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Comparison of Odorant Losses at the ppb-Level from Sampling Bags of Nalophan™ and Tedlar™ and from Adsorption Tubes.

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The issue of volatiles and odorant losses has already been addressed by different authors. The motivation came from the fields of breath analysis (Mochalski et al. 2013; Mochalski et al. 2009), atmospheric chemistry (Sulyok et al. 2001; Kim et al. 2012) and odour measurement (van Harreveld 2003; Hansen et al. 2011; Parker et al. 2010; Trabue et al. 2006). The aim in these fields is to collect samples for subsequent laboratory measurements. Frequently manufacturers of sample bags claim excellent stability of the stored substances. A closer look on the measurement procedure often shows an unrealistic background: The measurements were made with high concentrations of substances at an unrealistic level. The losses are different at a trace level, e.g. at the ppb-level near the odour thresholds of odorants, because the contribution of wall adsorption in the polymeric bags is comparatively greater.

The published contributions show some general trends but often suffer from deficits of the measurement procedure. The initial losses due to adsorption at the walls of the bags contribute to a great extent to the losses. Therefore a measurement starting with the freshly filled bags as the reference level for losses does not reflect the real situation of bag sampling. Other obvious problems are the stability of the sample gas generation at trace level concentrations.

The measurements for this study were made with a high sensitive trace gas measurement system. It uses online thermal desorption and a gas chromatography - time-of-flight mass spectrometry system. A calibration gas generator on basis of continuous evaporation and dilution has been used for the preparation of the sample gases in the ppb-range. Odorants from different chemical classes and of different molecular weight have been included in the study. Special care has been taken to avoid any losses due to leakage or cold spots in the measurement chain. Extensive measurements with different bag materials have been made, including the most common bags from Nalophan and from Tedlar. For comparison the same measurements have been made with adsorption tubes as a sampling method.

1. Introduction

The use of sampling bags is part of the measurement procedure of olfactometry. Although this step can corrupt the results due to losses only little is known of the processes which take part during the filling and the storage of the bags. Recently a publications has dealt with background odour of the bags in detail (Laor Y. et al. 2010) indicating that some odorants and other chemicals outgas from the bags.

The ideal material of a sampling bag should have the following properties:

1. Preserve the concentrations of all chemicals in the sample atmosphere from the time of sampling until the time of the measurement
2. Does not add any chemical to the sample gas
3. Easy preparation of bags at low expenses

In the European standard EN 13725 (EN 13725, 2003) three bag materials are referred to as qualified for olfactometric sample bags: FEP, PVF (Tedlar™) and PET (Nalophan™). For PVF a footnote states that background contaminations have been observed.

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The storage time in the EN 13725:2003 is limited to 30 hours. In the new German regulation VDI 3880 (VDI 3880, 2011) this interval is reduced to 6 hours. If a longer interval is necessary evidence has to be provided that the samples remain stable. Three bags have to be measured immediately and three other bags after the intended storage time. If the geometric means of the two measurements are within a factor of 1.5 the samples are accepted as stable.

2. Materials and Methods

2.1 Bag Materials and Adsorption Tubes

For the measurements the classical material polyethylene terephthalate (PET) (Nalophan™) and two other materials from Kalle Gmbh, Wiesbaden, Germany have been used, namely Nalobar™ and NaloSafe P™. Nalobar™ is a multi-layer composition of polyamide (PA) and polyethylene (PE) with PA on the inner surface, NaloSafe P™ is a multi-layer composition of PA and PE with a coating of ethylene vinyl alcohol (EVOH) on the inner surface as an oxygen barrier. The PVF (Tedlar™) bags (3 L bags of SKC Inc. with polypropylene fittings) were purchased from Analyt-MTC, Müllheim, Germany. For comparison also the background contamination of metalized foil balloons (polyethylene with vaporized aluminum layer) from M.Oertel Internethandel, Burscheidt, Germany has been measured. The adsorption tubes (Markes International GmbH, Neu-Isenburg, Germany) have been filled with Tenax TA™ (200 mg in stainless steel tubes).

2.2 Sample Gas Generation

For the preparation of the sample gases a trace gas generator on the principle of continuous evaporation was applied (HovaCal 3435SP-VOC, IAS GmbH, Frankfurt, Germany). The generator (Figure 1) has two evaporators for the calibration chemicals and for water (humidity). The odorants in a stock solution are pumped with the double stroke syringe pump into the main evaporator. A mass flow controller delivers the dilution air (catalytically purified air). A three stage dilution cascade with pressure regulators delivers the concentrations in three ranges between the ppm- and the ppt-level. The system is built from stainless steel components and heated to reduce adsorption losses. The continuous operation ensures a stable concentration also at the very low concentration ranges. The sample gases can be humidified by the second and third evaporator. Depending on the desired concentration range the flow of water from the second syringe pump is delivered to the appropriate evaporator and thus the sample gas flow.

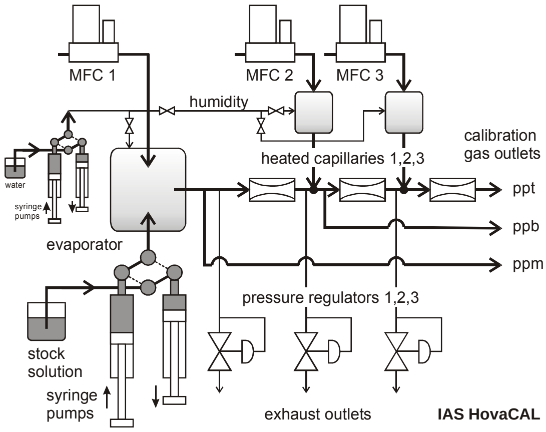


Figure 1: Trace gas generator HovaCal with three dilution stages and humidifier unit.

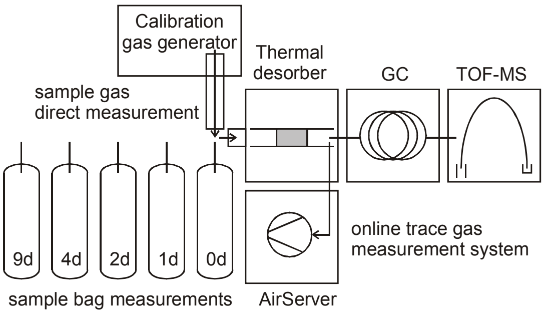


Figure 2: Measurement system for the measurement of sampling bags

2.3 Measurement System

Basis of the measurements is a trace gas measurement chain (Figure 2) consisting of a thermal desorber (Unity 2, Markes Int., Llantrisant, UK), a gas chromatograph (7890A, Agilent, Santa Clara, USA) and a time-of-flight mass spectrometer (BenchTOF, Markes/Almsco, Llantrisant, UK). For the sampling from the gas generator and the sampling bags an online sampling system (AirServer, Markes Int., Llantrisant, UK) has been modified to reduce losses of odorants.

2.4 Odorant mixtures

The odorants have been chosen from different chemical classes to cover different possible chemical interactions with the polymers of the sample bags. The odorants have been generated in three different stock solutions (Table 1) because chemical reactions between certain odorants have been observed. The solvent of the solutions has been methanol. The mixtures have been humidified to a level of 50% relative humidity at 20°C (approximately 15,000 ppm H_2O).

Table 1: Odorants used in the study with their molar masses, concentrations and odour thresholds.

No.	Chemical class	Name	Molar mass [g/mol]	Concentration [ppb]	Odour threshold [ppb]
Odorant mixture 1					
1	Aldehyde	Hexanal	100.16	44.76	0.28
2	Aldehyde	Furfural	96.08	58.56	k.A.
3	Aldehyde	α-Hexyl cinnamaldehyde, α-HCA	216.32	23.68	k.A.
4	Alcohol	Ethanol	46.07	0.00	520
5	Alcohol	n-Butanol	74.12	51.84	38
6	Alcohol	n-Hexanol	102.17	37.61	6
7	Alcohol	Phenol	94.11	49.58	5.6
8	Alcohol	p-Cresole	108.13	164.56	0.054
9	Alcohol/Monoterpene	Menthol	156.27	24.59	k.A.
10	Nitrogen	Indole	117.15	53.10	0.3
11	Nitrogen	Skatole	131.17	56.84	0.0056
12	Aromate	Toluene	92.1381	117.16	330
13	Aromate	Ethylbenzene	106.17	39.21	170
14	Aromate	1,2,3,4-Tetrahydronaphthalene, THN	132.2	32.18	9.3
15	Monoterpene	α-Pinene	136.23	30.22	18
16	Monoterpene	Limonene	136.24	32.90	38
17	Cyclic terpenes	α-Ionone	192.3	49.95	k.A.
18	Ester	Ethyl acetate	88.11	36.34	870
19	Ester	n-Hexyl acetate	144.21	30.77	1.8
20	Ketone	Acetone	58.08	98.45	42000
21	Ketone	Ethyl Methyl Keton, EMK	72.11	44.40	440
22	Ketone	Methyl isobutyl ketone, MIK	100.16	36.08	500
23	Ketone	Methyl n-amyl ketone, 2-Heptanone	114.18	38.46	6.8
24	Chlor	Dichloromethane	84.93	94.25	160000
25	Chlor	Chloroform	119.38	49.81	3800
26	Chlor	1,2-Dichloroethane	98.96	54.54	k.A.
Odorant mixture 2					
1	Ester	Ethyl n-butyrate, EB	116.16	38.59	0.04
2	Ester	Ethyl acetate, EA	88.11	50.88	870
3	Ester	Butyl acetate, BA	116.16	38.59	16
4	Sulfur	Dimethyl sulfid	62.14	81.16	3
5	Sulfur	Dimethyl disulfid	94.2	53.54	2.2
6	Sulfur	Carbon disulfid	76.14	66.24	210
Odorant mixture 3					
1	Amine	Butylamine, BAm	73.14	612.91	0.061
2	Amine	Propylamine, PAm	59.11	758.38	0.17

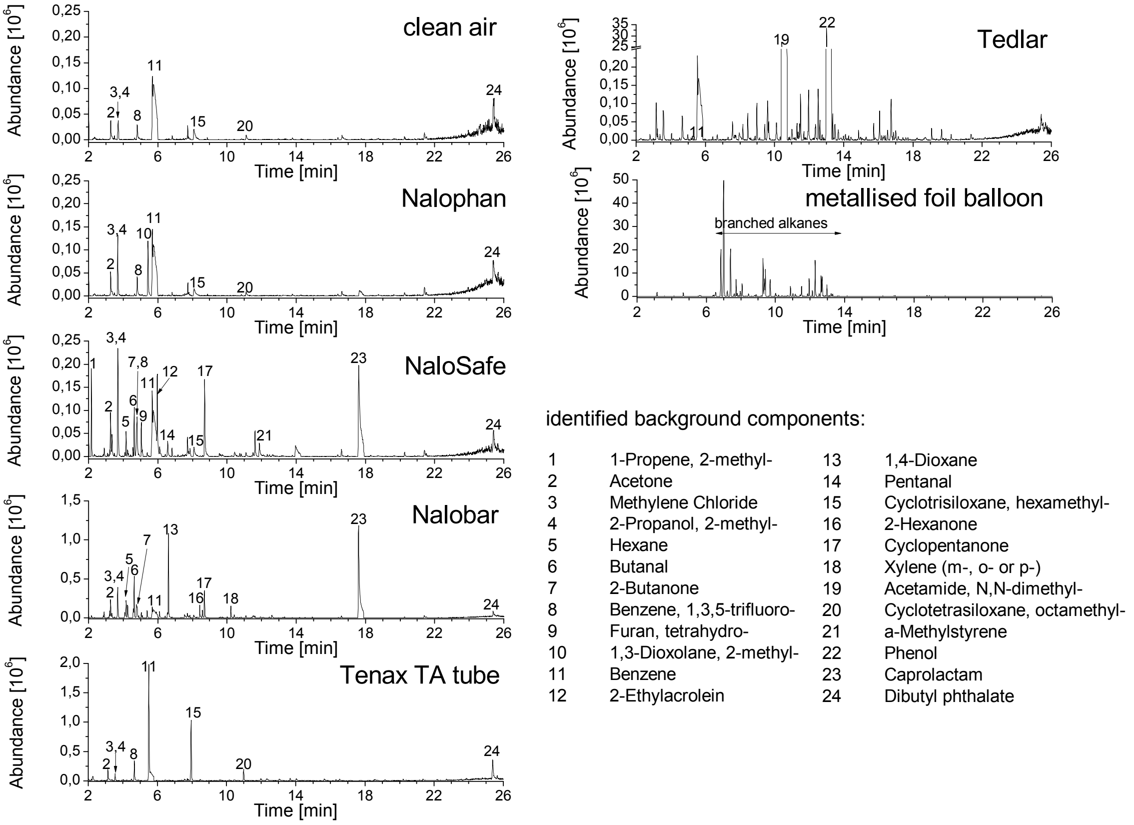
2.5 Measurement procedure

The measurements started with a measurement of the sample gas mixture as delivered by the calibration gas generator in the concentrations according to Table 1. The peak areas of the odorants from at least three sample bags are the basis for the calculation of losses. Immediately after these reference measurements the bags have been filled (with a priming step). The first series of bags has now been measured with approximately 15 min delay to the time of the filling. The other bags have been measured after storage times of 1, 2, 4 and 9 days.

3. Results

3.1 Background contamination

The measured background contaminations are shown in Figure 3. The chromatogram of ‘clean air’ is shown as reference. The substance traces are on a very low level and can be explained by artifacts from the Tenax™-filled cold trap of the thermal desorber. The chromatogram of Nalophan is nearly identical. Only the trace of dioxolane is a contaminant of the PET material. The polyamide and polyethylene-based bags of Nalobar and NaloSafe show more contamination, NaloSafe with its internal oxygen barrier is less contaminated than Nalobar. The chromatogram of the Tedlar bags is scaled by more than a factor of 100. Two well-known contaminants, acetamid and phenol, dominate the chromatogram. Even worse is the situation with the foil balloons which have been used by atmospheric chemists. Here branched alkanes are present in high concentrations.



identified background components:

1	1-Propene, 2-methyl-	13	1,4-Dioxane
2	Acetone	14	Pentanal
3	Methylene Chloride	15	Cyclotrisiloxane, hexamethyl-
4	2-Propanol, 2-methyl-	16	2-Hexanone
5	Hexane	17	Cyclopentanone
6	Butanal	18	Xylene (m-, o- or p-)
7	2-Butanone	19	Acetamide, N,N-dimethyl-
8	Benzene, 1,3,5-trifluoro-	20	Cyclotetrasiloxane, octamethyl-
9	Furan, tetrahydro-	21	a-Methylstyrene
10	1,3-Dioxolane, 2-methyl-	22	Phenol
11	Benzene	23	Caprolactam
12	2-Ethylacrolein	24	Dibutyl phthalate

Figure 3: Comparison of background contaminations.

3.2 Odorant losses

Figure 4 shows a selection of the results. The losses are referenced to the concentration of the sample gas, not the concentration of the freshly filled bags. These initial losses immediately after the filling are shown on the 0d-bars. The measurement uncertainty of trace gas measurements is high and indicated by the uncertainty intervals. If results are higher than 100% this may indicate fluctuations of the overall sensitivity of the measurement chain. The recovery data of the chlorine compounds and the ester are not shown. They generally show a small amount of losses even after 9 days of storage for both bags and the Tenax adsorption tubes respectively.

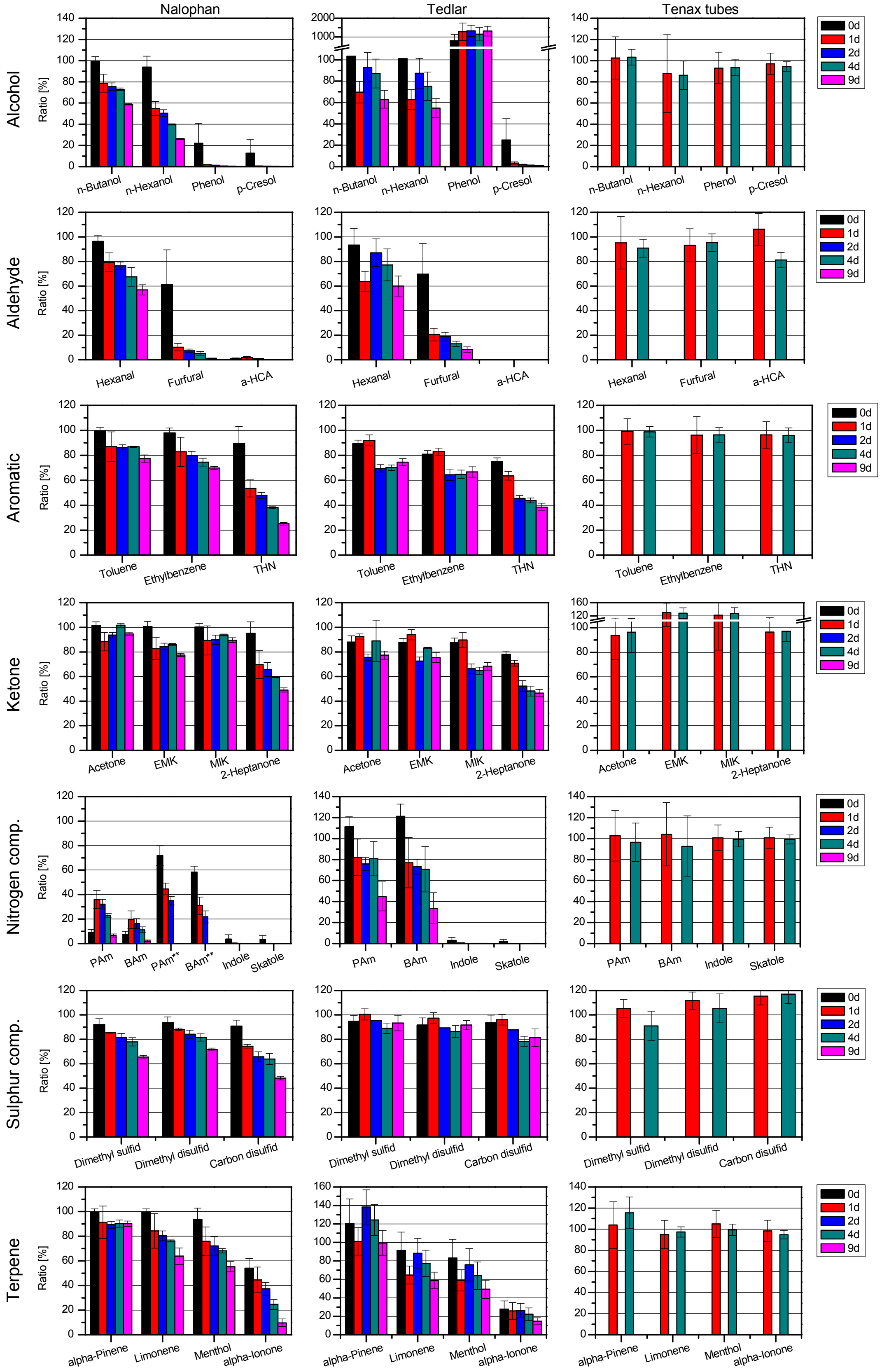


Figure 4: Odorant losses from Nalophan and Tedlar bags compared to adsorption tubes filled with Tenax. The recovery (i.e. losses) of each odorant is presented for the five time intervals.

4. Conclusions

The measurement of odorant losses from Nalophan or Tedlar sampling bags shows no distinct differences. The two materials show nearly the same pattern of the losses. P-cresole, indole and skatole get lost immediately during the filling of the bags. This can be explained by pronounced wall adsorption of these compounds. The continuous trend of the losses observed by the majority of the odorants is caused by the permeation though the polymers of the bags (Beghi 2008). The rate of the losses depends on the solution in the polymers and the subsequent diffusion driven by the concentration difference (Siracuse 2012).

A more detailed look at the data shows some minor differences between Nalophan and Tedlar bags. The losses of amines are smaller in Tedlar bags than in Nalophan bags. The humidity level seem to play a role in the case of Nalophan. Dry sample gas with propyl amine and butyl amine exhibits a much smaller initial loss (see the bar graph with the double star indication, PAM** and Bam**). The loss level after one day of storage is of the same amount as with the humid sample gas. Due to the fast equilibration of the humidity content (95% equilibration within 2-3 hours, data not shown) the mechanism of the loss by permeation is not affected by the initial humidity content. It seems that a high water level contributes to a higher amount of wall adsorption in the case of the two amines.

The issue of background contamination is of great importance. The well-known background odour of Tedlar bags can be explained by the phenol contamination. Even multiple cleaning steps with purified air cannot eliminate this contamination completely. From an odour measurement perspective the material Tedlar therefore is not suitable for olfactometric measurements of low odour concentrations.

The bags from Nalophan are economically much more favorable than Tedlar bags, since they can easily be made from hoses cut into the appropriate length.

The measurements with the adsorption tubes show a lower level of losses than the polymer bags. Adsorption tubes may be a better basis of a sampling and olfactometric measurement method in future if the methodology of sample reconstitution and dilution can be adapted to these samplers.

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