THE ODOR PERCEPTION OF KEY DEGRADATION PRODUCTS OF POLYAMIDE 6.6

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Abstract

Psychophysical research on indoor air has not focused on the odor of degradation products of polymers in building materials, e.g. the polymer Polyamide 6.6. Three of its odorous degradation products, cyclopentanone, pentanoic acid, and 2-methyl-pyridine, were measured in the form of single chemical compounds and their four mixtures. The results from 15 participants’ scaling of perceived odor similarity and ranking of odor preference showed that the cyclopentanone odor is masked by the other odor(s) of its mixtures. A new odor quality was formed when pentanoic acid and 2-methyl-pyridine were mixed. The three chemical compounds, thus, provided for four unique odor qualities, as revealed in a PCA. Moreover, the odor intensity ranks confirmed intermediacy of odor mixtures relative to these same four unique odor qualities. Our results confirm the importance of degradation products of polyamide 6.6 as contributors to indoor air quality.

This experiment is grounded in research on the “sick building syndrome” (SBS), (Berglund & Gidlöf Gunnarsson, 2000). In 1983, WHO introduced the concept SBS as a set of different symptoms (WHO, 1983). The indoor climate has been suspected to be the main cause. Sick buildings have been defined as modern buildings where occupants show symptoms similar to those caused by formaldehyde exposure, although the measured formaldehyde concentrations are usually too low to cause such symptoms. So far, research has failed to identify why these symptoms of SBS occur. Many different causes have been and still are proposed. The main cause of the symptoms is believed to be environmental, even though psychological factors may influence SBS as well (Berglund & Johansson, 1996; Norbäck, et al., 1990; Crawford, et al., 1996; Berglund & Gidlöf Gunnarsson, 2000; Berglund & Zheng, 2002).

The psychophysical approach to SBS has focused on the quality of the indoor air as regards odor, sensory irritation and acceptability as a function of concentration of volatile organic compounds (VOC). A main interest has been what VOCs may cause human sensory irritation (see e.g. Nielsen, et al., 2007). Although pattern analysis of VOC concentrations has shown that critical patterns can be identified in sick or healthy buildings, these patterns do not necessarily cause adverse or positive sensory reactions, respectively (Berglund, 1991).

In the present experiment, it is stressed that VOCs of other kind than those earlier studied could be capable of causing SBS, particularly semi-volatile compounds (SVOC). These are, for example, emitted from polymers in aged building materials. Together with wood, different kinds of polymers are the most common among the building materials. Many textiles are also made of polymers. Polyamide 6.6 (PA66) is, for example, one of the most common polymers in our indoor environments, used in e.g. carpets.
In current quality control of building materials, the VOCs emitted from new materials are measured and controlled short after the production of the materials. Conversely, many new compounds are formed and emitted from the materials during their use and also simply due to ageing (Lundgren, et al., 1999). Polymeric building materials are organic materials that will interact continuously with factors in their environment (i.e. UV-light, thermal oxidation, and chemical interactions with e.g. ozone). These interactions result in chemical degradation of the materials, and cause formations and emissions of volatile (VOC) and semi-volatile (SVOC) degradation products (Albertsson, et al., 2006).

The goal is to research the odor perception resulting from three of the degradation products that are common from the polymer PA66. In order to better understand how degradation products contribute to the indoor air quality of nonindustrial buildings, we measured the odor quality, the odor intensity, and preference of the products.

**The Experiment**

**Participants**

The 15 participants (7 men & 8 women) were between 20-30 years old. They were screened for pregnancy and tobacco use, and were required to be in good health and not have a cold. All participants were residents in the Greater Stockholm area. They received monetary compensation for their participation.

**Stimulus Materials & Procedure**

The degradation products of the polymer PA66 were extracted by headspace solid-phase microextraction (HS-SPME) after up to 1200 h of thermo-oxidation at 100°C. Chemical compounds were identified by gas chromatography-mass spectrometry (GC-MS), (Gröning & Hakkarainen, 2001). Out of the 18 identified degradation products of the polymer, three key degradation products were selected as stimuli, because they had different chemical structures and documented odor, Table 1.

The three selected degradation products were transferred with a Hamilton micro-syringe into a 250 ml amber glass jar and capped with aluminum foil. In order to exceed the Odor Threshold Volume (OTV), but still be well below stipulated Threshold Limit Values (TLV), a concentration of 1 ppm (corresponding to a volume of 0.5 µl) was selected. Due to its higher OTV and TLV, cyclopentanone was selected to be 2 ppm. Through preliminary odor tests, where the experimenters sniffed all stimuli, the three chemical compounds were perceived to be approximately of the same odor intensity. The experimental odor stimuli (three single components and their four possible mixtures) are presented in Table 2.

The duration of the experiment was 40-50 min for each participant. Three tasks were conducted:

**Task 1** was to compare all possible stimulus samples in pairs, and scale their similarity in odor quality on a scale from 0-100, where 0 means “not similar at all” and 100 means “totally similar”. The participants scaled the 49 pairs of the full matrix once (each sample in a pair was presented both first and second, e.g. AB–AC and AC–AB). To begin with, similarity was scaled of a selected set of 7 pairs in a ”training session”. In their similarity judgments, participants were asked to disregard differences in perceived odor intensity and try to focus on odor quality. To avoid odor adaptation, short breaks were always taken after every 7th pair.

**Task 2** was to rank the 7 different stimuli according to their perceived odor intensity, from lowest to highest intensity.

**Task 3** was to rank the 7 different stimuli according to their preference, from lowest preference to highest preference.
Table 2. Three single chemical components and their possible mixtures.

<table>
<thead>
<tr>
<th>Sign</th>
<th>Single component</th>
<th>Sign</th>
<th>Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>cyclopentanone</td>
<td>AB</td>
<td>cyclopentanone and pentanoic acid</td>
</tr>
<tr>
<td>B</td>
<td>pentanoic acid</td>
<td>BC</td>
<td>pentanoic acid and cyclopentanone</td>
</tr>
<tr>
<td>C</td>
<td>2-methyl-pyridine</td>
<td>AC</td>
<td>2-methyl-pyridine and cyclopentanone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ABC</td>
<td>cyclopentanone, pentanoic acid and 2-methyl-pyridine</td>
</tr>
</tbody>
</table>

Results

Similarity in odor quality

Overall, the participants “test-retest” reliability of the similarity scales was estimated and found to be good. Out of 15 participants, 13 produced similarity values of the two half matrices (2x21 cells) that were significantly correlated (r > 0.7, p<0.05).

The arithmetic mean of the similarity values was calculated for the two half matrices (e.g. AB–AC and AC–AB), and a symmetric similarity matrix for the group was formed. A Principal Components Analysis (PCA) was performed and the four-component solution explains 82.3 % of the total variance. These results are shown in Figure 1. The seven odor stimuli “form a circle”, which indicates that the perceived odor intensity of the stimuli was invariant and that the participants actually focused on and reported the perceived odor quality, not the odor intensity per se (see further Ekman & Engen, 1962; Engen, 1964).

Figure 1 shows that four different odor qualities were recovered in the PCA solution (Q1–Q4). Q1 represents the odor quality of stimulus A, Q2 of stimulus B, Q3 of stimulus C, and Q4 of stimulus BC. If existing in mixtures, the odor quality of stimulus A seems to be submerged in the quality of the other odor(s). Thus, Figure 1 shows that the mixtures containing A are perceived very similar to the other mixture component(s) but for A, i.e. AC=C, AB=B, ABC=BC. This is also apparent in the ten pairs with the highest perceived similarities. In this case, 7 pairs refer to the case when every stimulus is compared to itself (i.e. A–A, B–B, etc. ...ABC-ABC) and the 3 other pairs when compared to mixtures with A: ABC-BC, AC-C, and AB-B.

Table 1. Estimated odor and sensory irritation threshold for three chemical compounds selected as stimuli.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Chemical structure</th>
<th>OTV</th>
<th>TLV/TWA (ppm)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methyl-pyridine</td>
<td><img src="image" alt="Pyridine structure" /></td>
<td>43 ppb(^1)</td>
<td>5(^2)</td>
<td>1</td>
</tr>
<tr>
<td>pentanoic acid</td>
<td><img src="image" alt="Pentanoic acid structure" /></td>
<td>5 ppb(^1)</td>
<td>5(^3)</td>
<td>1</td>
</tr>
<tr>
<td>cyclopentanone</td>
<td><img src="image" alt="Cyclopentanone structure" /></td>
<td>1.7 ppm(^1)</td>
<td>25(^4)</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^1\)Devos, M., et al. (1990).
\(^2\)MSDS, www.sciencelab.com, USA
\(^4\)MSDS, www.sigmaaldrich.com
Perceived odor intensity and preference

The 15 participants’ average ranks of perceived odor intensity and of preference were calculated. Figure 2 shows that the average rank of perceived odor intensity and the average rank of preference are not well correlated statistically ($\tau = -0.4$, $p > 0.1$, $n=7$). Notably, the odor of stimulus A was ranked to be lowest in odor intensity, but it was ranked highest in preference.

In the plot of odor preference against perceived odor intensity, in Figure 2, all the 7 odor stimuli formed clusters similarly as in Figure 1. The odor intensity is ranked lower when A is included in the mixtures. This indicates that the odor of stimulus A is not only submerged in the quality of the other odor(s) in the mixtures, but also makes the odor intensity of the mixtures lower. However, since the participants were only to rank odor intensity and preference, the results cannot be interpreted to represent quantities of perceived odor intensity and of preference. The participants expressed that it was a difficult task to rank the odor stimuli. And, since the stimuli are clustered together similarly in Figure 1 and 2, it is most accurate to interpret Figure 2 as clusters containing close rank values.

Discussion

The participants had been asked to scale the similarity of pairs of odor stimuli and then focus on odor quality and try to disregard potential odor intensity differences. This may have succeeded because according to Figure 1, the participants performed surprisingly well in the similarity task. The circle in Figure 1 shows that similarity in odor quality was considered rather than similarities in odor intensity (cf. Figure 2; e.g., B and AB vs. C and AC would have been expected to be approximately equal in intensity). Moreover, scales of similarity in
odor intensity would not place the 7 odor stimuli at the periphery of the circle (cf. Ekman & Engen, 1962; Engen, 1964).

As mentioned before, the odor of stimulus A might have been submerged in the quality of the other odor(s) of a mixture. This seems to be exemplified in Figure 1 where the four principal qualities (Q1-Q4) are represented by the odors of stimulus A, B, C and BC. Stimulus B and C produce a new odor quality (BC, representative of Q4). The odor qualities of mixtures containing stimulus A (AB, AC, ABC) are found at nearly the same positions in the PCA solution as the stimuli without stimulus A (B, C, BC), i.e. AB=B, AC=C, ABC=BC.

The odor of stimulus A would have no influence on odor quality of its mixtures. This is validated in Figure 2 where perceived odor intensity is plotted against preference. If stimulus A would have an influence on the odor quality when being in a mixture, it would most likely also have an influence on preference, e.g. generate a lower preference rank. However, the clusters in Figure 2 show that the mixtures containing stimulus A cannot be separated from the corresponding odors without A. For example, ABC has a lower average rank than BC; AB has a higher average rank than B; and AC has a lower average rank than C. Since the participants were forced to rank the preference, these results indicate that stimuli containing A are perceived most similar to those not containing stimulus A.

Indeed, Figure 2 shows that stimulus A seems to produce a lower intensity of a mixture compared to when the mixture does not contain stimulus A. These ranks of odor intensity follow the same principle as predicted by the vector model for perceived odor intensity (Berglund, 1974; Berglund, et al., 1976; see also Moskowitz, 1976). Notably, mixtures containing odor component A (AB, AC, ABC) are in the intensity-preference plot positioned very close in rank to its other component odors (B, C, or BC). It could be a coincidence that the mixtures containing A are ranked to have lower odor intensity than those without A. As in the preference ranks, the only certain fact is that the mixtures containing A is positioned in the same clusters as the versions without A, because they are perceived as similar.

Our results bring further understanding to how mixtures of odors are perceived. The odor components of one mixture are perceived as a homogenous perception in which odor quality and odor intensity blend. Some components form a new odor quality (e.g. component odor B + component odor C = component odor BC), whereas other components do not contribute to a new odor quality (e.g. component odor A + component odor B = component odor B), (cf. Moskowitz, 1976). The odor perception of chemical mixtures is clearly complex, and needs to be further researched. In the future, it would be interesting to add even more degradation products of PA66 and create mixtures of 4 and/or 5 odor components.

Acknowledgments

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References


