Key odorants in the artificial leather of car interiors

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Abstract

Application of an aroma extract dilution analysis (AEDA) to the volatiles isolated from a PVC based automotive artificial leather with representative odour characteristics by solvent extraction and solvent-assisted flavour evaporation (SAFE) revealed 22 odour-active compounds in the flavour dilution (FD) factor range of 4 to 64. The three compounds with the highest FD factor of 64 were plastic-like, pungent smelling 1-hexen-3-one, mushroom-like smelling 1-octen-3-one, and plastic-like smelling acetophenone. Quantitation of these three compounds was accomplished by stable isotope dilution assays (SIDAs). On the basis of the obtained concentrations and oil as matrix, an odour reconstitution model was prepared that clearly reflected the typical odour of the artificial leather. Omission tests in combination with quantitative descriptive analyses (QDAs) showed that 1-hexen-3-one contributed most to the overall odour, but 1-octen-3-one and acetophenone modified the sensory impression of the mixture. Quantitation of 1-hexen-3-one in a variety of other PVC materials, including baby toys, inflatable beach toys, and a flexible PVC tubing for beverage industry applications finally showed that the problem of odour-active amounts of 1-hexen-3-one is not limited to artificial leather.

Introduction

The interior of new cars often exhibits a more or less strong odour. Many modern consumers consider this "new car odour" as unpleasant and it has been shown that it may have a huge influence on the purchase decision [1]. As a consequence, the automotive industry currently tries hard to reduce the interior odour towards an almost odourless new car. A targeted minimization approach, however, requires knowledge of the causal compounds and their source materials. So far, little data has been published on this topic. Polyurethane foams included in headliners and floor carpets have been identified as source of fishy smelling compounds such as benzyldimethylamine (BDMA) and pentamethyldipropylenetetramine (PMDPTA) [2, 3]. The role of PVC materials, however, was yet unclear.

The aim of the present study was to get an insight into the major compounds contributing to the odour of PVC based artificial leathers. Such materials are widely used in the automotive industry for upholstery and interior covers. On the one hand, artificial leathers are very versatile, allowing for a wide range of optical (colour, gloss) and haptic adjustments. On the other hand, they are very resistant against scratching and aging [4]. However, PVC materials are known to be highly odorous and numerous volatiles emitted from PVC have been characterized including plasticizers, solvent residues, unreacted monomers, and secondary degradation products [5]. However, little information is available on the odour activity of volatiles emanated from PVC materials [6, 7].

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Experimental

Materials

The automotive artificial leather was provided by a German car manufacturer. It was ~1 mm thick and consisted of a main layer of expanded PVC, which was glued to a polyester fabric on the back side and covered by a layer of dense PVC and a transparent lacquer film on the front side. A flexible PVC tubing for industrial beverage handling was obtained from ESSKA.de (Hamburg, Germany). All other PVC products were purchased from local shops in Freising, Germany. For analyses, the materials were cut into small pieces by scissors or knives and further crushed by use of a cryomill (Retsch, Haan, Germany) at −196 °C.

Reference odorants

1-Hexen-3-one and acetophenone were purchased from Sigma-Aldrich (Taufkirchen, Germany). 1-Octen-3-one was from Alfa Aesar (Karlsruhe, Germany).

Workups

Solvent extraction was accomplished by using dichloromethane. Extraction time was 72 h. Light was excluded during extractions. Non-volatile material was removed by solvent-assisted flavour evaporation (SAFE) [8]. SAFE distillates were concentrated by using a Vigreux column (50 cm × 2 cm). For the volatile isolate used for gas chromatography-olfactometry and aroma extract dilution analysis (AEDA), 150 g material and 1 L solvent were used and the distillate was concentrated to 1 mL.

Gas chromatography-olfactometry (GC-O)

GC-O was performed by using a gas chromatograph equipped with a cold-on-column injector and a DB-FFAP column, 30 m × 0.32 mm i.d. × 0.2 µm film thickness, or a DB-5 column, 30 m × 0.32 mm i.d. × 0.2 µm film thickness (both J&W, Agilent Technologies, Waldbronn, Germany). The eluate of the column was split 1:1 using a glass splitter and the volatiles were simultaneously transferred to an FID and a tailor-made sniffing port [9]. AEDA was done as detailed in [10].

Quantitations

These were accomplished by stable isotope dilution assays using the following stable isotopically substituted analogues of the target compounds as internal standards: ($^{2}H_2$)-1-hexen-3-one [11], ($^{2}H_4$)-1-octen-3-one [12], and ($^{2}H_5$)acetophenone (Sigma-Aldrich). Work-up was done as detailed above. Internal standards were added at the beginning of the extraction period. Selective recording of analytes and standards was done by GC-MS analysis using a GC×GC-TOFMS system [13] and concentrations were calculated as detailed in [13].

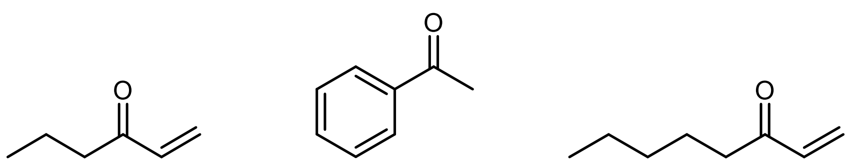
Sensory tests

These were performed by a trained panel of males and females, aged 23-36. Odour threshold values were determined according to the ASTM method [14]. Odour reconstitution models were prepared in odourless sunflower oil. Descriptors used in the QDAs were collected by a preceding free choice profiling test. During QDAs, descriptors were defined by reference solutions of the following odorants: 1-hexen-3-one (pungent, plastic), 1-octen-3-one (mushroom), (*E*, *Z*)-2,4-decadienal (fatty), nonanal (citrusy, soapy), and ethyl 2-methylbutanoate (fruity). For each descriptor the intensity was rated on a seven-point scale using 0.5 increments and a range from 0 to 3 with 0 = not detectable, 1 = weak, 2 = moderate, and 3 = strong.

Results and discussion

Odorant screening by GC-O and AEDA

Automotive artificial leather with a characteristic odour was obtained from a car manufacturer. The volatiles were isolated using solvent extraction and SAFE. GC-O of the concentrated volatile fraction using an FFAP column resulted in 22 odour-active zones. Application of an aroma extract dilution analysis revealed flavour dilution (FD) factors in the range of 4 to 64 (data not shown). Ten odorants showed an FD factor of 4, four showed an FD factor of 8, and five showed an FD factor of 16. The remaining three compounds exhibited an FD factor of 64, thus were the most potent odorants in the extract. Among them, two compounds showed an odour reminiscent of plastic and the third compound smelled like mushrooms. Comparison of their odour qualities and their retention indices on the FFAP column with published data suggested them to be 1-hexen-3-one, acetophenone, and 1-octen-3-one. These structure assignments were confirmed by GC-O analysis of reference compounds in parallel to the artificial leather extract using the FFAP column as well as a DB-5 column and by GC-MS analysis (Figure 1).



1-hexen-3-one	**acetophenone**	**1-octen-3-one**
odour: plastic-like, pungent	odour: plastic-like	odour: plastic-like
RI_{DB-5}: 775; RI_{FFAP}: 1093	RI_{DB-5}: 1312; RI_{FFAP}: 1654	RI_{DB-5}: 979; RI_{FFAP}: 1293

Figure 1: Most potent odorants (FD 64) in the automotive artificial leather

Quantitation of 1-hexen-3-one, 1-octen-3-one, and acetophenone

Quantitation of 1-hexen-3-one, 1-octen-3-one, and acetophenone in the automotive artificial leather was accomplished by stable isotope dilution assays using ($^2H_2$)-1-hexen-3-one, ($^2H_4$)-1-octen-3-one, and ($^2H_5$)acetophenone as internal standards. Results revealed concentrations of 0.40 µg/kg for 1-hexen-3-one, 41.0 µg/kg for 1-octen-3-one, and 5600 µg/kg for acetophenone (Table 2). Comparison of these data with the odour threshold values of the three compounds in water, which were determined to be 0.00069 µg/kg (1-hexen-3-one), 0.016 µg/kg (1-octen-3-one), and 26 µg/kg (acetophenone), confirmed their high odour potency.

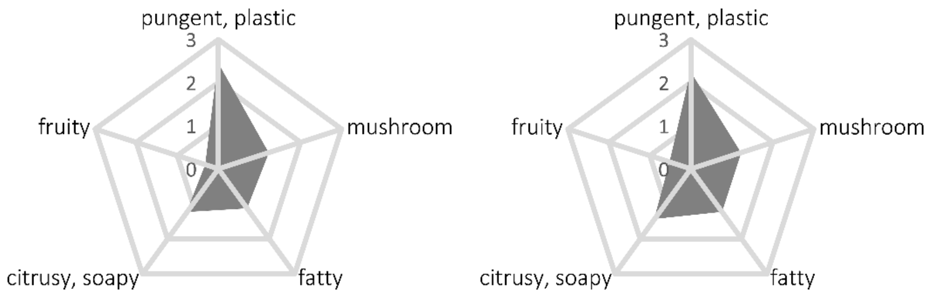
Table 1: Concentrations of the major odorants in the automotive artificial leather

Odorant	*Odour*	*Concentration (µg/kg)*[a]
1-hexen-3-one	plastic-like, pungent	0.40 ± 0.01
acetophenone	plastic-like	5600 ± 26
1-octen-3-one	mushroom-like	41.0 ± 1.0

[a] mean of triplicates ± standard deviation

Odour reconstitution and omission experiments

On the basis of the quantitative data detailed in Table 1, a reconstitution model was prepared from the pure compounds and oil as matrix. The model was compared orthonasally with the artificial leather in a QDA. Results showed a good agreement of the odour profiles of the original material and the model (Figure 2).



artificial leather **odour reconstitution model**

Figure 2: Orthonasal odour profiles of the artificial leather (left) and the odour reconstitution model (right) as obtained by QDA

To get a deeper insight into the individual odour contribution of the three odorous components, omission tests were performed. Omission of one component resulted in three binary mixtures that were compared to the complete model in triangle tests. The three tests revealed significant differences, indicating that all three compounds contributed to the odour of the mixture (Table 2). However, omission of 1-hexen-3-one was detected with higher significance (p = 0.00004) than omission of 1-octen-3-one (p = 0.01) and acetophenone (p = 0.005). Thus, 1-hexen-3-one obviously played a key role for the odour of the artificial leather.

Table 2: Results of omission tests applied to the artificial leather odour reconstitution model

Odorant omitted	*Correct answers*	*p value*	*Significance*
1-hexen-3-one	26/40	0.00004	***
acetophenone	26/50	0.005	**
1-octen-3-one	25/50	0.01	**

Results of the triangle tests were confirmed by QDA of the three binary mixtures and by QDA of models containing only one of the three compounds (Figure 3). Omission of 1-hexen-3-one clearly reduced the plastic-like note. On the other hand, the model containing only 1-hexen-3-one (Figure 3, upper left) showed a profile that was already quite close to the profile of the tertiary mixture (Figure 2, right).

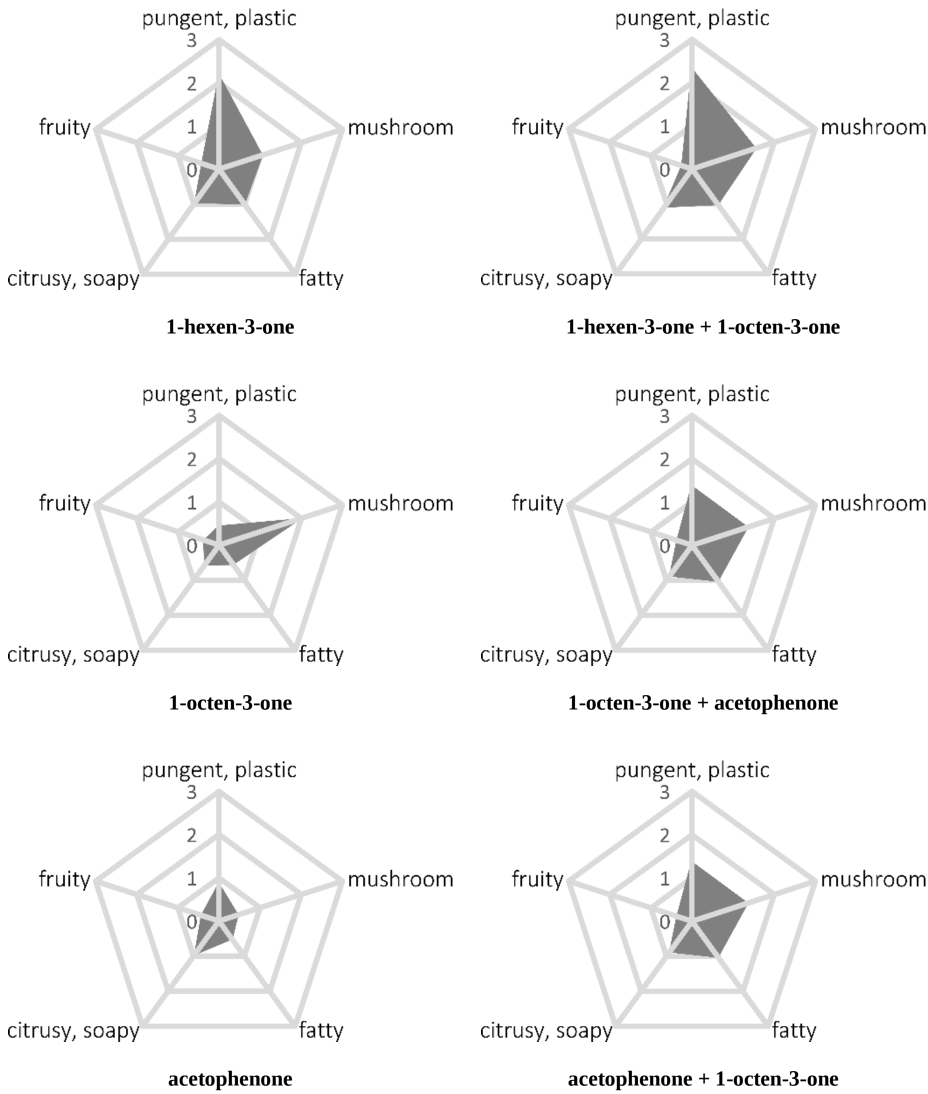


Figure 3: Orthonasal odour profiles of single compound models (left) and binary mixtures (right) obtained by omitting one or two compounds from the complete artificial leather odour reconstitution model

Concentrations of 1-hexen-3-one in other PVC products

To put the 1-hexen-3-one concentration found in the automotive artificial leather into perspective, we quantitated the compound in various other PVC products. Among them was a small water fun toy in the form of a dolphin, a baby toy in the form of a dinosaur, two inflatable beach balls, swimming aids in the form of inflatable armbands, and a PVC tubing intended for industrial beverage handling. Results (Table 3) showed concentrations in the range of 0.621 to 11.8 µg/kg. Thus, the 1-hexen-3-one concentration in all analysed materials was higher than the concentration previously determined in the automotive artificial leather. The highest concentration was found in an inflatable beach ball, but high concentrations were also determined for the baby toy in the form of a dinosaur (10.1 µg/kg), another inflatable beach ball of different brand (7.34 µg/kg), and the beverage tubing material (6.93 µg/kg). Clearly lower 1-hexen-3-one concentrations were found in the inflatable armbands (1.81 µg/kg) of a well-known brand and the rather highly priced water fun toy in the form of a dolphin (0.621 µg/kg).

Table 3: Concentrations of 1-hexen-3-one in various PVC products

PVC material	*Concentration of 1-hexen-3-one (µg/kg)*[a]
water fun toy dolphin	0.621 ± 0.033
baby toy dinosaur	10.1 ± 0.8
inflatable beach ball I	7.34 ± 0.25
inflatable beach ball II	11.8 ± 1.1
inflatable armbands (swimming aids)	1.81 ± 0.08
beverage tubing	6.93 ± 0.34

[a] mean of triplicates ± standard deviation

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