrations of the non-treated bags are half the treated ones, even at concentrations higher than 100 OU_E/m^3 . Taking into account these last results, the background odour from sampling bag has an important effect over the odour concentration of a wide range of samples.

4. Conclusions

The Nalophan® used for taking odour samples can transfer to the sample contained in the bag, a variable quantity of volatile compounds which are responsible for a background odour. The concentration of the odour from the Nalophan® depends on the position that it was taken from within the commercially available roll that is normally used for the fabrication of the sample bags. The concentration being greater the further within the roll that the pieces of Nalophan® come from (less exposure of the film). It

has been demonstrated, however, that the background odour of the bags can be reduced (independently of which part of the roll the pieces are from) using a thermal treatment of 60°C. This allows not only the improvement of the detection limit of this measurement technique, but also the taking of samples using bags with the same (and minimum) background odour concentration (or contamination.). Furthermore, it has been possible to check what is the influence of the background contamination from the Nalophan® on the odour concentration of real samples, demonstrating that important masking effects can be presented, even in cases in which the odour concentration is higher than 100 OU_E/m³. Related to this last issue, although very interesting results have been obtained, it is necessary to continue studying the influence of background odour on real samples.

5. References

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