A Model for Estimation of the effect of residual odour in sampling bags on odour concentration measurement

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Abstract: Based on the European standards, an odor concentration can be expressed as a concentration of the European Reference Odour Mass (EROM). Thus, a "very accurate" odor concentration measurement must be able to be expressed as a continuous value. By comparing the "very accurate" odor concentration measurement and the odor concentration measurement by the standard method, a mathematical model is developed to describe the effect of background odor from manufactured odor sampling bags or residual sample odors from a used sample bag on the sample’s odor concentration measurement at different confident levels.

Keywords. Odor, sample, bag, model, Tedlar™, polyethylene, PVF, background, residual, error.
Introduction

The most widely used sample bags for collecting odorous air samples are Tedlar™ (polyethylene, PVF), because they are considered to be inert to a wide range of chemicals and have a relatively low cost. Tedlar™ is the industrial standard in the United States and is the preferred sample container (bags) by the European standard (CEN, 2003) for storing odorous air samples. However, Tedlar™ is not a perfect material for storing odors. Scientists have found evidence that Tedlar™ adsorbs and desorbs some chemical species (McGarvey and Shorten, 2000; van Harreveld, 2003). McGarvey and Shorten (2000) found that Tedlar™ bags readily absorbed low molecular alcohols and significantly absorbed aromatic compounds, and the absorption could not be removed by simple flushing. They concluded that Tedlar bags could not be reliably reused and even their initial use should be limited to short holding period. Keener et al. (2002) reported that Teldar™ bags emit significant amount of acetic acid and phenol and adsorb indole and statole. Koziel et al. (2004) compared 5 types of air bags and found all new bags had chemical impurities of different species at varied magnitudes, e.g. new commercial Tedlar™ bags had measurable concentrations of DMAC and phenol, while foil bags had measurable concentrations of acetic, propionic, butyric, valeric and hexanoic acids. Parker et al. (2003) reported that the background odors in new Tedlar™ bags have a manufacture background odor typically ranging from 20 to 60 OU_E /m³. Background odor concentrations over 100 OU_E /m³ from new Tedlar™ bags have been noted in some batches in the CEN standard due to release of solvent from the film (CEN, 2003). Due to its cost and strength, Tedlar™ bags are reused in some cases. Odorous air samples remain residuals on the surface of the used sample bags. The background odors from manufactured sample bags or odour residuals of samples may cause a measurement bias. The objective of this study is to develop a model to estimate the impact of the background odors in sampling bags on the odor concentration measurement of source samples.
Development of a model to estimate the impact of background odors on the odor concentration measurement

The standard method for the odor concentration measurement by both ASTM (ASTM E679-91, 1991) and CEN (CEN, 2003) standards is designating an odorous air sample to an olfactometry consisting of a qualified human panel and an olfactometer. The sample is initially diluted to a level where none of the panelists can detect the odour. Then the concentration of the sample is increased by a factor of 2 until 50% of the panel can detect the odour. Thus, the resulting odor concentration measured with the standard method is a discrete value. To simplify the methodology discussed, assume that all members in the panel have the same sensitivity. Then, odor concentrations measurement by the standard method will be discrete and differentiated by a factor of 2 for the sequential measurements. An odor concentration measurement can be expressed as a Dilution Factor to Detection Threshold (DTs) in the ASTM standard (ASTM E679-91, 1991) or a concentration of the European Reference Odour Mass (EROM) in the CEN standard (CEN, 2003). When expressed in EROM, the “very accurate” odor concentration measurement of a sample can be expressed as a continuous value. The relationship of a sample’s “very accurate” odor concentration (a continuous value) and the odor concentration measured with the standard method can be expressed as:

\[ S = C_0 \cdot 2^N + R_S \]  

(1)

where:

- \( S \) = a sample’s “very accurate” odor concentration (a continuous value);
- \( C_0 \cdot 2^N \) = a sample’s odor concentration measured with the standard method (a discrete value);
- \( C_0 \) = the lowest scale of the olfactometry system,
- \( N \) = a power coefficient representing a dilution level;
\( R_S \) = the difference between a sample’s “very accurate” odor concentration and the odor concentration measurement by the standard method, \( 0 \leq R_S < C_0 \cdot 2^N \).

Similarly, a “very accurate” odor concentration measurement for the background odor of a sample airbag can be expressed as:

\[
B = C_0 \cdot 2^M + R_b \quad \text{………………………………………………………………………………… (2)}
\]

where:

\( B \) = a “very accurate” odor concentration for a sample bag’s background odor (a continuous value),

\( C_0 \cdot 2^M \) = the odor concentration for a sample bag’s background odor measured with the standard method (a discrete value),

\( C_0 \) = the lowest scale of the olfactometry system,

\( M \) = a power coefficient representing a dilution level;

\( R_b \) = the difference between the “very accurate” odor concentration for a sample bag’s background odor and the odor concentration measurement by the standard method, \( 0 \leq R_b < C_0 \cdot 2^M \).

The interaction of different odorant chemical species is very complicated and far from fully understood. When mixed together, the odor strength of different odorants may be enhanced or suppressed (ref ). To simplify the question discussing, an assumption is made that only summation effect exists between the sample odor and the bag background. This assumption is conservative for the case that the sample odor and the bag background is not same, which makes the result of this study secure. Thus, the odor concentration measured with the standard method will be same for a sample with or without a background odor from the sample bag if

\[
S + B < C_0 \cdot 2^{N+1} \quad \text{………………………………………………………………………………………….. (3)}
\]
Equation (3) indicates a condition in which the odor concentration of a sample is stronger after adding a background odor from the bag it is stored than that of the odor concentration of a sample only, but not one dilution level higher than that of the sample only.

Substitute S and B with equation (1) and (2), then

$$R_S + C_0*2^M + R_b < C_0*2^N$$

...(4)

Assume that both $R_S$ and $R_b$ are evenly distributed within their ranges. The probability of $R_S$ within the range of 0 to $(1-\alpha)*C_0*2^N$ is $1-\alpha$. Similarly, the probability of $R_b$ within the range of 0 to $(1-\alpha)*C_0*2^M$ is $1-\alpha$, where $(1-\alpha)$ is the statistical confidence level. Substitute $R_S$ and $R_b$ with the largest value in their ranges at the $(1-\alpha)$ confidence level to equation (4):

$$(1-\alpha)*C_0*2^N + C_0*2^M + (1-\alpha)*C_0*2^M < C_0*2^N$$

...(5)

Thus:

$$N > M + \text{Int}\left\{\frac{\log(2-\alpha)-\log\alpha}{\log 2}\right\}$$

...(6)

Let: $N_{\text{MIN}} = M + K$, thus:

$$K = \text{Int}\left\{\frac{\log(2-\alpha)-\log\alpha}{\log 2}\right\}$$

...(7)

Where: $K$ is the minimum power coefficient applicable to equation (3).

Equation (7) indicates that a sample's odor concentration measurement will be not impacted by the bag background odor at the $(1-\alpha)$ confidence level when the sample's odor concentration is at least $K$ dilution levels higher than that of the bag background odor.

The power coefficient $K$ varies, as shown in Figure 1, with the confidence level of $(1-\alpha)$. When $\alpha=0.01$, $k=7$ ($2^7 =112$). This indicates that when a sample's odor concentration is 112
times larger than that of the sample bag background odor, the odor concentration measurement for a sample with or without sample bag background odor will be same at a 99% confidence level. Similarly, when $\alpha=0.04\sim0.05$, $k=5$ ($2^5=32$); When $\alpha=0.07\sim0.11$, $k=4$ ($2^4=16$); When $\alpha=0.12\sim0.21$, $k=3$ ($2^3=8$). The CEN standard requires that sample bags' background odor concentration should be at least a factor $2^5$ lower than that of the samples that will be introduced to the bags. This requirement, as discussed above, is based on 95% of confidence level.

![Graph of K vs. $\alpha$](image)

**Figure 1 K vs. $\alpha$**

**Measurement of bag background odors**

Experiments are conducted to measure background odors from new commercial Tedlar bags (SKC Inc., USA), in-house made new Tedlar bags, and used bags in the olfactometry laboratory at the University of Alberta. Used sample bags are purged 150 times with a programmed bag cleaning device that withdraws and adds air to the sampling bag. With the same device, new bags are purged 10 times prior to test. The experiment results are summarized in Table 1.
Table 1. Background odors from new and used bags

<table>
<thead>
<tr>
<th>Bags</th>
<th>Flushes</th>
<th>Measurements</th>
<th>Range (OUE /m3)</th>
<th>G. Mean (OUE /m3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SKC</td>
<td>10</td>
<td>30</td>
<td>8~71</td>
<td>19</td>
</tr>
<tr>
<td>In-house</td>
<td>10</td>
<td>30</td>
<td>6~71</td>
<td>17</td>
</tr>
<tr>
<td>Used</td>
<td>100</td>
<td>22</td>
<td>15~40</td>
<td>26</td>
</tr>
</tbody>
</table>

Based on equation (7), bag background odors will not impact sample measurement results at the 95% confidence level when odor concentrations of samples are equal or higher than 608 (OUE /m3) for new SKC Tedlar bags (19x2^5=608), 544 (OUE /m3) for new In-house Tedlar bags, and 832 (OUE /m3) for used Tedlar bags. This type of samples can only be found within a swine barn or close to a manure earth storage. For collecting samples with low concentrations, the confidence level will be decreased. Thus, development of methodology for further cleaning sample bags is necessary.

**Conclusions**

A mathematical model is developed in this study for estimation the impact of the background odors on sample measurement results at different statistical confidence level. Experiment is conducted to measure background odors from new and used air bags. Based on the calculation result with the model developed, to get rid of impact of bag background odors, odor concentrations of samples should be equal or higher than 608 (OUE /m3) for new SKC Tedlar bags, 544 (OUE /m3) for new In-house Tedlar bags, and 832 (OUE /m3) for used Tedlar bags. For collecting samples with low concentrations, the confidence level will be decreased. Thus, development of methodology for further cleaning sample bags is necessary.

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