Reducing Odour Sample Degradation: A Comparative Study of Nalophan, Tedlar® and PTFE Sample Bags

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Abstract

Degradation is inherent part of odour sampling and olfactometery 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 and the future EN13725 standard may go even further to propose a 6 hour limit, as observations have shown samples can degrade by an order of ten magnitude in a span of less than 24 hours. This study will aim to measure sample degradation from a variety of sources over a span of 48 hours. Samples will be stored in Nalophan, Tedlar®, and the newly introduced PTFE bags. Initial 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 will focus on samples that are subjected to lower pressure and temperature similar to those found in standard cargo planes. These samples will be compared to those which have been stored at standard conditions (room temperature at 1 atmosphere).

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 olfactometeric laboratory for Analysis. Recent advancements in field olfactometery, 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. Field olfactometery has accentuated the issue of sample degradation during storage and transport. A unique capability of field olfactometers 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. 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, Tiziano et al., 2012) 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 (Tiziano et al. 2012) that Ammonia and H2S among other chemicals easily escapes from Nalophan sample bags. The current European standard imposes a 30 hour 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 hours and 30% loss of H2S (Hansen et al. 2011). These chemicals are commonly found in waste water treatment plants, landfills, agricultural process, and compositing 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 hours Tedlar® bags have losses of less than 5% on sulfur compounds. However, Ammonia (40% in 24 hours and 60% in 30 Hours), Phenol (50% in 24 hours) 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 a property material of 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 therefore eliminate the chances of sample contamination, 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 (Tiziano et al. 2012).

This paper presents results of a comprehensive study of odour degradation rate inNalophan, 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.

Materials and Methods

The three types of bags used in this experiment were Nalphan, Tedlar® (0.002" thick) and PTFE (0.002" 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.

Samples used in these studies were collected from four processes: i) Waste Water Treatment plant, ii) Agricultural facility (Swine and cow manure), iii) a compost facility, and iv) a refinery in a process where high benzene concentration could be detected in the indoor air. 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 bio-filter using Scentroid SB10 vacuum chamber. Samples from the agricultural site were collected from an open manure pile using the Scentroid SF450 Flux chamber. Samples were taken from the ambient air of a transfer station at a compost facility also using a Scentroid SB10 vacuum chamber. Samples from the refinery were collected at from ambient air using SB10 vacuum chamber.

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

Experiment 1 – Sample degradation due to storage at room temperature.

The samples were stored at room temperature (21.5℃) 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.

Experiment 2: sample degradation due to temperature and pressure variations of air freight

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

Experiment 3: Sample cross contamination in shipping

The third 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 was 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. In total 4 carton boxes were setup three of each with two (2) samples of 10L 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.

Equipment Used for Odour Measurement

To conduct all odour analysis the Scentroid SM100 portable field olfactometer was used. This equipment allows the panelists to conduct odour analysis from ambient or stored samples. 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. 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 panelists that had undergone n-butanol sensitivity analysis in accordance to the EN13725 standard.

Results and Discussions

In the first experiment samples that were stored at room temperature were analyzed for odour degradation. The raw data is shown in Table 1 and 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. Odours from the manure source also seem to be similar to Waste water treatment plant partially due to the loss of Ammonia and H2S. But the losses were closer between Tedlar® and PTFE with moderately better odour preservation in PTFE likely due to the excellent VOC preservation of both Tedlar® and PTFE. 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 laboratory in Calgary, Alberta, Canada to determine the losses of Benzene from the bags as it was determined to be the key odour causing chemical. The results shown in Table 2. As can be seen Benzene sample retention is unacceptable in Nalophan and Tedlar. PTFE provides a good holding time for Benzene.

TABLE 1 Odour degradation of samples preserved at standard temperature and pressure

	Source	0 hrs	2 hrs	3 hrs	4 hrs	7 hrs	10 hrs	14 hrs	24 hrs
Nalophan	WWTP	1250	1063	875	813	738	688	600	538
	Agriculture	2700	2133	1701	1566	1350	1215	1026	918
	Compost	750	518	480	465	435	390	360	308
	Refinery	3300	2574	2310	2013	1683	1485	1188	891
Tedlar®	WWTP	1400	1288	1190	1148	1078	1008	966	924
	Agriculture	2600	2366	2314	2210	2132	2028	1950	1898
	Compost	815	717	668	644	611	562	513	481
	Refinery	3500	3010	2730	2520	2100	1820	1750	1575
PTFE	WWTP	1155	1097	1063	1040	1028	982	959	901
	Agriculture	2950	2744	2626	2567	2508	2478	2390	2331
	Compost	910	865	828	801	783	764	764	746
	Refinery	3250	2925	2860	2828	2763	2600	2535	2470

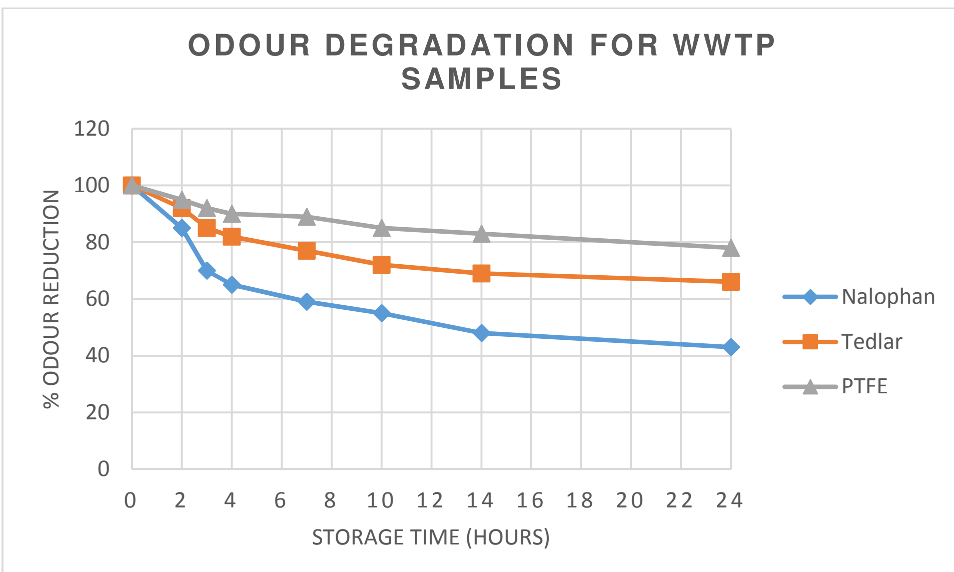

Figure 1.A Odour decay graph of WWTP samples preserved at standard temperature and pressure for all three bag types.

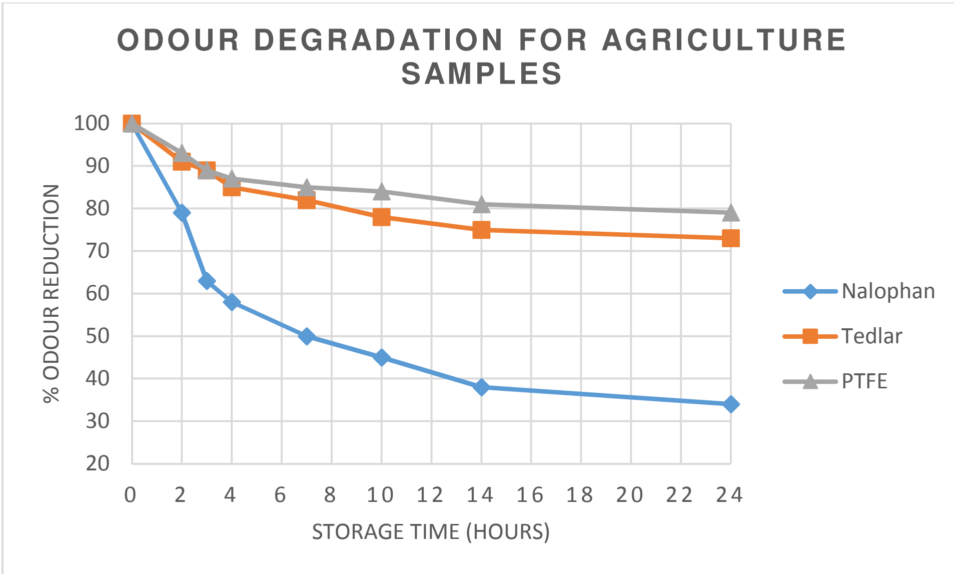

Figure 1.B Odour decay graph of Agriculture samples preserved at standard temperature and pressure for all three bag types.

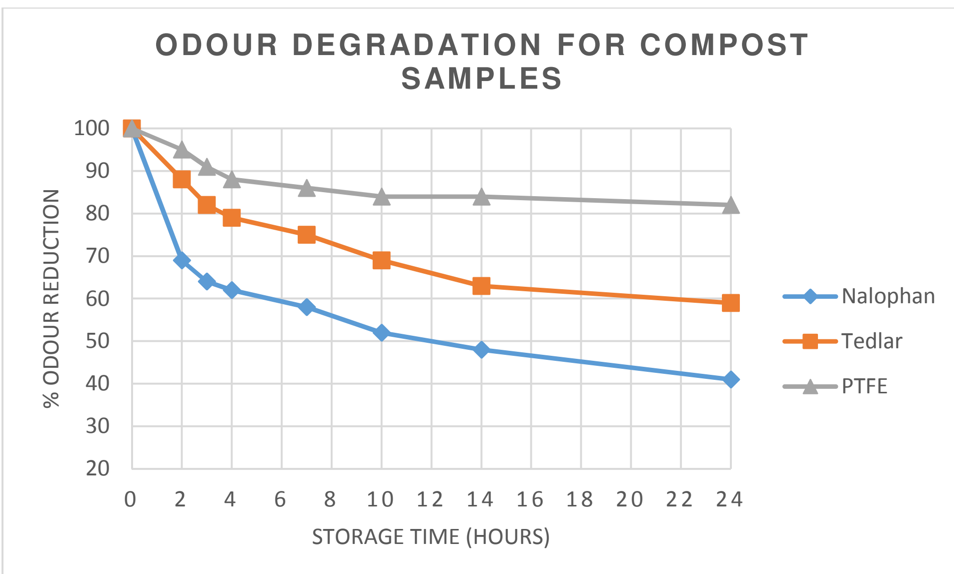

Figure 1.C Odour decay graph of compost samples preserved at standard temperature and pressure for all three bag types.

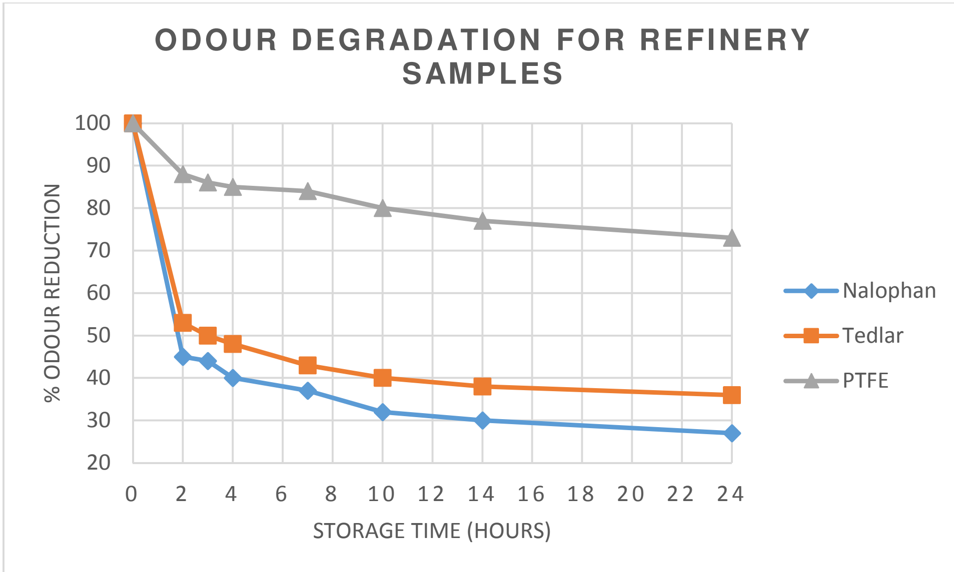

Figure 1.D Odour decay graph of refinery samples preserved at standard temperature and pressure for all three bag types.

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

The second experiment evaluate the effects of pressure and temperature drops associated with air fright on odour samples. The odour degradation data is shown in Table 3 and Graph 2 show 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 the effects of sample degradation is less than samples stored in Nalophan. Samples that have a higher humidity had a higher sample 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 3 Odour degradation of WWTP samples subjected to pressure and temperature conditions of air freight.

Material	0 hrs	2 hrs	3 hrs	4 hrs	7 hrs	10 hrs	14 hrs	24 hrs
Nalophan	1355	827	772	718	664	596	542	515
Tedlar®	1009	737	696	676	636	615	555	535
PTFE	1239	1053	1004	942	892	855	805	781

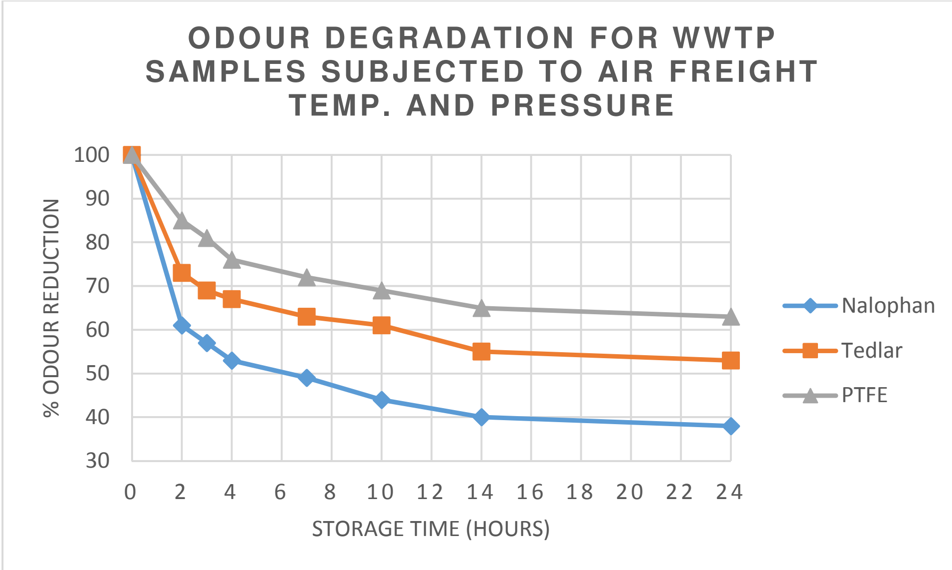

Figure 2 Odour decay graph of samples subjected to pressure and temperature conditions of air freight.

In the third experiment extend of cross contamination on samples stored in the same container are measured. Table 4 shows the initial and 24 hour odour concentration of each sample. Table 5 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

Table 4 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 5 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 Nalophan	0	270	518	673	750
Box 3 Tedlar®	0	106	207	320	420
Box 4 PTFE	0	45	99	145	178

Conclusion

Sample degradation is based on a number of factors including: sample composition, pre-dilution to minimize condensation, Sample bag material, transportation method, and duration of storage. In this paper the effects of sample bag material and transportation is studied. The data clearly shows an improved sample preservation in PTFE over traditionally used materials such as Nalophan or even Tedlar®. The effects are more predominant in samples with high concentration of Hydrogen Sulfide and Ammonia. When bags are subjected to lower pressure the permeability of the bag is further exposed and therefore odour degradation is accelerated. This is especially an issue if the bag is filled to 80% or higher of its maximum volume. It is therefore recommended that sample bags should be filled to 70% of their volume. 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 was most significant in Nalophan and least in PTFE bags. If possible Air freight should be avoided as reduced temperature and pressure on commercial carriers can further accelerate odour degradation. It is the recommendation of this author that samples that require more than a few hours of transit to a stationary lab should be analyzed using portable olfactometers or field olfactometers. The advantages of increased accuracy gained by stationary laboratories is insignificant to the odour degradation caused by long distance shipping and air freight.

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