

Managing Odour Sample Degradation through On-Site Olfactometry and Proper Sample Transportation and Storage

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Degradation is inherent part of odour sampling and olfactometry analysis. There are many techniques that can be deployed in order to minimize sample degradation, such as nitrogen-based pre-dilution and sealed transportation vessels. Despite the best efforts to keep the volatilization at bay - sample degradation has forced European and American standards to implement a thirty (30) hour expiration on all odour samples. German standard VDI3880, and possible the soon to be revised EN13725 standard, limit sample storage to 6 hours unless it can be shown that the sample degradation is within acceptable limit. On-site olfactometers such the Scentroid SM100, can be used, and are widely used in Canada, as part of the quality assurance program by measuring samples immediately after acquisition and immediately prior to analysis by the laboratory to ensure odour degradation is within these defined limits. However, observations have shown samples can degrade by an order of ten magnitudes in a span of less than 24 hours. This study provides data on sample degradation from a variety of sources over a span of 24 hours. Samples will be stored in Nalophan, Tedlar®, and the newly introduced PTFE bags. Data has shown that the much higher density of PTFE provides slower sample degradation than Tedlar® or Nalophan. This is especially true of samples with high humidity, Ammonia, or H₂S. To properly simulate shipping conditions a portion of the study focuses on samples that are subjected to lower pressure and temperature similar to those found in standard cargo planes. These samples are compared to those which have been stored at standard conditions (room temperature at 1 atmosphere). Further study has been made on degradation of sample with highly volatile compounds such as ozone.

1. Introduction

The process of odour impact assessment of a facility starts with air sampling. Samples must be taken from the correct sources, stored in appropriate containers, and transported to an olfactometric laboratory for analysis. Recent advancements in on-site olfactometry, such as the introduction of the Scentroid SM100, have in some instances eliminated the need for sample storage and transportation by allowing the olfactometer to be deployed at the emission source. This is referred to in the EN13725 standard as direct olfactometry (see section 3.1.15 and Section 7.2). On-site olfactometry has accentuated the issue of sample degradation during storage and transport. A unique capability of on-site olfactometry is to allow the users to conduct odour analysis before and after a sample has been stored and shipped to the laboratory. Measurements made at the time of sampling can now be compared with those made just before laboratory analysis to accurately quantify the total sample degradation. Laboratories following VDI3880 may even be required to perform this test to ensure sample degradation falls within the dictated limits if the sample storage exceeds 6 hours.

It has been concluded that sample degradation falls into four (4) categories:

- A- Sample loss due to permeability of the sample container
- B- Sample cross contamination due to close proximity of high concentration samples with lower ones.
- C- Sample contamination by chemicals released from sample containers (background odour).

D- Sample decomposition due to interaction with Oxygen or other reactive gases.

The first 3 categories of sample degradation are directly influenced by the choice of the container (i.e. sample bag) material. There has been numerous studies (Hansen et al., 2011; Mochalski et al., 2013; Harreveld, 2003; Coyne et al., 2011; Hsieh et al., 2003, Zarra et al., 2012, N. Akdeniz 2011) conducted on different bag materials to reduce or eliminate sample degradation. In Europe and parts of Asia, Nalophan is wide used due to its low cost and ease of use. Nalophan is a one-time use bag that is supplied in a tubular roll. The tube can be made into a bag easily with minimal tools. Virgin Nalophan has low chemical emission and therefore does not severely contaminate weaker samples. However it has been shown (Zarra et al. 2012) that Ammonia and H₂S among other chemicals easily escapes from Nalophan sample bags. The current European standard imposes a 30 h expiration period on all samples after which odour analysis cannot be performed. Studies have shown losses of 50-90 % of certain chemicals such as Phenols, Carboxylic Acids, and indoles in less than 24 h and 30 % loss of H₂S (Hansen et al. 2011). These chemicals are commonly found in waste water treatment plants, landfills, agricultural process, and composting plants. H₂S for example has an extremely strong odour and therefore even small losses can drastically affect the odour threshold of the sample.

In most of North America and some parts of Asia and South America, Tedlar® is the most commonly used material for sample bags. Tedlar® has a much better holding properties than Nalophan especially for sulfur compounds. In 24 h Tedlar® bags have losses of less than 5 % on sulfur compounds. However, Ammonia (40 % in 24 h and 60 % in 30 h), Phenol (50 % in 24 h) and certain other chemicals still escape from the Tedlar® sample bag (Coyne et al., 2011). Furthermore virgin Tedlar® has a strong odour and can severely contaminate a weaker sample (e.g. ambient samples and those from outlet of odour filters). The cost of Tedlar® sample bags also forces most labs to re-use the sample bags by attempting to purge them with heated air and nitrogen. The process is not always perfect and can result in further sample contamination. Lastly Tedlar® is offered only by DuPont® which decided to reduce and eventually stop production of this material.

Recently, Scentroid introduced PTFE sample bags to be used for odour sampling. PTFE sample bags have existed for a while but their cost was not comparable to Tedlar® and therefore not feasible. New processes have allowed Scentroid sample bags to be priced similarly to Tedlar® sample bags and therefore be a good alternative to Tedlar®. PTFE sample bags have a number of distinct and critical advantages to Tedlar® or Nalophan: i) PTFE sample bags have no background odour and thus eliminate the chances of sample contamination as shown in the first experiment of this paper, ii) The non-stick properties of PTFE allow the bags to be quickly and thoroughly cleaned and reused reducing chances of contamination as well as sample bag costs, and iii) the higher density of PTFE significantly reduces its permeability and therefore reduces sample degradation and cross contamination (Zarra et al. 2012).

This paper presents results of a comprehensive study of odour degradation rate in Nalophan, Tedlar®, and PTFE bags. The study considers real world conditions associated with sample storage and shipment. The effects of lower temperature and reduced pressure on sample degradation is presented. The issue of cross contamination between strong and weak odour samples stored separately in sample bags but in the same shipping container is carefully explored. The objective is to provide scientific data to support good sampling techniques and strategies to minimize odour degradation.

2. Materials and Methods

The three types of bags used in this experiment were Nalophan, Tedlar® (0.002 inches thick) and PTFE (0.002 inches thick). The Tedlar® and PTFE bags were manufactured by IDES Canada Inc. Tedlar® bags were purged with heated air using the Scentroid SP20 Heated Air Purger and flushed with Nitrogen to ensure minimal background odour. PTFE bags were nitrogen purged and vacuumed as per IDES standard procedure prior to use. All bags used have a volume of 10 L and equipped with PTFE valves. The Tedlar and PTFE bags have dimension of 12x19 inches and the Nalophan is made of 250 mm wide tube.

Samples used in these studies were collected from four processes: i) Waste Water Treatment plant, ii) a compost facility, iii) a refinery in a process where high benzene concentration could be detected in the indoor air, and iv) food processing plant where an ozone based mitigation technology was used. Process samples were taken in triplets for analysis based on each of the three experiments described below. Samples from the wastewater treatment plant were collected at the inlet and outlet of a biofilter using Scentroid SB10 vacuum chamber. Samples were taken from the ambient air of a transfer station of a compost facility also using a Scentroid SB10 vacuum chamber. Samples from the refinery were collected from ambient air using SB10 vacuum chamber. Samples from the food processing plant were collected at the chimney that exhausted air treated with ozone.

The experiments were designed to fully measure sample degradation and contamination on all possible scenarios.

2.1 Experiment 1 – Background odour from sample bag

In this experiment 4 sample bags were filled with nitrogen and analysed 2 hours later to determine the background odour given off by each material. The sample bags used were Nalophan, virgin Tedlar sample bag, preconditioned Tedlar, and PTFE sample bags. The Precondition Tedlar sample bag was subjected to 30 hours purging in an oven at 110 °C in accordance to the usual technique practiced in Canada for removing background odour in Tedlar sample bags. Samples were stored at a cleanroom facility at 21°C and not subjected to any UV emitting light source.

2.2 Experiment 2 – Sample degradation due to storage at room temperature

The samples were stored at room temperature (21.5 °C) and 1 atmosphere. The samples were kept a minimum of 50 cm from each other in a well-ventilated room with odour filtered air delivery system. Samples were measured at time of collection and then at 2, 3, 4, 7, 10, 14, and 24 hours post sampling. Samples were not subjected to sunlight or any UV emitting artificial lighting.

2.3 Experiment 3 – sample degradation due to temperature and pressure variations of air freight

The third experiment was performed on samples stored at 90 kPa absolute pressure (a drop of 10 kPa) and at 13 °C in accordance with typical conditions in transport planes such as those used by FedEx or DHL (Singh et al., 2010). The samples were analysed at the same time period as in Experiment 1. Sample measurement was conducted in less than 60 seconds and the samples were returned to the environmental chamber. Pressure drop was created using Scentroid 50 L Vacuum chamber SB50.

2.4 Experiment 4 – sample degradation of highly reactive compounds

The fourth experiment involved samples taken from the stack exhausting odour air being treated with ozone. The experiment involved direct olfactometry using SM100 concurrently to sampling. Further measurements were made every 30 min for up to 6 hours.

2.5 Experiment 5 – Sample cross contamination in shipping

The fifth experiment aims to determine the affect and extend of cross contamination between samples stored in the same container. Therefore, samples of varying odour intensity were stored in carton boxes and sealed using shipping tape. The boxes were opened after 24 hours to measure the change in odour intensity of each sample. Headspace odour measurements were made of the box at 6, 12, 18 and 24 hours prior to opening the box containing the samples. Head space measurements were made on samples collected from the box. In total 4 carton boxes were setup, three of each with two (2) samples of 10 L capacity. The samples are selected from a UV filter inlet with odour concentration of roughly 2000 OU and outlet of odour concentration of 50 OU. Box 1 was designed at the control point with no odour samples (empty), Box 2 contained the inlet and outlet samples in Nalophan bags of 10 L capacity. Box 3 contained samples stored in Tedlar® bags and Box 4 contains samples stored in PTFE bags.

2.6 Equipment Used for Odour Measurement

To conduct all odour analysis the Scentroid SM100 portable olfactometer was used. This equipment allows the panellists to conduct odour analysis from ambient or stored samples as well as to conduct direct olfactometry. The total range of the SM100 is from 2 OU to 30,000 OU. It has been showed in a number of previous studies by independent researchers that the Scentroid SM100 produces results that are directly comparable to those obtained by certified odour laboratories following the EN13725 standard (Bokowa, 2012). We selected to use the SM100 instead of the Scentroid SC300 or the SS600 stationary olfactometer due to its portability and capacity for direct olfactometry. The portability of the unit allowed the research team to make sample measurement at site and when samples were received. All samples were measured using 2 panellists that had undergone n-butanol sensitivity analysis in accordance to the EN13725 standard. Each sample was analysed 3 times (3 rounds) and each round consisted of a minimum of 5 steps and a dilution step of less than 2. The SM100 was equipped with a specialized valve

for binary forced choice analysis. The valve allows the panel leader to administer diluted sample or neutral air to the panellist. The panel leader then manually increases the dilution and randomizes the presentation until both panellists can correctly distinguish the diluted sample from neutral air with certainty. This is to follow the EN13725 standard in all aspects except the use of 2 panellists instead of 4.

3. Results and Discussion

In the first experiment each sample bag was filled with nitrogen and analysed in 2 hours to determine the background odour originating from the bag material. The results are shown in Table 1. As can be seen PTFE has no background odour while new Tedlar has significant background odour.

Table 1: Odour degradation of samples preserved at standard temperature and pressure

Bag Material	Nalophan	Virgin Tedlar®	Pre-Cond Tedlar®	PTFE
Odour Concentration (OU)	9	42	7	0

In the second experiment, samples that were stored at room temperature were analysed for odour degradation. The odour decay for all samples is shown in Figure 1. In general Nalophan has the highest odour decay followed by Tedlar®, and PTFE has the best odour preservation. Certain samples such as those from a compost facility have the most sample degradation in Nalophan compared to Tedlar® and PTFE. This is partially due to the high loss rate of H₂S from Nalophan bags. For waste water treatment plant odour samples have high degradation in both Nalophan (60 % in 24 hours) and Tedlar® (35 %) but far better in PTFE sample bags (23 %). This could be explained in part by the losses of Ammonia from Tedlar® and Nalophan bags. Samples from the refinery have significant loss in Nalophan and Tedlar® compared to PTFE. To determine the source of this loss, samples bags were sent to an external laboratory to determine the losses of Benzene from the bags as it was determined to be the key odour causing chemical. The results are shown in Table 2. As can be seen Benzene sample retention is extremely poor in Nalophan and Tedlar while PTFE provides an acceptable holding time for Benzene.

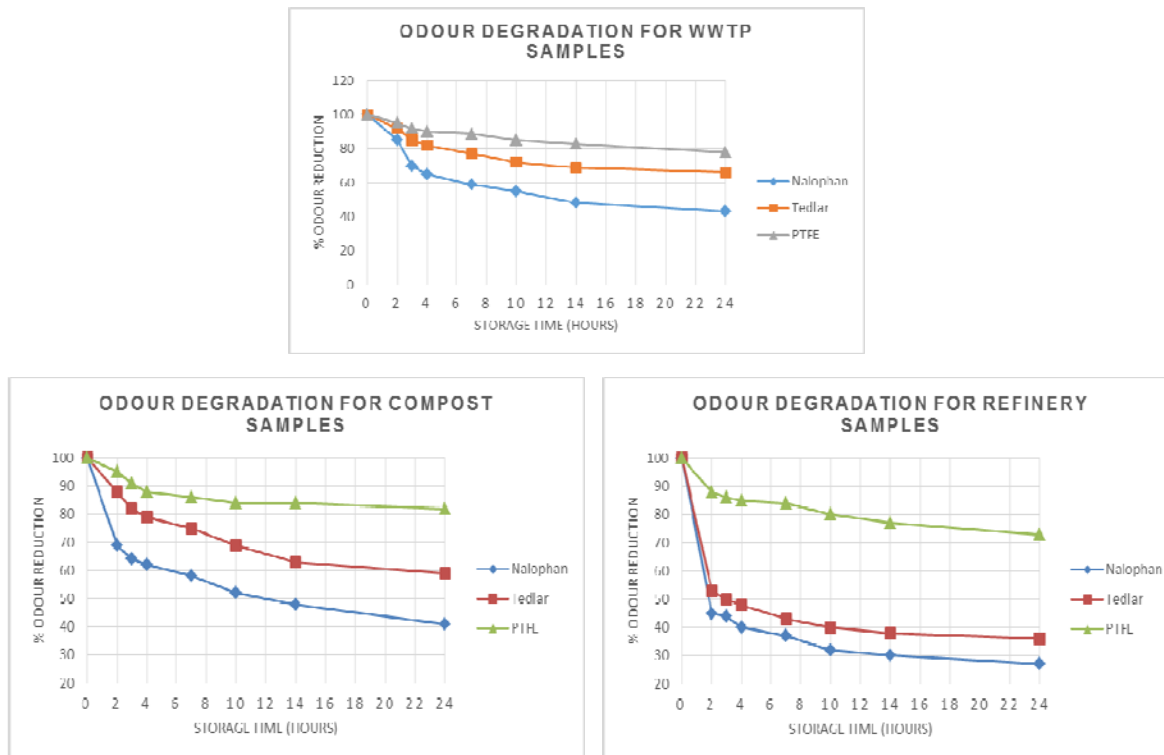


Figure 1: Odour decay graph of WWTP, Compost, and Refinery samples preserved at standard temperature and pressure for all three bag types.

The third experiment evaluates the effects of pressure and temperature drops associated with air fright on odour samples. The odour degradation data, shown in Figure 2, demonstrate the effects of pressure and temperature on sample degradation. Pressure drop clearly increases the rate at which samples escape the bags due to permeability of the material. In Tedlar® and PTFE these effects on sample degradation is far less than samples stored in Nalophan bags. Samples that have a higher humidity have a higher degradation in all bags due to condensation. The condensation was only occurring during depressurization and temperature drops. The water droplets evaporate when the sample is returned to room temperature.

Table 2: Degradation of Benzene concentration in Nalophan, Tedlar®, and PTFE bags

Material	Concentration in the tank (ppm)	After 10 min (ppm)	After 45 min in (ppm)
Nalophan	100	51	35
Tedlar®	100	65	53
PTFE	100	88	85

In the fourth experiment degradation of samples with highly reactive compound ozone were considered. Figure 3 shows the sample degradation as a percentage of the initial odour concentration as collected using direct olfactometry. The results show an extremely rapid degradation regardless of the bag material. The majority of the odour degradation is due to the reaction of the ozone with the odorous compounds while stored in the sample bag, and mostly takes place within the first 30 min of storage. In normal operation odorous gas that is emitted from the stack is diluted by ambient air and therefore the reaction is stopped.

In the fifth experiment, extend of cross contamination on samples stored in the same container are measured. Table 3 shows the initial and 24 hour odour concentration of each sample. Table 4 shows the headspace odour concentration. A box containing no samples was used as the control point for the experiment. As can be noted, the empty box had a background odour of 7 OU while the box containing the Nalophan sample bags had the highest odour concentration. While PTFE sample bags had the least odour cross contamination it is still necessary for sampling technicians to sort weak and strong samples and store them separately. The chemical composition should also be similar to avoid creating samples of new chemical composition which can lead to odours exceeding even the sample with the highest odour concentration.

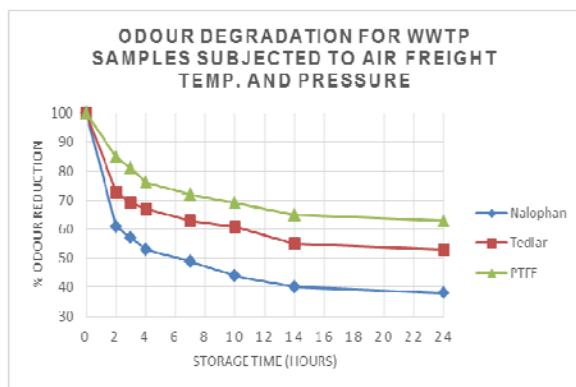


Figure 2: Odour decay graph of samples subjected to pressure and temperature conditions of air freight.

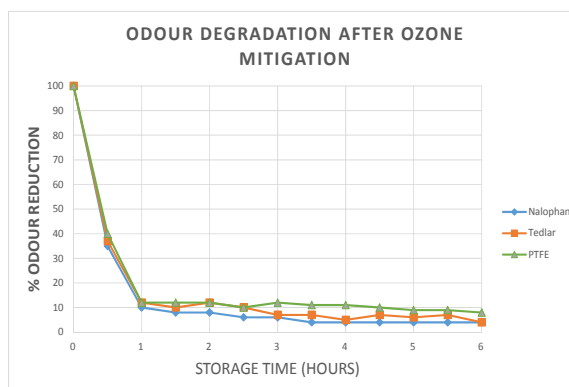


Figure 3: Odour decay graph of samples taken from exhaust of ozone treated air.

Table 3: Odour concentration changes due to cross contamination of samples stored in carton boxes

	Initial	6	12	18	24
Box 2	60	135	280	390	524
Nalophan	2540	2010	1850	1367	1053
Box 3	40	59	163	229	280
Tedlar®	2890	2551	2392	2184	1900
Box 4	55	61	73	89	103
PTFE	2610	2513	2395	2209	2150

Table 4: Head space odour concentration of carton boxes with high concentration odours stored inside.

	Initial	6	12	18	24
Box 1 Empty	0	6	7	8	7
Box 2	0	270	518	673	750
Nalophan					
Box 3	0	106	207	320	420
Tedlar®					
Box 4	0	45	99	145	178
PTFE					

4. Conclusion

Sample degradation is based on a number of factors including: sample composition, pre-dilution (as a means of minimize condensation), Sample bag material, transportation method, and duration of storage. In this paper the effects of sample bag material and transportation as well as sample composition is studied. The data clearly shows an improved sample preservation in PTFE over traditionally used materials such as Nalophan or Tedlar®. The effects are more predominant in organic samples with high concentration of Hydrogen Sulfide and Ammonia such as those from a compost facility. When bags are subjected to lower pressure odour degradation is accelerated with a more rapid odour loss in Nalophan bags. Further study of cross contamination during shipping has shown that samples of varying composition and concentration can start to exchange due to the permeability of the sample bag material. The exchange leads to significant cross contamination. If possible samples of similar type and concentration should be stored together and preferably for as short a period as possible. The cross contamination is most significant in Nalophan and least in PTFE bags. Sample pre-dilution at the source with nitrogen is an excellent technique for reducing sample loss and cross contamination. If possible, air freight should be avoided as reduced temperature and pressure on commercial carriers can further accelerate odour degradation. Samples with highly volatile compounds, such as those collected from exhaust of ozone generators should be analyzed as soon as possible and ideally using direct olfactometry. If samples containing ozone are analyzed even within a few hours of collection a much lower odour concentration will be measured. It is the recommendation of this author that samples that require more than a few hours of transit to a stationary lab or samples with ozone and other highly reactive compounds, should be analyzed using portable or direct olfactometers. The advantages of increased accuracy gained by stationary laboratories maybe insignificant to the odour degradation caused by long distance shipping and air freight.

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