Chemical and Odor Evaluation of Various Potential Replacement Films for Sampling Bags

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ABSTRACT

Tedlar (polyvinyl fluoride) has been the material of choice for sampling bags used in the environmental and odor assessment fields; however, as of 2011, the material is being phased out of production for this application. ALS Columbia and St. Croix Sensory evaluated various potential replacement film materials and bag construction configurations with the goal of finding the optimal combination that is well suited for both chemical odor analysis (e.g. ASTM D5504 reduced sulfur compound sampling, modified EPA TO-15 volatile organic compound sampling) as well as odor panel evaluation (e.g. ASTM E679-04, ASTM E544-99, EN 13725:2003). Many factors contribute to the success of the bag including film type, size of the bag (surface area), valve stem type, bag shape/seam sealing, septum material, bag material permeability, and bag material off gassing/adsorption.

Preliminary results confirm published data that Tedlar sample bags contain several artifacts (e.g. phenol and/or N,N-dimethylacetamide) which may affect both chemical analysis and odor analysis. Therefore, Tedlar material for sample bags is not necessarily the 'Gold Standard' for sample bag material. Pros and cons of each of the material types and configurations that were tested are presented in this paper, as well as recommendations for types of bags to use for different odor related sampling applications.

KEYWORDS

Tedlar bag, bag artifact, Tedlar replacement film, bag background, bag odor.

INTRODUCTION

Tedlar (polyvinyl fluoride) has been the material of choice for sampling bags used in the environmental and odor assessment fields (for both chemical and sensory/odor panel analysis);

however, as of 2011, according to various sample bag manufacturers, the Tedlar material is being phased out of production for this application (Sigma Aldrich 2012, Keika Ventures 2012). Along with Tedlar, Nalophan (polyethylene terephthalate) is also mentioned as an acceptable sample bag film type in the European standard EN 13725, Air quality - Determination of odour concentration by dynamic olfactometry (CEN 2003). As of 2011, Tedlar is the predominant material used for sampling bags in the United States, while Nalophan is more widely used in Europe and Australia (Parker 2010). For most olfactory applications, 10L size bags (or larger) are preferred, while for most chemical evaluations, smaller bags (1L) are more commonly used.

Several researchers have documented the phenomenon of sample bag chemical artifacts and/or background odors. Both Tedlar and Nalophan are known to have background odor levels which may be reduced by flushing and/or heat conditioning the bags prior to use. Miller and McGinley found that preconditioning Tedlar bags by flushing with odor free air at an elevated temperature reduced odor background levels to within 2x the reporting limit; they found that Nalophan background odor levels could be reduced simply by placing the bags in an odor free environment for a period of time (Miller 2008).

Since sample bags are used for a wide range of applications (from ambient odor evaluation to source testing), and have different analyses performed (e.g. olfactory testing/odor panel evaluation, permanent gas analysis, reduced sulfur compound analysis, and/or speciated volatile organic compound (VOC) analysis), users may have different needs in terms of cleanliness and performance.

Although there are many applicable ASTM standards related to physical, thermal, electrical, and chemical performance of plastic films (e.g. ASTM D1434, ASTM D882, etc.), to date, none of these performance standards specifically address the film's performance related to air sampling applications. Most likely different applications of bag sampling would merit different acceptance criteria (for example, source level samples vs. ambient level samples). There is, however, a need for testing in a standardized fashion to ensure basic quality and consistency, and that the product meets the user's needs.

When considering characteristics of sample bags for the odor assessment field, factors such as film cleanliness, inherent odor, permeability, reactivity, and fitting style all contribute to what will be referenced as an "ideal" bag (Table 1). Logically, bag film characteristics such as cleanliness (presence of artifacts) and permeability can directly impact sample integrity. Although not addressed in this paper, acceptable recovery and stability of odorous compounds of interest in the sample bags is a critical performance evaluation criterion.

In addition to bag film characteristics, bag fitting characteristics such as fitting material and septum material can impact sample integrity since these materials can also off-gas and/or adsorb chemical compounds of interest (for example, some septa types are known to emit carbonyl sulfide and carbon disulfide—two reduced sulfur compounds of odor interest. In addition, bags with stainless steel fittings are not suitable for reduced sulfur compound sampling/analysis since the compounds of interest may react with the stainless steel and recovery may be poor). Figure 1 presents a photograph of an example 1L size Tedlar bag with polypropylene fittings (as is often used for reduced sulfur compound sampling/analysis), showing the bag fitting and the septum assembly. Many bag fittings include a re-sealable septum to facilitate access to the sample with a gas-tight syringe.

Table 1. Characteristics of an Ideal Sample Bag Film and Bag Fitting

The "Perfect" Sample Bag Film	Fitting

• "Cleanliness"—though impractical to think there will be no artifacts:
  o Artifacts should not be target analytes
  o Concentrations of artifacts should be below standard reporting limits
• If there are large concentrations of artifacts, consider producing a larger bag (a smaller surface: volume ratio decreases interference)
• No inherent odor to the bag
• There should be a lack of permeability of small compounds
• The film should be able to retain sulfur compounds for a minimum of 24 hours and target VOCs for three days
	• The fitting should not off-gas sulfur compounds that is either intrinsic to the septum or fitting silicone lubrication:
	• The septum should be as small and thin as possible
	• Septa should also be cured at higher temperatures to diminish off-gas potential
	• Fittings with lubrication eliminated all together are desirable
	• Fitting material should be inert to target analytes and/or sample matrix to prevent losses

Figure 1. Photograph of 1L Tedlar Bag with Polypropylene Fitting and Septum Assembly

METHODS

ALS Columbia performed chemical testing on various Tedlar replacement film sample bags, as well as several commercially available Tedlar sample bags, to characterize typical artifact frequency, identifications, and concentrations. The bags were first inspected upon receipt for tears or flaws. Next, the bags were evacuated and filled with humidified high purity air and allowed to equilibrate before being subjected to various analytical tests. The Nalophan and Tedlar E bags were analyzed at a later date than the rest of the bags, and therefore had a revised preparation protocol which included flushing twice with high purity nitrogen, evacuating the bag fully, and then filling with high purity nitrogen (dry).

It is important to note that this testing was performed in controlled laboratory conditions (temperature, humidity, etc.) and care was taken to minimize the bag exposure to ambient chemicals that may have been present in the laboratory (used for environmental sample extractions, etc.). After equilibration, the filler gas in the bags was analyzed for a list of 75 volatile organic compounds (VOCs) plus the top 20 tentatively identified compounds (TICs, as identified using a NIST library search feature) via EPA Method TO-15 (modified for use of bags instead of canisters). This technique utilizes cryogenic concentration and gas chromatography with mass spectrometry detection (GC/MS) in full scan mode. For all bag samples, 100 mL of sample was analyzed. Ambient room air was also monitored via EPA Method TO-15 daily throughout the duration of the experiments, to provide additional information for potential cross-contamination sources in case the bags displayed leaks or permeation over the duration of testing.

Bags were also analyzed for a list of 20 reduced sulfur compounds, including hydrogen sulfide, carbonyl sulfide, methyl mercaptan, and carbon disulfide, via ASTM Method D5504. This technique utilizes gas chromatography with sulfur chemiluminescence detection (GC/SCD).

Finally, the Nalophan and Tedlar E bags were also analyzed for oxygen (as an indicator of bag leakage and/or permeability) via EPA Method 3C (modified for single injections). This technique utilizes gas chromatography with thermal conductivity detection (GC/TCD).

Table 2 summarizes the various bag types investigated in this paper.

Table 2. Bag Types Evaluated in this Study

Bag Name	Type	Size	Fitting/Other Characteristics
Tedlar A	Tedlar (Polyvinyl fluoride)	1L	Polypropylene, approx. 11 mm butyl rubber septum. Heat sealed edges with metal grommet.
Tedlar B	Tedlar (Polyvinyl fluoride)	1L	Polypropylene, approx. 2.5 mm fluoropolymer faced septum. Heat sealed edges with polypropylene grommet.
Tedlar C	Tedlar (Polyvinyl fluoride)	1L	Polypropylene, approx. 4 mm OD teflon faced septum. Heat sealed edges with polypropylene grommet.
Tedlar D	Tedlar (Polyvinyl fluoride)	1L	Polypropylene, approx 2.5 mm butyl rubber septum. Heat sealed edges with polypropylene grommet.
Tedlar E	Tedlar (Polyvinyl fluoride)	10L	Polypropylene, approx. 11 mm OD butyl rubber septum. Heat sealed edges with polypropylene grommet.
Nalophan	Nalophan (polyethylene terephthalate)	10L	Teflon tubing and stopper at one end with cinched stainless steel clamp at other end.
Kynar	Polyvinylidene difluoride (PVDF)	1L	Polypropylene, approx. 10 mm OD butyl rubber septum. Heat sealed edges with polypropylene grommet.
New Film A	Proprietary	1L	Polypropylene, approx. 10 mm OD butyl rubber septum. Heat sealed edges with metal grommet.
New Film B	Proprietary	1L	Polypropylene, approx. 10 mm OD butyl rubber septum. Heat sealed edges with metal grommet.

RESULTS

Figure 2 displays the total number of VOC artifacts detected via modified EPA TO-15 analysis in various sample bag film types. Reduced sulfur compounds are not included in the VOC assessment. Four different Tedlar bag types are represented, as well as one Kynar and two different new replacement films.

Among the four Tedlar types, there is notable variation in the number of VOCs detected as artifacts. Two of the Tedlar types were analyzed in duplicate, and for Tedlar B, even two different bags of the same type yielded very different results (one bag had 11 VOCs detected, while the other had only one). Even with this small sample size, one can see the need for standardization of these materials.

In this comparison, overall the replacement films yielded a higher number of detected VOCs than the Tedlar. Nalophan exhibited the fewest artifacts of all the alternate films. It should be noted that when performing chemical analysis using sample bags, it is more desirable from a laboratory perspective for a bag to have fewer total VOC artifacts (even if they are higher concentration) rather than a high number of VOC artifacts at lower concentrations. In general, any laboratory performing routine analysis using sample bags will make accommodations to work around these artifacts. In some cases, the artifacts may interfere with chemical or odor analysis and cause a high bias and/or cause laboratory reporting limits to be elevated. For example, chromatographic interference caused by the size of the large N,N-dimethylacetamide peak (a common artifact in many Tedlar bags) requires that a smaller aliquot (100mL as opposed to ALS Columbia’s standard 1L aliquot) be used for sample analysis; with this dilution of the sample size there is a 100 fold increase in reporting limits for the modified EPA TO-15 analysis.

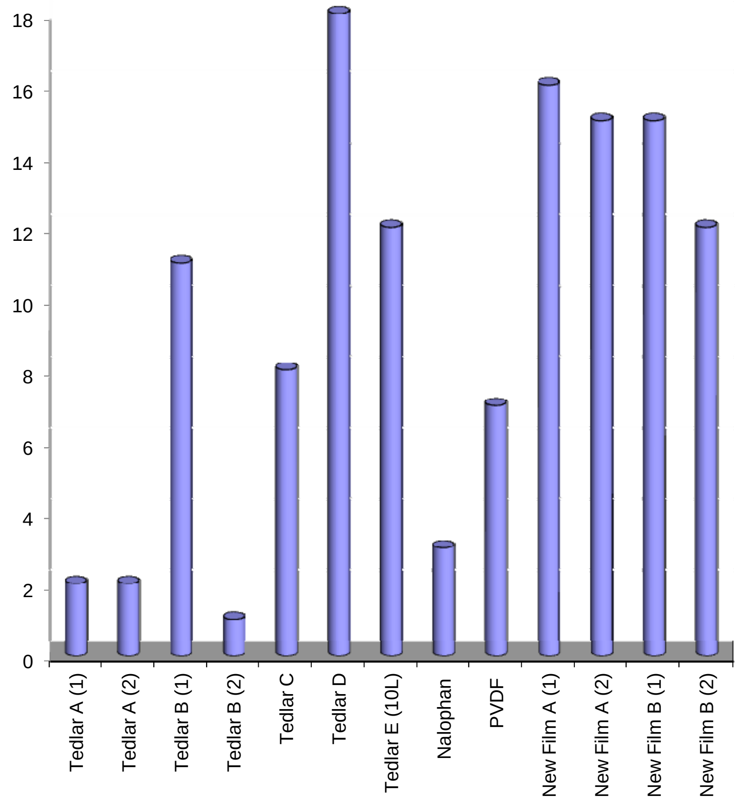

Figure 2. Total Number of VOC Artifacts Detected in Various Sample Bag Film Types

For olfactory work, the AC'SCENT laboratory olfactometer has an instrument lowest detection limit of 8; meaning the sample is diluted 8x at the assessor level. Background odor levels for blank Tedlar bags have been documented at anywhere from at least 12-30 OU and up to 100 OU (Laor 2010, Miller, 2008, van Harreveld 2003). Nalophan also has similar background odor levels (Laor 2010, M iller 2008). Following the laws of Olfactomatics, odor values (dilution ratios) cannot be added or subtracted (McGinley 2000); therefore, there is no way to adjust a result (i.e. “blank subtract”) because of an artifact caused bag odor. For instance, if a bag artifact compound causes the test result to be 20 OU, and a bag from the same lot is filled with an air sample, the odorant in the air sample may cause a test result of 50 OU. The laws of Olfactomatics require the result to be reported as 50 OU and not corrected down to 30 OU for the observed background level. Odor character can help determine the source of background odors. Typical background odor character descriptors for Tedlar bags include “plastic” and “vinyl”.

The two most frequent VOC artifacts detected in most commercially available Tedlar bags are phenol and N,N-dimethylacetamide. These compounds are generally thought to be attributable to the bag manufacturing process (Trabue 2006, van Harreveld 2003). Other VOCs detected in the different bag types include various alcohols, aldehydes, ketones, gasoline range hydrocarbons, and solvents. Table 3 presents a list of selected detected VOCs, their maximum detected concentrations, and odor detection threshold range information for comparison. Acetaldehyde, n-hexanal, 2-methylpentane, and phenol were detected in at least one bag at concentrations exceeding published odor thresholds. While most of the maximum detected concentrations shown in Table 3 are below published odor thresholds, it is possible that these concentrations contribute individually (to sensitive assessors) or additively/synergistically to overall odor artifact detection. It is also possible that there are additional odorous compounds emitted from sample bags which are not most effectively captured by the EPA Method TO-15 (a whole air sampling method). For example, Trabue et al. (2006) also measured background levels of acetic acid in Tedlar bags, in addition to phenol and N,N-dimethylacetamide; acetic acid is not recovered well via EPA TO-15. It is also possible that some of the odor threshold references are outdated and biased high since many of them originate over 20-30 years ago, when different sample introduction techniques were used in dynamic olfactometry.

Table 3. Bag Film Artifact Concentrations vs. Odor Thresholds

Compound	Bag(s) Detected	Odor Character	Maximum Concentration Detected, µg/m^3	Odor Threshold, µg/m^3	Reference
Acetone	Kynar, Tedlar E	Minty chemical, sweet	310	4.7E4 – 1.6E6	Ruth 1986
Acetaldehyde	New Film A	Green, sweet, fruity	54	0.2 - 4140	Ruth 1986
t-Butanol	Kynar, Tedlar B	Camphor-like	116	2.19E5	Ruth 1986
2-Butoxyethanol	Kynar	Sweet, ether, musty	37	483 - 1690	AIHA 1986
N,N-Dimethylacetamide	Tedlar A, Tedlar C, Tedlar D, Tedlar E	Amine, burnt, oily	7200	1.63E5	Ruth 1986
2-Ethylhexanol	New Film A	Musty	166	399.9 – 734.2	Ruth 1986
n-Hexanal	Kynar	Green, grassy leaves	56	28-67	Louhelainen 2001
2-Methylpentane	Tedlar B	Petroleum	1561	288.6	Ruth 1986
α-Methyl styrene	New Film A	Sweet, aromatic	132	249 – 9.6E5	Ruth 1986
Methyl methacrylate	Tedlar C, Tedlar E	Arid, fruity, sulfidy	31	205 - 1394	Ruth 1986
n-Pentane	Tedlar B, Tedlar D	Gasoline-like	66	6.6E3 – 3.0E6	Ruth 1986
Phenol	Tedlar A, Tedlar B, New Film A, Tedlar C, Tedlar D, Tedlar E	Medicinal, sweet	1200	178.6 – 2.2E4	Ruth 1986
2-Propanol (Isopropanol)	Nalophan, Tedlar E	Rubbing alcohol	42	7.84E3 – 4.9E5	Ruth 1986

Reduced sulfur compound artifacts were assessed separately from VOCs, via ASTM Method D5504. Figure 3 displays the total number of reduced sulfur artifacts detected via ASTM D5504 analysis in various sample bag film types. Many bags had two main compounds present:

carbonyl sulfide and carbon disulfide; both of these compounds are associated with butyl rubber which is often used as the bag septum material. This finding is consistent with the work of Mochalski et al. (2009), and additionally they hypothesized that the carbonyl sulfide and carbon disulfide may be emitted during heating of the bags during bag production. A few of the other bag types displayed detected concentrations of hydrogen sulfide and/or methyl mercaptan. Concentrations of reduced sulfur compounds ranged from approximately 13-280 $\mu g/m^3$. In most cases, these concentrations are above published odor detection threshold levels, and could possibly contribute to the overall odor.

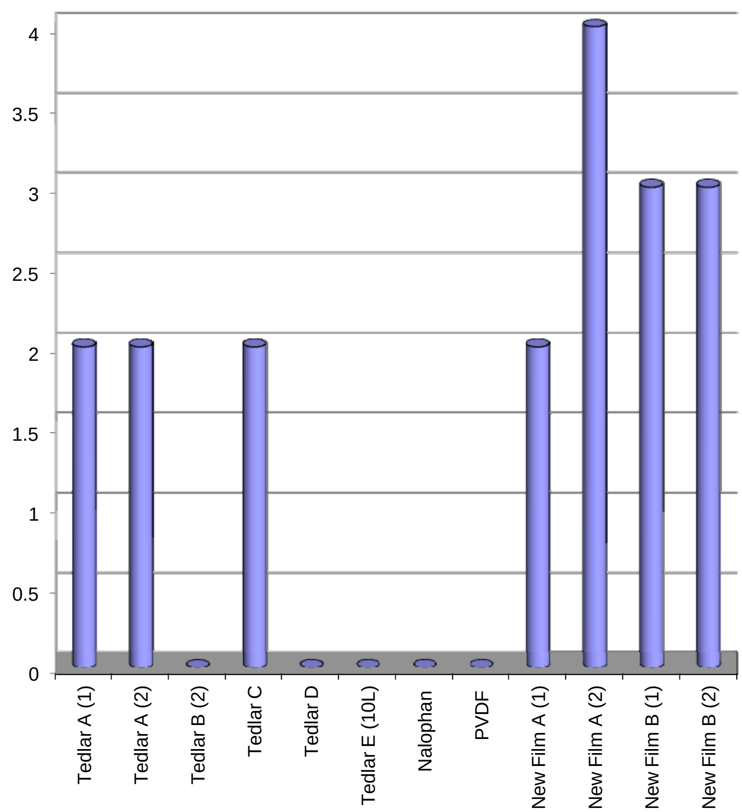

Figure 3. Total Number of Reduced Sulfur Artifacts Detected in Various Sample Bag Film Types

For the Nalophan and Tedlar E bags, ALS Columbia analyzed the bags on multiple days to investigate if there was a noticeable change in artifact detections and/or concentrations detected over time. For real world samples, Laor et al. (2010) investigated the effect of sample storage on olfactory testing in Tedlar and Nalophan bags, and observed both increased odor activity and decreased odor activity for stored samples. Odor decay rates are known to be different for different chemical classes and different bag materials (van Harreveld 2003). In this experiment, for bag artifacts, an overall increase in the chemical concentrations was observed from the first day to day seven.

Figure 4 presents the decay curves for the various VOC artifacts seen in Nalophan bags in this study, as measured on Day 1, Day 3, and Day 7. Figure 5 presents the decay curves for the various VOC artifacts seen in Tedlar E (10L) bags in this study, as measured on Day 1, Day 3, and Day 7.

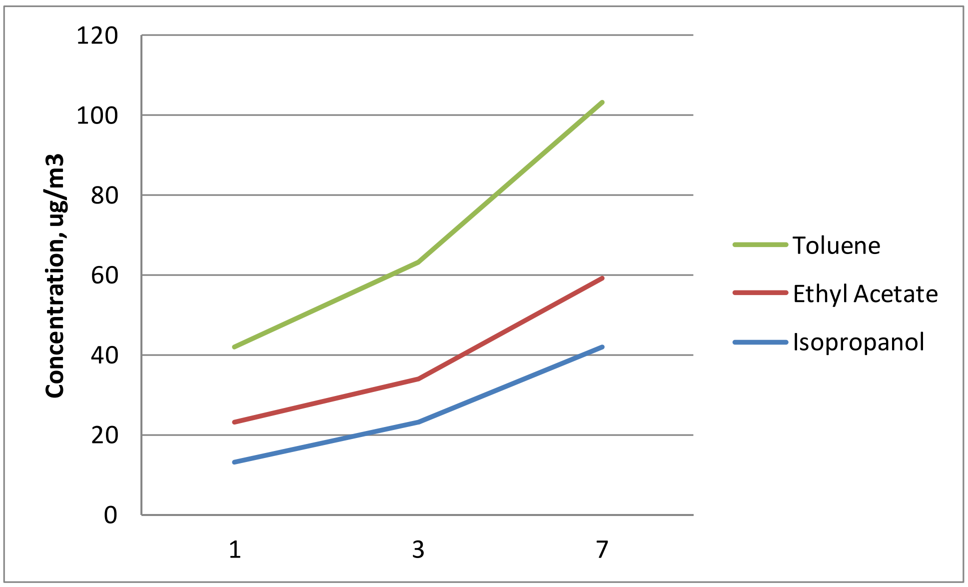

Figure 4. Nalophan Bag Artifacts Over Time

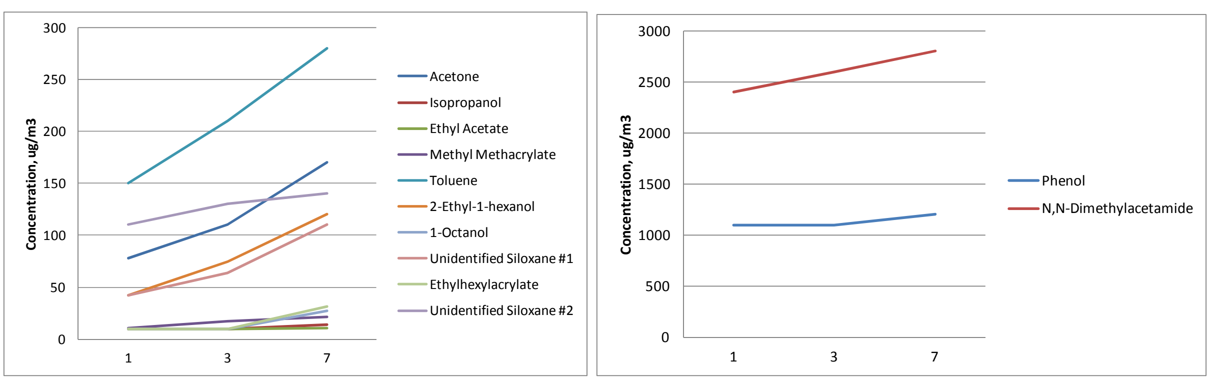

Figure 5. Tedlar E (10L) Bag Artifacts Over Time (Phenol and N,N-Dimethylacetamide Charted Separately for Scale)

For the Nalophan and Tedlar E bags, ALS Columbia also conducted fixed gas testing, to assess permeability using the oxygen concentration as an indicator of bag leakage.

Figure 6 presents the oxygen intrusion rates (showing normalized oxygen % concentrations) for both bags, charted over the duration of the experiment. The Nalophan bag displayed a slightly faster rate of oxygen intrusion than the Tedlar E bag. This test does not distinguish between permeation of the bag material and leaking from the bag fitting, seams, or elsewhere.

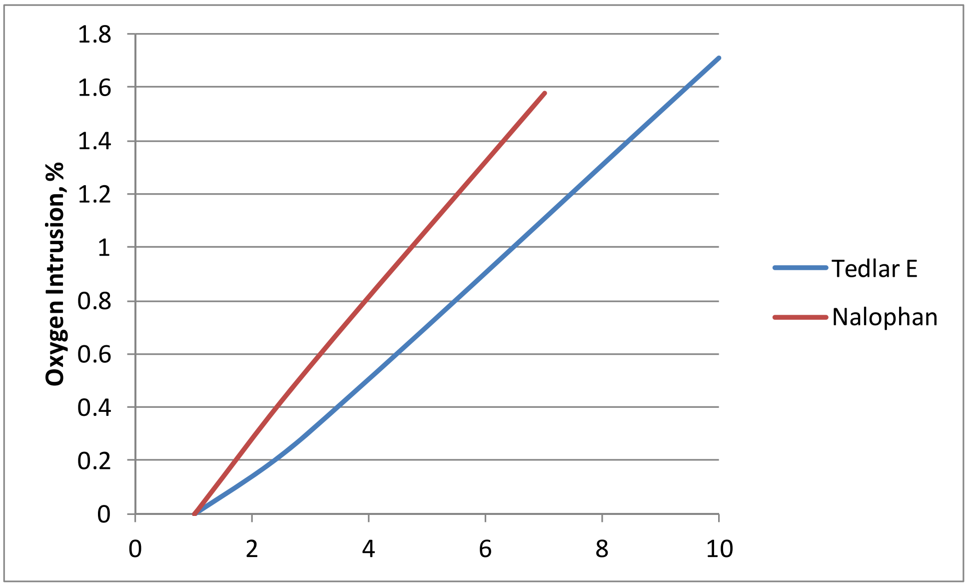

Figure 6. Oxygen Intrusion Rates for Tedlar E and Nalophan Bags

CONCLUSIONS

There is no "gold standard" currently available for sample bag films; each bag film and bag configuration has its benefits and drawbacks. The end user must decide which bag material type and configuration is appropriate for their sampling event and quality objectives. This paper investigated the characteristics of common sampling bags used in the odor assessment field, examining factors such as film cleanliness, inherent odor, and permeability. Overall, there is a need for oversight and/or testing in a standardized way to challenge the bags in a controlled environment and characterize the artifacts, to assist users in selecting a bag that suits their needs.

RECOMMENDATIONS/FUTURE WORK

Overall, a bag film with negligible quantities of inherent target analytes and no intrinsic odor in the bag is desirable. If the bag material does contain artifacts, they should be of low concentration. The bag should be impermeable (especially for sulfur-containing compounds) for a minimum period of 24 hours. The bag fitting should be as small as possible as to minimize any potential off-gassing of target compounds or large inherent artifacts.

The authors of this paper recommend that a standardized procedure be developed for assessing the performance of gas sample bags for various odor related applications. Testing would include factors such as evaluation of analyte stability and recovery (not addressed in this paper), determination of background odor/chemical artifacts, permeation, etc. Table 4 presents recommended testing procedures.

Table 4. Suggested Standardized Tests for Sample Bag Performance

Test Parameter	Test Method	Holding Times	Test Modes
Odor testing	EN13725:2003	1, 4, 8 , 12, 24, 30 hours	Preconditioning options
VOC testing-artifacts & recovery	EPA TO-15 and/or EPA TO-17	24-72 hours	
Sulfur gas testing-artifacts & recovery	ASTM D5504	24 hours	
Permeability testing (oxygen)	EPA 3C	24-72 hours	

All the tests in Table 4 above would be performed by filling the bags with a neutral/high purity gas such as zero air, odor free air, etc.

Future work should also include film reactivity, fitting style, and determining an “acceptable” range of recovery of odorous compounds of interest, possibly via the input of an industry workgroup or roundtable.

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