

Research Article

Odor-Active Compounds in Flexible Polyurethane Materials

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Received 25 January 2024; Revised 17 April 2024; Accepted 23 April 2024; Published 29 May 2024

Academic Editor: Faming Wang

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Flexible polyurethane (PU) materials find extensive use in upholstery, mattresses, and automobiles, yet the molecular background of their odor is still inadequately understood. To address this gap, we aimed at identifying major odorants in fifteen samples representing eight common types of flexible PU materials. The volatiles isolated from the samples were subjected to activity-guided screening via gas chromatography-olfactometry. Structures were assigned by comparing odor, retention data, and mass spectra to those of authentic reference compounds. This approach led to the identification of 50 odorants, 39 of which had not previously been described in PU. The odorants belonged to a wide range of compound classes, including tertiary amines, fatty acid oxidation products, short-chain aldehydes, trioxocanes, pyrazines, aromatic hydrocarbons and heterocycles, chlorinated compounds, phenol derivatives, fragrance compounds, and nitriles. For some odorants, further insights were gained into their origins and release behavior. For example, the odorous 1,4-dimethylpiperazine had been used as a catalyst, and propanal was shown to be not only a PU odorant but also the precursor of an odor-active trioxocane. Additionally, the quantitation of acetaldehyde and propanal suggested their continuous regeneration from the samples. While the sources of other compounds still have to be clarified, the data obtained in this study could pave the way for odor reduction strategies in the production of PU materials, ultimately resulting in an improved odor and consumer experience.

1. Introduction

Polyurethane- (PU-) based polymers are the fifth most produced type of plastics worldwide, with a global production volume of over 20 million metric tons per year [1]. The polyurethane backbone is formed in the polyaddition reaction of polyisocyanates and polyols. In the presence of water, hydrolysis of the polyisocyanates generates CO₂ and amines. CO₂ acts as a blowing agent, turning the PU material into a foam, whereas the amines react with further isocyanate to urea derivatives [2]. The reactions are exothermic and accelerated by catalysts, mainly tertiary amines [2, 3]. The most commonly used polyisocyanates are methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), together accounting for 90% of the total isocyanate usage [4]. The polyol is typically a polymeric compound with either a polyether or a polyester backbone [2]. Apart from the main constituents, manufacturers can choose from a multitude of additives, allowing them to fine-tune the composition of PU

materials so that they have the properties best suited for their intended use. These include, but are not limited to, surfactants, antioxidants, crosslinking agents, flame retardants, colorants, and auxiliary blowing agents [2].

The vast number of options for modifying a PU material's characteristics makes them arguably one of the most variable plastic types and suitable for a wide range of applications. PU materials can be roughly categorized into flexible foams, rigid foams, and CASE (coatings, adhesives, sealants, and elastomers), with flexible foams having the largest market share [2, 5]. Flexible PU foams are used primarily in upholstered furniture and mattresses, as well as in automotive vehicles in the form of seating and acoustic insulation [2]. Given that adults sleep eight to nine hours a day and spend up to more than an hour daily inside vehicles [6, 7], humans in industrialized countries are thus close to flexible PU materials during a significant part of their lives.

Beds and car passenger cabins can be regarded as specific microenvironments whose air quality has the potential to

substantially affect health and well-being [6, 8]. One critical dimension of air quality is odor [9, 10]. Odors perceived as unpleasant can impair subjective well-being, even though substance concentrations are well below toxicological levels. In particular, Asian customers often express dissatisfaction with the interior odor of newly purchased vehicles [11]. Furthermore, it has been shown that a person's hedonic rating of an odor can influence sleep quality [12]. Hence, controlling material odor has become a pressing concern, and end-product manufacturers resort to implementing increasingly strict olfactory specifications [13]. However, the PU industry's efforts to meet these requirements are severely complicated by a lack of knowledge on PU odorants. This gap is rooted in the fact that studies on emission predominantly focus on the major volatiles [14–16], which often exhibit comparably high odor thresholds [17]. In contrast, trace components with low odor threshold concentrations in the $\mu\text{g}/\text{kg}$ or even ng/kg range are easily overlooked [18]. Especially in PU materials, there exist many potential entryways for such trace constituents. More than a dozen components can be combined to produce a single PU material, each obtained from technical-grade feedstocks containing numerous impurities. Additionally, the heat released when urethane and urea moieties form could promote the thermal generation of compounds not initially present in the raw materials.

To identify PU odorants and discern them from the bulk of volatiles not present in odor-active concentrations, sensory activity-guided screening by means of gas chromatography-olfactometry (GC-O) is indispensable. So far, only few studies have used GC-O to selectively target odor-active compounds in PU foams. In one of the first scientific publications to address the issue, cyclic acetals derived from propylene oxide were found to cause a musty odor in PU foams. The authors identified the underlying polyols as the source of the odorous constituents [19]. In 2006, Mayer and Breuer reported the detection of pyrazines in an earthy-smelling PU foam and speculated that these were introduced by amine catalysts [20], which can also serve as precursors of highly volatile amines like trimethylamine [21]. Two other studies investigated odorants in larger sets of four and six foams, respectively [22, 23]. The researchers carried out GC-O experiments with emission samples trapped on an adsorber material. Their combined findings suggested that aldehydes, aliphatic and aromatic hydrocarbons, alcohols, ketones, ethers, amines, acids, and esters could play a role in the odor of PU foams.

In conclusion, the existing literature provided some first insights into the molecular background of PU odor. However, the topic was clearly understudied, particularly considering the complexity and versatility of PUs. The present work is aimed at expanding the knowledge in this field by (1) using GC-O and gas chromatography-mass spectrometry (GC-MS) to characterize the odorants in a variety of flexible PU materials intended for use in mattresses or vehicles and (2) developing hypotheses on the origins of odor-active compounds based on their molecular structures.

2. Materials and Methods

2.1. Samples. PU materials were provided by European PU manufacturers via the industry associations EUROPUR

and EURO-MOULDERS. They were chosen to represent the most important types of flexible PU produced in Europe. The selection (Table 1) included molded and slabstock foams as well as an elastomer. The isocyanate was either MDI, TDI, or an MDI/isophorone diisocyanate (IPDI) mixture, and the polyol was either a polyether or polyester polyol. A glossary briefly explaining the technical terminology is incorporated in the Supplementary Material file (Table S1). Eight types of flexible PU were analyzed, and two samples of each type were requested from separate manufacturers. PU-15 constituted the sole exception since no adequately similar product was available. Companies were asked to send authentic materials taken directly from ongoing production. After curing, the samples were left to ventilate at the production site for 2–7 days. Slabstock foams were cut to the desired measurements ($25 \times 20 \times 15 \text{ cm}$) prior to shipment. The molded materials remained intact. Upon arrival at the research facility, PU samples were placed into individual moisture barrier bags, wrapped air-tight, and stored at 4°C . The manufacturer of PU-15 additionally provided the polyether polyol used in the production of this PU material.

2.2. Reference Odorants. The following compounds were obtained commercially (c.f. Supplementary Material file, Table S2, for compound names): **1–8**, **11**, **12**, **14–20**, **22–25**, **27–33**, **35**, **37–39**, **41–46**, **48**, and **49** (Merck, Darmstadt, Germany); **40**, **47**, and **50** (Thermo Fisher Scientific, Waltham, MA, USA); **9** (Carl Roth, Karlsruhe, Germany); **10** (Apollo Scientific, Stockport, England); and **36** (Cayman Chemicals Company, Ann Arbor, MI, USA). **21** was gifted by Symrise (Holzminden, Germany). **26** and **34** were synthesized as detailed previously [24, 25]. **49** and **50** were freshly distilled before use.

Odorant **13** was obtained from dipropylene glycol (22.3 mmol) and **50** (31.3 mmol) in the presence of an acidic cation exchange resin (Amberlite™ IR120-H; 0.71 g) and anhydrous sodium sulfate (10 g) in dichloromethane/*n*-pentane (5 + 1, $v + v$; 100 mL) [26]. After stirring under reflux for 2 hours, the solids were filtered off. The filtrate was washed with aqueous sodium carbonate solution (0.25 M; $2 \times 50 \text{ mL}$) and dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure.

2.3. Stable Isotopically Substituted Odorants. ($^2\text{H}_2$)-**32** was purchased from Aromalab (Martinsried, Germany). ($^{13}\text{C}_2$)-**49** was from Merck. ($^2\text{H}_2$)-**50** was purchased from CDN Isotopes (Montreal, Canada). ($^2\text{H}_6$)-**30** was synthesized from piperazine (18 mmol) and iodo($^2\text{H}_3$)methane (35 mmol), and ($^2\text{H}_5$)-**31** was synthesized from morpholine (6.4 mmol) and iodo($^2\text{H}_3$)ethane (13 mmol). In both cases, the reactants were dissolved in dichloromethane (100 mL) and stirred under reflux. After 3 hours, the reaction was quenched with aqueous sodium hydroxide solution (0.001 M; 100 mL), and the desired product was extracted with dichloromethane ($3 \times 30 \text{ mL}$). The combined organic phases were dried over anhydrous sodium sulfate and filtered, and the filtrate was made up to 100 mL. The concentrations of ($^2\text{H}_6$)-**30** and ($^2\text{H}_5$)-**31** in these stock solutions were determined by

TABLE 1: Technical characteristics of the PU material samples.

Sample	Type	Isocyanate	Polyol	Morphology
PU-1	Molded MDI foam	MDI ^a	Polyether	Molded
PU-2	Molded MDI foam	MDI ^a	Polyether	Molded
PU-3	Acoustic viscoelastic molded MDI foam	MDI ^a	Polyether	Molded
PU-4	Acoustic viscoelastic molded MDI foam	MDI ^a	Polyether	Molded
PU-5	Molded TDI foam	TDI ^b	Polyether	Molded
PU-6	Molded TDI foam	TDI ^b	Polyether	Molded
PU-7	Viscoelastic slabstock TDI foam	TDI ^b	Polyether	Slabstock
PU-8	Viscoelastic slabstock TDI foam	TDI ^b	Polyether	Slabstock
PU-9	High-resilience slabstock TDI foam	TDI ^b	Polyether	Slabstock
PU-10	High-resilience slabstock TDI foam	TDI ^b	Polyether	Slabstock
PU-11	Slabstock polyether foam	TDI ^b	Polyether	Slabstock
PU-12	Slabstock polyether foam	TDI ^b	Polyether	Slabstock
PU-13	Slabstock polyester foam	TDI ^b	Polyester	Slabstock
PU-14	Slabstock polyester foam	TDI ^b	Polyester	Slabstock
PU-15	Elastomeric spray skin	MDI ^a /IPDI ^c	Polyether	Elastomer

^aMethylene diphenyl diisocyanate; cf. Supplementary Material file, Table S1. ^bToluene diisocyanate; cf. Supplementary Material file, Table S1. ^cIsophorone diisocyanate; cf. Supplementary Material file, Table S1.

GC-FID (cf. Supplementary Material file) with methyl octanoate as the internal standard using response factors of 0.962 and 0.946, respectively, as obtained from the analysis of mixtures of methyl octanoate with **30** and **31**.

2.4. Miscellaneous Chemicals. Dichloromethane, diethyl ether, and *n*-pentane were purchased from CLN (Freising, Germany) and freshly distilled through a column packed with Raschig rings before use. Dipropylene glycol (99%), Amberlite™ IR120-H, anhydrous sodium sulfate, morpholine, piperazine, iodo(²H₃)methane (≥99.5% deuterium), iodo(²H₃)ethane (99.5% deuterium), silica gel (0.040–0.063 mm), and *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride were obtained from Merck. The silica gel was purified before use as described in the literature [27]. *n*-Hexane was from Thermo Fisher Scientific, and Miglyol® 812 was purchased from Caesar & Loretz (Hilden, Germany).

2.5. Gas Chromatography. GC-FID and GC-O analyses were performed with a GC-FID and a GC-O/FID instrument. GC-MS analyses were conducted with four different instruments: a static headspace GC-MS instrument with a Paul trap mass analyzer, a two-dimensional heart-cut GC-GC-HRMS/O instrument with an orbitrap mass analyzer, a comprehensive two-dimensional GC×GC-MS instrument with a time-of-flight (TOF) mass analyzer, and a GC×GC-MS instrument with a TOF mass analyzer and an autosampler with headspace solid phase microextraction (SPME) sampling option. Details on the individual instruments are available in the Supplementary Material file.

2.6. Odorant Screening. In accordance with industry guideline VDA 270 [28], all PU samples were placed in a clean glass vessel prior to the workup and exposed to a temperature of 80°C for a duration of two hours. After that, foams

(60 g) were cut into pieces (~1 cm³) with defatted stainless steel scissors and ground into a powder at the temperature of liquid nitrogen (−196°C). The elastomer PU-15 (60 g) was cut into pieces (~1 cm²), but not ground. The material was transferred to round bottom flasks, and freshly distilled dichloromethane (2 L) was added. The mixture was stirred overnight at ambient temperature and then filtered. Nonvolatiles were removed from the extract by means of automated solvent-assisted flavor evaporation (aSAFE) at 40°C with the valve opening for 0.2 s every 15 s [29]. The polyol (10 g) was diluted with dichloromethane (50 mL), and the mixture was subjected directly to aSAFE. The distillate was dried over anhydrous sodium sulfate (50 g) and concentrated to a final volume of 1 mL using a Vigreux column (50 × 1 cm) and a microdistillation device [30].

The PU volatile isolates were stepwise diluted 1:2 with dichloromethane to obtain dilutions of 1:2, 1:4, 1:8, and so on. The concentrate and the diluted solutions were subjected to an aroma extract dilution analysis (AEDA) [31], meaning that consecutive GC-O/FID runs using the DB-5 or the FFAP column were conducted as detailed in the Supplementary Material file until the dilution was high enough not to perceive a single odorant in the whole GC run. Each odorous region was assigned a dilution factor (DF), which corresponded to the dilution factor of the highest diluted solution in which the odor was still perceptible.

Complementary screening for odorants in the sample headspace was performed using the static headspace GC-MS/O instrument. A portion (3 g) of the sample was cut into pieces (~0.5 cm diameter) and sealed inside a crimp-top headspace vial (120 mL). After equilibration (20 min) at 40°C in the autosampler rack, a portion of the headspace (10 mL) was injected with a gastight syringe and subjected to a GC-MS/O measurement as detailed in the Supplementary Material file.

2.7. Fractionation. *n*-Hexane (1 mL) was added to a portion (0.8 mL) of the concentrated volatile isolate, and the dichloromethane in the mixture was removed at 40°C. A water-cooled (12°C) glass column (20 × 1 cm) filled with a slurry of purified silica gel (8 g) in *n*-pentane was prepared. The sample was loaded onto the column with a glass Pasteur pipette, and elution was performed with *n*-pentane/diethyl ether mixtures (5 × 50 mL) in the following volumetric ratios: 100 + 0, 90 + 10, 70 + 30, 50 + 50, and 0 + 100 [27]. The five resulting eluate fractions A–E were concentrated to 0.2 mL.

2.8. Odorant Quantitation. For the quantitation of **30–32**, a portion of the sample (0.1–4 g) was ground into a powder at the temperature of liquid nitrogen (–196°C) and immersed in dichloromethane or diethyl ether (30–500 mL). After the addition of the stable isotopologues (0.10–45 µg) and equilibration, the volatiles were isolated following the workup procedure described above. Samples were worked up in triplicate. The dried aSAFE distillates were concentrated to a final volume of 0.1–1 mL. Subsequent GC-MS analysis allowed for the separate recording of the standard and analyte ion intensities. For the quantitation of **30** and **31**, the GC×GC-MS instrument was used. The quantitation of **32** was performed with the heart-cut GC-GC-HRMS/O instrument. Concentrations were determined with a calibration line obtained from the injection of mixtures of standard (0.957–7.83 ng) and analyte (1.04–10.8 ng) in different ratios (~1:5 to 5:1) followed by linear regression. Individual internal standards, quantifier ions, and calibration lines are available in the Supplementary Material file, Table S33.

For the quantitation of **49** and **50**, a portion (0.01–0.5 g) of the sample was cut into pieces (~0.5 cm diameter) and placed in an amber glass headspace vial (20 mL). (¹³C₂)-**49** (6.3–52 ng) and (²H₂)-**50** (2.9–280 ng) solved in a tap water/methanol mixture (4 + 1, *v* + *v*) were added as internal standards, and the samples were left to equilibrate at room temperature. Then, headspace SPME sampling was performed as detailed in the Supplementary Material file, with 1 mg of solid *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) as the derivatization reagent. Eight headspace samples of each PU material were prepared simultaneously and analyzed successively. Concentrations were determined with a calibration line obtained from the analysis of mixtures of standard (35.4–510 ng) and analyte (33.8–500 ng) solved in different ratios (~1:10 to 10:1) in a tap water/methanol mixture (4 + 1, *v* + *v*) followed by linear regression.

The concentration of **50** in sample PU-11 was determined in triplicate by stirring ground foam powder (0.05 g) and (²H₂)-**50** (29 µg) overnight in dichloromethane (35 mL). Toward the end, PFBHA (500 µg) was added, and the mixture was left to react for one more hour. The extract was subjected to aSAFE, and the volatile fraction was concentrated to a total volume of 10 mL prior to being analyzed with the GC×GC-MS instrument. Concentrations were determined as detailed for **30–32** with standard amounts of 0.290–1.45 ng and analyte amounts of 0.387–1.94 ng and the addition of PFBHA to the calibration solutions.

2.9. Determination of Odor Threshold Concentrations. Orthonasal odor threshold concentrations (OTCs) were determined in accordance with the guidelines published by the American Society for Testing and Materials [32]. A solution with an odorant concentration 150 times above the estimated OTC was stepwise diluted (1:3) with deionized water or Miglyol 812®, an odorless mixture of medium-chain triglycerides. Then, a portion (10 mL) of each test solution was transferred to an odor-neutral vessel and offered to the assessors alongside two identical cups containing only the solvent in the style of a forced-choice test. The tests were conducted by 15–18 trained assessors in a room solely used for sensory evaluations. The OTC of the panel was calculated as the geometrical mean of the individual OTC values.

3. Results and Discussion

3.1. Overall Odor of PU Materials. Before investigating the molecular background, we performed a quick assessment of the overall odor of the 15 flexible PU materials by sensory testing. Following the conditioning period according to VDA 270 [28], three trained assessors (two males and one female, aged 24–54 years) sniffed the samples in a free-choice profiling (Table 2). An odor note subjectively termed “wall paint-like” was perceived to some extent in the majority of samples and most often was accompanied by odors described as earthy and musty. On the other hand, certain foams evoked very distinct odor impressions described by the assessors as, e.g., “rum-like” (PU-11) or “old furniture-like” (PU-5). Notably, some samples emitted a fishy odor upon initial opening, which usually dissipated rapidly. An exception was observed in the polyester foams, in which the fishy impression was stronger and persisted over time. Besides this, the similarity between foams of the same type (cf. Table 1) was not remarkably higher than between foams of different types. This was, for example, evident in the slabstock viscoelastic foams. PU-7 exhibited a slightly roasty odor, whereas PU-8 carried a pronounced phenolic note.

3.2. Odorants in PU Materials. The volatiles were isolated from the PU samples by means of solvent extraction and aSAFE. To exclude workup artifacts, a blank sample was worked up in parallel. A portion of the concentrated isolate was diluted stepwise and subjected to an AEDA as detailed in Section 2.6. A total of 30 AEDAs were performed using the DB-5 and FFAP columns, the detailed results of which are included in the Supplementary Material file, Tables S3–S32. Analysis of the volatile isolates revealed between 10 and 61 odorants with DFs ≥ 4. The highest number of odorants was observed in the volatile isolate of the spray skin PU-15. The isolate obtained from viscoelastic molded MDI foam PU-3 contained the lowest number of odorants. In both cases, the overall sample odor was not noticeably stronger or weaker compared to the remaining foams. Hence, no clear relation was found between odor intensity and the number of odorants, indicating that a higher number of odor-active compounds did not necessarily imply highly potent odorants.

TABLE 2: Olfactory characteristics of the PU materials.

Sample	Odor impression ^a
PU-1	Musty, wall paint
PU-2	Sweetish, musty, wall paint
PU-3	Wall paint, earthy, fishy
PU-4	Wall paint
PU-5	Musty, old furniture, glue
PU-6	Sweetish, musty, wall paint
PU-7	Roasty, wall paint, sweetish
PU-8	Ink, phenolic
PU-9	Pungent, old furniture, fatty
PU-10	Wall paint, earthy, fishy, sweetish
PU-11	Rum, sweetish, phenolic, plastic
PU-12	Earthy, wall paint, lighter fluid
PU-13	Fishy, rotten
PU-14	Very fatty, fishy, pungent
PU-15	Earthy, plastic, wall paint

^aAs perceived by three trained assessors after a sample conditioning period (2 hours at 80°C).

In order to generate structure proposals for the odorants, retention indices and odor impressions were first compared to entries in online databases [33, 34]. If this did not result in a structure proposal, prefractionation in combination with two-dimensional GC-MS/O was applied to the respective volatile isolate in an attempt to obtain mass spectral data of the analyte in question. The isolate underwent fractionation via silica gel chromatography to remove matrix constituents and minimize coelutions. Odorants were localized in the fractions by means of GC-O. If a fraction contained a previously unidentified odorant, it was analyzed with the heart-cut GC-GC-HRMS/O instrument (cf. Supplementary Material file). Whenever an odor was perceived in the eluate of the second column, the mass spectrum linked to the respective retention time was checked against a mass spectral database [35].

All structure proposals were verified by preparing a solution of the authentic reference compound at a concentration similar to that estimated in the volatile isolate. Both solutions were then subjected to consecutive GC-O runs. Provided that the odor qualities and retention properties on both the DB-5 and the FFAP columns were indistinguishable, the finding was confirmed through GC-MS by analyzing the isolate and the reference solution under identical conditions. This approach resulted in the unequivocal identification of 4 to 23 odorants per sample, totaling 50 odorants identified in the 15 samples. The relatively low percentage of identification, ranging from 20% to 67%, can be largely attributed to the scarcity of preexisting data on PU odorants. While comprehensive databases are available for odorous and odorless volatiles in foods and beverages [33, 34], there is currently no comparably extensive resource for nonfood materials.

Among the 50 compounds, only **13** [19]; **31**, **49**, and **50** [22]; **37** and **40** [23]; and **39** [20] had been previously identified as odorants in flexible PU materials. Furthermore, **9**

and **11** [36], **22** [37], and **30** [38] had been reported as PU volatiles, but not as PU odorants. The remaining odorants had, to the best of our knowledge, never been reported in flexible PU. The 50 odorants belonged to various compound classes, which will be discussed individually in the following sections. The compound classes included tertiary amines, fatty acid oxidation products, short-chain aldehydes, trioxocanes, pyrazines, aromatic hydrocarbons and heterocycles, chlorinated compounds, phenol derivatives, fragrance compounds, and nitriles.

3.2.1. Tertiary Amines. In the volatile isolates of PU-13 and PU-14, a fishy-smelling compound was perceived. In both cases, 1,4-dimethylpiperazine (**30**; Figure 1) had been used as a catalyst during manufacturing. The isolate of PU-13 additionally contained fishy-smelling odorant 4-ethylmorpholine (**31**). The manufacturer confirmed that **31** was not an ingredient in this foam, but in another product stored for postcuring at the same site.

Both **30** and **31** were assigned a DF of 2 in the AEDA of the PU-13 volatile isolate, which was surprisingly low given the intense fishy odor of the foam. As amines, **30** and **31** are fairly polar molecules, so they may not have transferred sufficiently into the nonpolar solvent during the extraction. Additionally, the DF depends on chromatographic behavior, which was not ideal for **30** and **31**. In past publications, both reasons have been presumed to lead to an underestimation of amines in dilution analyses [39, 40]. Consequently, the DFs did not provide insight into which amine accounted primarily for the foam's fishy odor. Aiming to answer this question nonetheless, we determined the concentrations and the OTCs of **30** and **31**. Since it was unclear which was the better approximation for the PU foam, the OTCs were determined in both water and odorless oil. From this, odor activity values (OAVs) were calculated by dividing the first by the latter [18]. Results (Table 3) revealed higher OAVs of **30** regardless of the solvent. This finding suggested that catalyst **30** was the predominant cause for the fishy odor and aligned with the odor quality of PU-14, in which **30**, but not **31**, was detected.

Overall, the impact of amines within the scope of this study was rather low. This can most probably be attributed to advancements in PU catalysis. Until a few decades ago, low-boiling compounds such as triethylamine, 4-ethylmorpholine, and 4-methylmorpholine were primarily used, with the disadvantage of imparting a fishy odor to the foam. Modern amine catalysts are typically less volatile or equipped with a reactive group [41]. The latter are incorporated into the polymer backbone during foaming, resulting in a significantly reduced emission from the final PU materials. It is noteworthy that out of the 15 samples, fishy-smelling amines were only detected in the volatile isolates of slabstock polyester foams PU-13 and PU-14. Compared to polyether-based systems, fewer catalysts are suitable for use in polyester foams [5], possibly leading manufacturers to rely to a higher degree on traditional catalysts like **30**.

Furthermore, our results did not provide evidence that highly volatile amines like trimethylamine are still major odor-causing agents in PUs, as suggested previously [21].

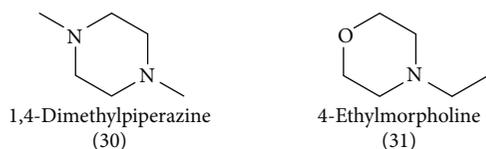


FIGURE 1: Odor-active amines detected in the volatile isolates of PU-13 and PU-14.

Only when evaluating a sample's odor upon the first unwrapping, a fishy note was occasionally observed. The odor ceased to be perceptible after just a brief storage period. At this point, screening via static headspace GC-MS/O did not indicate the presence of fishy-smelling odorants.

3.2.2. Fatty Acid Oxidation Products. Close to a third of the 50 odorants were medium-chain carbonyl compounds (Figure 2). This included a ketone (**1**), lactones (**4**, **7**), saturated aldehydes (**37**, **38**, and **40**), and unsaturated aldehydes (**2**, **3**, **12**, **26**, **32–34**, **36**, and **43**). Within this group, oct-1-en-3-one (**1**) and (2*E*)-non-2-enal (**12**) showed the highest abundance. Each was identified as an odorant in 10 out of 15 samples.

Most of the compounds had previously been detected in other plastic products, such as polyvinyl chloride-based toys (**1**, **4**, **12**, **26**, **34**, **36**, and **43**) [42] or polypropylene materials (**1**, **3**, **7**, **12**, **26**, **36–38**, **40**, and **43**) [43]. A well-known formation pathway of these odorants is fatty acid oxidation [44]. Consequently, Wiedmer et al. proposed lubricants derived from vegetable oils as their source [42]. In the context of PU, vegetable oils are also relevant as a feedstock for bio-based polyols, which are currently seen as a promising route toward more sustainable PU production [2]. However, no such raw materials were used in the samples examined in this study, leaving lubricants as the more likely explanation. **1** and **12** are among the most potent odorous oxidation products of linoleic acid [44], the main fatty acid in many industrially important plant oils, including soybean and sunflower oil [45]. The abundance of **1** and **12** thus reinforces the assumption that the compounds shown in Figure 2 originated from vegetable oils.

Polyester foam PU-14 contained more unsaturated aldehydes than any other sample. Fatty, plastic-like smelling compounds **12**, **26**, and **34** were assigned high DFs (64–512), which was consistent with the pronounced fatty odor of the foam. Additionally, a fishy-smelling compound in the volatile isolate was identified as (4*Z*)-hept-4-enal (**32**). Quantitation revealed a concentration of 67.8 $\mu\text{g}/\text{kg}$ foam, corresponding to an OAV of 7800 based on the OTC in water [33] and an OAV of 15 based on the OTC in oil [46]. However, PU-14 also contained the amine **30**, which reached OAVs of 1.4 (water) and 56 (oil). Hence, it was not possible to unequivocally attribute the fishy odor to one or the other compound. Nevertheless, the data suggested that odorants other than amines can inflict a fishy off-odor on PU.

3.2.3. Short-Chain Aldehydes. An odor note described as “wall paint-like” was perceptible in most samples. Screening

conducted by headspace GC-MS/O proved the emission of acetaldehyde (**49**) and propanal (**50**; Figure 3), whose fresh green odor corresponded well to the paint-like olfactory impression. Neither **49** nor **50** were detected in the volatile isolates, presumably due to their low boiling points of 20.8 and 48.0°C [47]. Therefore, we determined their concentrations to approximate their odor contribution. Quantitation was performed using static headspace SPME-GC×GC-MS. Eight headspace samples were prepared simultaneously by spiking portions of the same PU material with $^{13}\text{C}_2$ -substituted **49** and deuterated **50**. The eight samples were then analyzed successively to cover a period of ~25–40 hours. We found that each PU material emitted **49** and **50**, and a continuous increase in concentration, as exemplified for PU-5 in Figure 4, was observed for most of them. The curves of all 15 samples are available in the Supplementary Material file, Figures S1–S15.

Initially, the monitoring of the concentration over time had been intended as a preliminary experiment, designed to assess the time required for standard and analyte to reach equilibrium. Instead, it led to the intriguing finding that, apparently, **49** and **50** were continuously regenerated from the samples. Al-Rashid et al. made a comparable observation when they found that both freshly produced and aged foams emitted acetaldehyde and that the emission increased with the foam age [48]. As a possible reason, they named the depletion of antioxidants in the foam. This assumption fits the mechanism proposed by Allan et al., according to whom **49** and **50** are oxidative degradation products of polyether polyols [49].

Between the samples, both the aldehyde concentration levels and the regeneration rates differed considerably. For the first headspace sample of each series, acetaldehyde concentrations between 11.5 $\mu\text{g}/\text{kg}$ (PU-3) and 407 $\mu\text{g}/\text{kg}$ (PU-4) were determined. Propanal concentrations ranged from 4.85 $\mu\text{g}/\text{kg}$ (PU-14) to 170 $\mu\text{g}/\text{kg}$ (PU-4 and PU-7). For the eighth sample of each row, acetaldehyde concentrations were between 20.1 $\mu\text{g}/\text{kg}$ (PU-8) and 5170 $\mu\text{g}/\text{kg}$ (PU-10), and propanal concentrations ranged from 17.1 $\mu\text{g}/\text{kg}$ (PU-13) to 3880 $\mu\text{g}/\text{kg}$ (PU-7). The propanal concentration in slabstock polyether foam PU-11 reached such elevated levels that the headspace method was no longer practical. Utilizing an alternative method based on solvent extraction, a concentration as high as 229 000 $\mu\text{g}/\text{kg}$ was determined. By contrast, the polyester foams PU-13 and PU-14 showed comparably low concentrations and only minimal increases (cf. Supplementary Material file, Figures S13 and S14). Polyester polyols exhibit better oxidative stability than polyethers [2]. Consequently, reactions leading to the formation of **49** and **50** are less likely to occur. Other than that, there was no discernible trend in terms of PU type and aldehyde concentration. However, although the concentrations diverged substantially, they mostly exceeded the OTCs of 16 $\mu\text{g}/\text{kg}$ water (**49**) [50] and 9.3 $\mu\text{g}/\text{kg}$ water (**50**) [51]. For 12 of the 15 samples, this was true for both compounds throughout the entire measuring series.

3.2.4. Trioxocanes. An earthy-smelling odorant with RI values of 1121 (DB-5) and 1409 (FFAP) was detected in 11

TABLE 3: Concentrations, odor threshold concentrations, and odor activity values of amines **30** and **31** in foams PU-13 and PU-14.

	Concentration (mg/kg) ^a		OTC _{oil} ^b (mg/kg)	OTC _{water} ^c (mg/kg)	OAV _{oil} ^d		OAV _{water} ^e	
	PU-13	PU-14			PU-13	PU-14	PU-13	PU-14
30	1330 ± 190	677 ± 73	12	500	110	56	2.7	1.4
31	24.6 ± 0.3	N.d. ^f	6.6	38	3.7	N.d. ^f	0.65	N.d. ^f

^aMean of triplicates ± standard deviation. ^bOrthonasal odor threshold concentration in an odorless mixture of medium-chain saturated triglycerides. ^cOrthonasal odor threshold concentration in deionized water. ^dOdor activity value; odorant concentration in the sample divided by the odor threshold concentration in an odorless mixture of medium-chain saturated triglycerides. ^eSee footnote d, but based on the odor threshold concentration in deionized water. ^fNot determined.

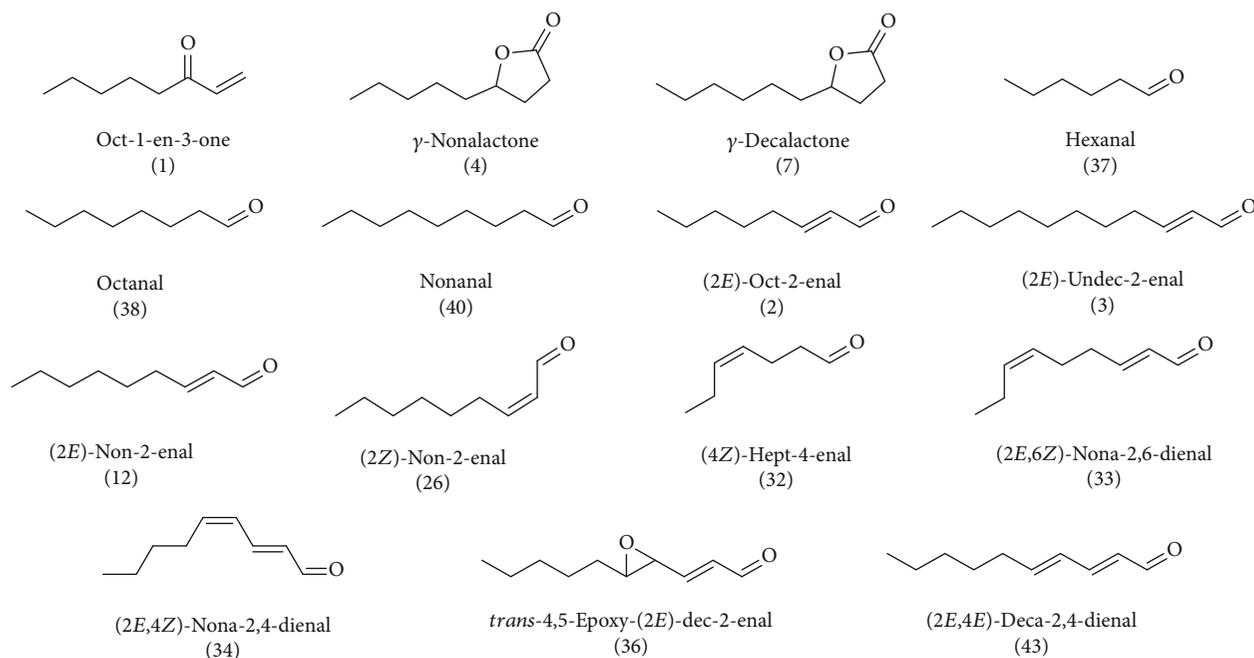


FIGURE 2: Odor-active fatty acid oxidation products detected in the volatile isolates of PU samples.



FIGURE 3: Odor-active short-chain aldehydes detected in the headspace of PU samples.

of the 15 PU samples. Its exact mass was determined by high-resolution mass spectrometry and corresponded to the sum formula $C_9H_{18}O_3$. Such compounds were previously identified by Harris et al. as cyclic acetals of dipropylene glycol and propanal [19]. Therefore, we hypothesized that the unknown odorant would be formed in the acid-catalyzed reaction of those two reagents (Figure 5). Indeed, GC-O and GC-MS measurements confirmed that the reaction mixture contained the same odor-active 2-ethyl-4,7-dimethyl-1,3,6-trioxocane (**13**) as the PU samples. Additionally, we detected **13** in a polyether polyol sample. This was in agreement with the results of Harris et al., who isolated **13** from PU foam, polyether polyols, and propylene oxide treated with a Lewis acid. The industrial conversion of propylene oxide to polyether polyols is catalyzed

by metal hydroxides or metal cyanides. In the first case, subsequent catalyst removal is often achieved through the addition of acid [52]. Harris et al. proposed the formation of **13** at this stage, either directly from propylene oxide or from higher molecular weight species.

Both the synthetic product and the PU volatile isolates contained a mixture of 2-ethyl-4,7-dimethyl-1,3,6-trioxocanes, 2-ethyl-4,8-dimethyl-1,3,6-trioxocanes, and 2-ethyl-5,7-dimethyl-1,3,6-trioxocanes. The occurrence of multiple positional isomers can be explained by the low regioselectivity of the propoxylation reaction [38]. Further peaks were attributed to stereoisomers. Interestingly, only one odorous region evoked a strong earthy impression during GC-O. This illustrates a characteristic feature of odorants, which is that positional and stereoisomers may vary extremely in their olfactory potency. Other examples of this principle are 3-ethylphenol (OTC 0.85 $\mu\text{g}/\text{kg}$ water) and 4-ethylphenol (OTC 13 $\mu\text{g}/\text{kg}$ water) [33] and the chiral wine lactone, whose eight stereoisomers exhibit OTCs spanning over seven orders of magnitude [53].

3.2.5. Pyrazines. Odorant screening in the PU skin PU-15 revealed three pyrazines (Figure 6), namely, 3-isobutyl-2-

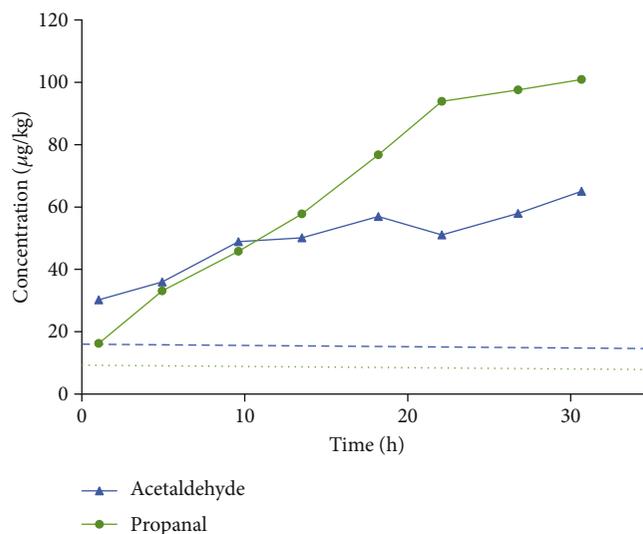


FIGURE 4: Concentrations of acetaldehyde and propanal in PU-5 determined after defined periods in a sealed headspace vial. Horizontal lines indicate the orthonasal odor threshold concentrations of acetaldehyde (dashed) and propanal (dotted) in water.

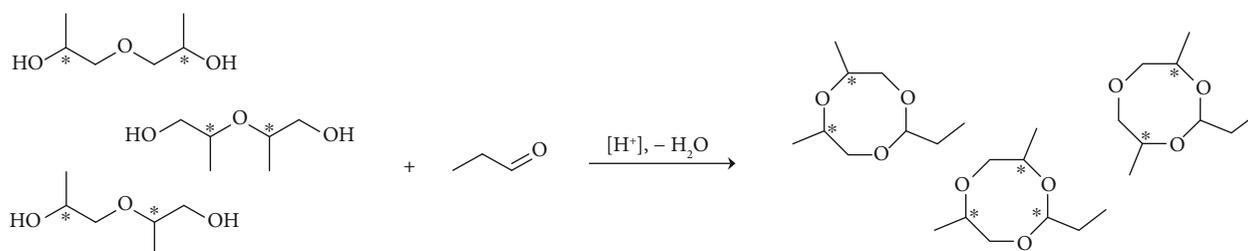


FIGURE 5: Synthesis of 2-ethyl-2,2,6,6-tetramethyl-1,3,6-trioxocanes from dipropylene glycols and propanal. Asterisks indicate the positions of chirality centers.

methoxypyrazine (**24**), 3-isopropyl-2-methoxypyrazine (**39**), and 2,3-diethyl-5-methylpyrazine (**41**), with DFs between 32 and 128. Pyrazines were previously described as odor-active substances in PU, and Mayer and Breuer hypothesized that amine catalysts might constitute a source of these compounds [20]. However, the manufacturer of PU-15 stressed that only metal catalysts, but no amine catalysts, were used for this product. Additionally, the pathway suggested by the authors involves the temperature-induced breakdown of amines into aminoketones, which may react further to form pyrazines, but the generation of enough heat to favor a reaction of this kind is unlikely to occur in the thin PU skin. Thus, the origin of the pyrazines in PU-15 was most probably not an amine catalyst. Alternatively, trace amounts of the odorants could have entered the sample through cross-contamination or impure raw materials. **24**, **39**, and **41** exhibit very low OTCs between 0.0039 and 0.031 µg/kg water, making even minute quantities detectable by GC-O.

3.2.6. Aromatic Hydrocarbons and Heterocycles. In molded MDI foams PU-1 and PU-2, the aromatic nitrogen heterocycle acridine (**11**; Figure 7) was one of the most potent odorants (DFs 32 and 64). In contrast, GC-O did not indicate the presence of **11** in the volatile isolate of any other foam type. Technical MDI is produced from aniline and formaldehyde,

with methylenedianiline as an intermediate [38]. Aromatic amines can self-condense in the presence of acids [54], and model experiments have shown that 2,2'-methylenedianiline can undergo acid-catalyzed cyclization to 9,10-dihydroacridine and acridine at high temperatures [55]. Such conditions are encountered during MDI production [38]. Variations in the process parameters and, subsequently, in the quality of MDI might account for why **11** was detected in only two of the five MDI-based PU samples.

One metallic-smelling odorant in foam PU-10 was identified as 4-phenyl-1-cyclohexene (**25**). The compound was previously reported as a pyrolysis product of styrene-butadiene rubber, and the authors proposed its formation in a Diels-Alder reaction of styrene and 1,3-butadiene [56]. Styrene has been identified as an emission of flexible PU mattress cores [14], and both styrene and 1,3-butadiene have been found among the volatiles released by pyrolyzed PU foams [57]. In foam PU-11, phenanthrene (**29**) was detected. The foam sample was dyed in a dark gray tone. Gray or black tinting in plastics is often achieved by adding carbon blacks. These pigments are most often produced by incomplete combustion of heavy oils containing aromatic hydrocarbons [58].

3.2.7. Chlorinated Compounds. Three odor-active substances were identified as chlorinated aromatic amines (Figure 8),

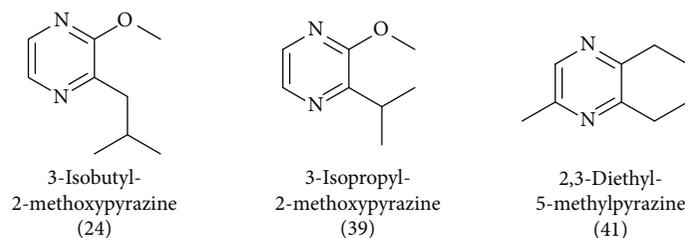


FIGURE 6: Odor-active pyrazines detected in the volatile isolate of PU-15.

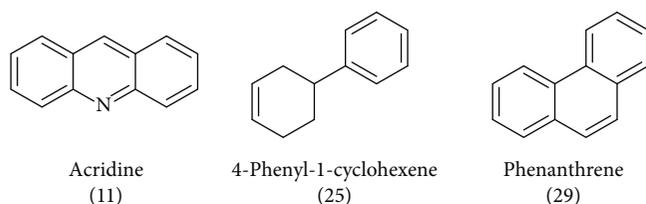


FIGURE 7: Odor-active aromatic hydrocarbons and heterocycles detected in the volatile isolates of PU samples.

each only occurring in one PU sample. They exhibited a musty (**10**) or fecal (**44**, **47**) odor quality. Like **11**, these odorants may have been introduced by the isocyanate component. The industrial synthesis of MDI and TDI involves phosgene and amines, which are often solved in chlorobenzene [38].

A fourth compound with a plastic-like odor was detected in seven samples and with DFs of 16–64. The comparison of the electron ionization MS fragmentation pattern with mass spectra compiled in a database [35] did not procure a match. Therefore, we attempted to derive the structure from the available information on the odorant. A sum formula of C_7H_9OCl was determined by high-resolution mass spectrometry, corresponding to three double bond equivalents. Retention indices were 1125 (DB-5) and 1620 (FFAP). After silica gel fractionation, the odorant was recovered in fraction C (*n*-pentane/diethyl ether 70 + 30, $v + v$). This behavior indicated a molecule of medium polarity. To gain insights into functional groups within the molecule, we added PFBHA, a derivatization agent selective for carbonyl compounds, to the volatile isolate of PU-11. The treatment did not result in a loss of odor activity, suggesting that the oxygen atom was not incorporated within an aldehyde or ketone, but rather an alcohol or ether functionality. Unfortunately, structure elucidation attempts beyond this point remained unsuccessful. Two more odor-active organohalogenes were phenolic compounds and will be discussed in the following section.

3.2.8. Phenol Derivatives. The group of phenolic odorants included phenol (**22**), two alkylphenols (**16**, **48**), 2'-hydroxyacetophenone (**14**), four alkoxyphenols (**6**, **23**, **27**, and **35**), and two halogenated compounds (**17**, **20**). Overall, 10 of 15 samples contained at least one of the compounds shown in Figure 9. Viscoelastic slabstock TDI foam PU-8, in particular, stood out due to an intense phenolic odor. This olfactory impression matched the AEDA results, which

revealed **22** (DF 1024), **20** (DF 128), and **23** (DF 128) as potent odorants.

Prior studies have identified some of these odorous phenols in different types of plastics, including polypropylene (**48**, **6**) [43], polyvinyl chloride (**22**, **6**) [42], and polyphenylene ether (**23**) [20]. The findings of Frank et al. pointed toward phenolic antioxidants as their source [43]. In PU, sterically hindered phenols are primarily used to protect polyethers from oxidation [59]. Odor-active phenols could result from their heat-induced degradation or be present as impurities in the antioxidant mixture [20]. Additionally, phenols serve as reversible blocking agents for aromatic isocyanates [60].

Particularly interesting is the detection of 2-bromo-4-methylphenol (**20**) and 2,4,6-trichloroanisole (**17**) in five and three foams, respectively. In a study conducted on Gouda cheese, Mills et al. showed that **20** can originate from 4-methylphenol (**48**) and bromine [61]. With regard to PU, bromine is relevant in the context of flame retardants [62], but the foam samples in question did not contain this type of additive. Cross-contamination from other formulations prepared with brominated flame retardants might explain the odorant's presence. Odorant **17** is a well-known contaminant in water disinfected by chlorine treatment [63]. Moreover, **17** is a main cause of the so-called "cork taint" in wine [64].

3.2.9. Fragrance Compounds. The last group of unambiguously identified odorants was termed "fragrance compounds," according to their function in, for example, cosmetic products [65]. Every PU volatile isolate contained at least one of the odorants displayed in Figure 10. Theoretically, it would be possible that side reactions throughout the production chain generated traces of some of these highly potent odorants. However, we found no record of a natural formation of **5**, **8**, and **46** in the scientific literature. Thus, an external source of the compounds seemed more plausible. Their joint presence suggested a transfer from cosmetic products or cleaning agents. Buchecker et al., who detected **8** and **15** in the interior air of newly fabricated cars, drew a similar conclusion [66]. They pointed out that workers could involuntarily introduce odorants during vehicle production.

To further investigate at which point the suspected contamination of our samples occurred, we first evaluated the blank samples. These showed no presence of fragrance compounds, indicating that the contamination did not take place in the laboratory. Consequently, production, postcuring storage, and packaging were left as possible exposure sites.

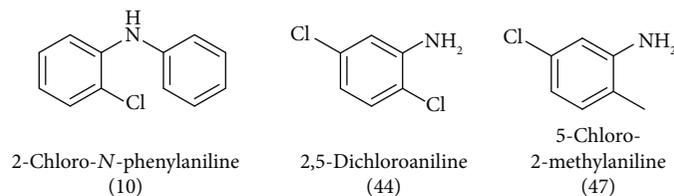


FIGURE 8: Odor-active chlorinated amines detected in the volatile isolates of PU samples.

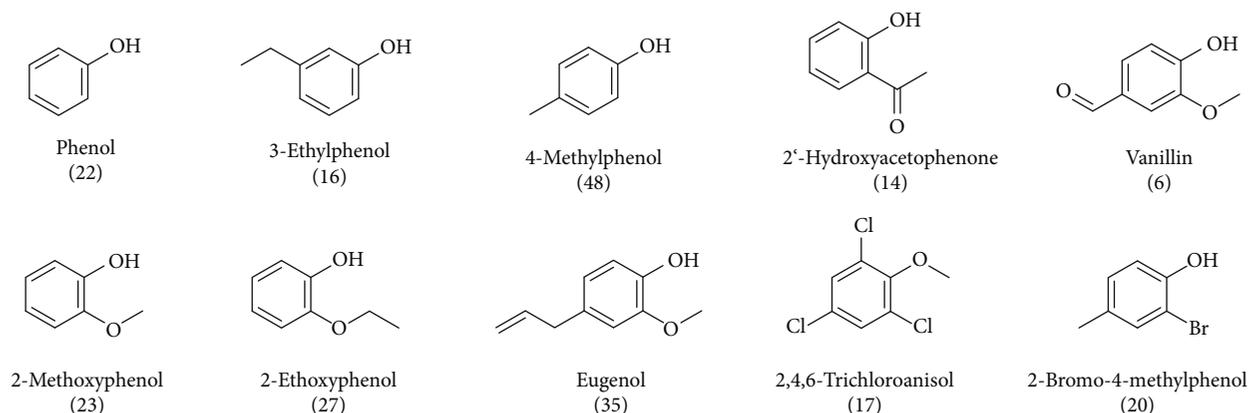


FIGURE 9: Odor-active phenol derivatives detected in the volatile isolates of PU samples.

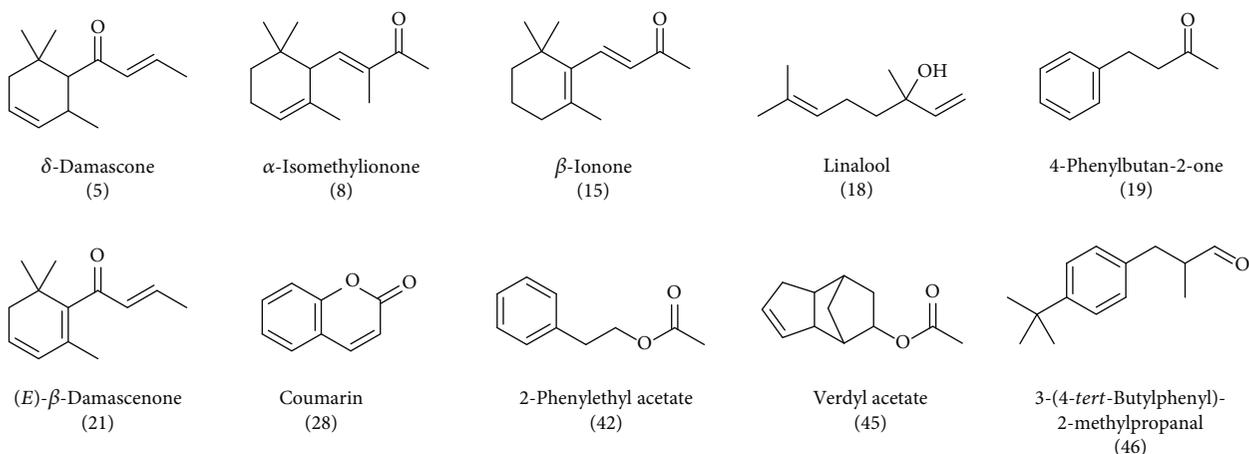


FIGURE 10: Fragrance compounds detected in the volatile isolates of PU samples.

Moreover, no substantial change in the odorant composition was observed when PU-15 was resampled with the instruction to handle it only with gloves, suggesting that the fragrance compounds were primarily transmitted through the ambient air. This aligned with earlier research demonstrating that PUs readily adsorbed organic volatiles [67, 68].

3.2.10. Nitriles. TDI-based foams PU-5 and PU-9 exhibited a similar odor quality described as “old furniture”-like. The volatile isolates contained multiple odorants matching this odor impression. One was assigned particularly high DFs of 1024 (PU-5) and 256 (PU-9). For this compound, RI values of 1235 (DB-5) and 1623 (FFAP) were determined. By performing heart-cut GC-GC-HRMS/O on fraction B, a

peak whose spectrum resembled *n*-decanenitrile was annotated to the odorous region. The proposal was consistent with the determined sum formula $C_{10}H_{19}N$, but the RI of *n*-decanenitrile on the DB-5 column was approximately 50 units higher than that of the unknown. A comparison of the mass spectra brought to light minor differences in the fragmentation pattern, most notably a lower relative signal intensity for *m/z* 110 (Figure 11). These findings indicated that the odorant in question was a skeletal isomer of *n*-decanenitrile with one or multiple branching sites along the carbon backbone. For the other compounds evoking the “old furniture”-like impression, we determined a sum formula of $C_{10}H_{17}N$. Their retention indices (1126–1224 on the DB-5 column) and the comparable odor quality suggested a structural similarity

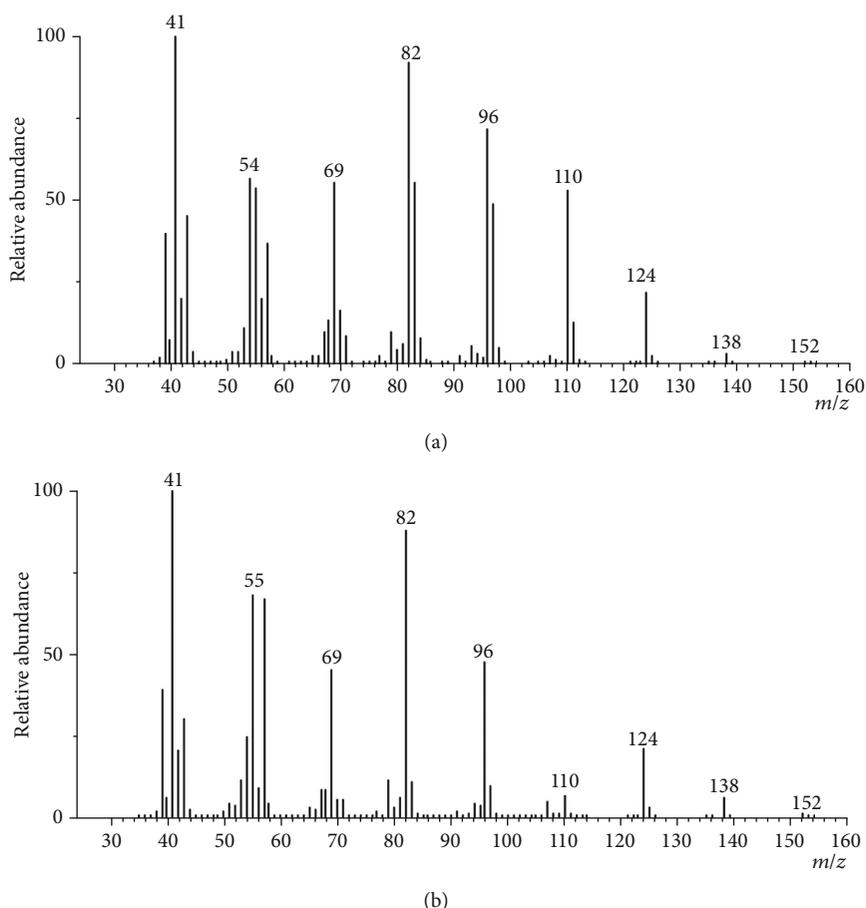


FIGURE 11: Electron ionization mass spectra of (a) *n*-decanenitrile and (b) the unknown isomeric C_{10} -nitrile detected in the volatile isolates of PU-5 and PU-9.

to the above-mentioned C_{10} -nitrile. Hence, they were most likely C_{10} -nitriles with a carbon-carbon double bond.

Nitriles are relevant in PU production in the form of styrene-acrylonitrile graft polyols, which are used to alter the mechanical properties of the foam [2]. The manufacturers of PU-5 and PU-9 confirmed that both foams were based on this type of polyol. However, the structure of the C_{10} -nitriles could not be deduced from either the radical starter or acrylonitrile. With the precursors unknown, the positions of both the unsaturation and the side chain were rather challenging to predict. Full structure elucidation for the compounds was thus not achieved.

4. Conclusion

Fifty odorants were identified in fifteen flexible PU samples using GC-O and GC-MS. With one exception, none of the compounds were part of the formulation. Instead, they were most likely the result of (i) cross-contamination, (ii) introduced as by-products in the raw materials, or (iii) formed during the production process. Consequently, manufacturers may mitigate odor problems by (i) preventing an odorant transfer from external sources, (ii) judiciously selecting the raw materials, and (iii) optimizing process parameters. Due to the extreme versatility of PU materials, however, a general

recommendation for improving PU odor is not practical. Rather, our data suggest that odor issues must largely be addressed on a case-by-case basis.

Most of the compounds had not been detected in earlier studies on PU volatiles and odorants, presumably because of their low concentrations. Thus, the present work further confirmed that the investigation of odorous trace constituents requires a specialized analytical approach and that GC-O should be considered the method of choice for characterizing odorants in a complex matrix. Understanding the molecular background is a crucial step toward targeted improvement of PU material odor. This, in turn, can lead to better air quality in those indoor environments where PU materials are primarily used, especially in confined spaces like vehicle interiors.

Nomenclature

Coumarin:	Chromen-2-one
(<i>E</i>)- β -Damascenone:	(2 <i>E</i>)-1-(2,6,6-Trimethylcyclohexa-1,3-dien-1-yl)but-2-en-1-one
δ -Damascone:	(2 <i>E</i>)-1-(2,6,6-Trimethylcyclohex-3-en-1-yl)but-2-en-1-one
γ -Decalactone:	5-Hexyloxolan-2-one

<i>trans</i> -4,5-Epoxy- (<i>2E</i>)-dec-2-enal:	(<i>2E</i>)-3-[(<i>2S,3S</i>)- and/or (<i>2E</i>)-3- [(<i>2R,3R</i>)-3-pentylloxiran-2-yl]prop- 2-enal
Eugenol:	2-Methoxy-4-prop-2-enylphenol
2'-Hydroxyacetophenone:	2-Hydroxy-1-phenylethanone
β -Ionone:	(<i>3E</i>)-4-(2,6,6-Trimethylcyclohexen- 1-yl)but-3-en-2-one
α -Isomethylionone:	(<i>3E</i>)-3-Methyl-4-(2,6,6-trimethylcyclohex-2-en-1-yl)but-3-en-2-one
Isophorone diisocyanate:	5-Isocyanato-1-(isocyanatomethyl)- 1,3,3-trimethylcyclohexane
Linalool:	3,7-Dimethylocta-1,6-dien-3-ol
2,2'-Methylenedianiline:	2-[(2-Aminophenyl)methyl]aniline
Methylene diphenyl diisocyanate:	Mixture of 1,1'-methylenebis (4-isocyanatobenzene), 1-isocyanato-2- [(4-isocyanatophenyl)methyl] benzene, and 1,1'-methylenebis (2-isocyanatobenzene)
γ -Nonalactone:	5-Pentylloxolan-2-one
4-Phenyl-1-cyclohexene:	Cyclohex-3-en-1-ylbenzene
Phosgene:	Carbonyl dichloride
Propylene oxide:	2-Methyloxirane
Toluene diisocyanate:	Mixture of 2,6-diisocyanato-1- methylbenzene and 2,4-diisocyanato- 1-methylbenzene
2,4,6-Trichloroanisole:	1,3,5-Trichloro-2-methoxybenzene
Vanillin:	4-Hydroxy-3-methoxybenzaldehyde
Verdyl acetate:	3a,4,5,6,7,7a-Hexahydro-1 <i>H</i> -4,7- methanoinden-5-yl acetate

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no competing financial interest.

Acknowledgments

We thank the EUROPUR and EURO-MOULDERS member companies that provided samples for this study for their generous support. We also thank Adri Aerts from Vita, Michel Baumgartner from EUROPUR, Gunther Guetens from Ascorium, and Stephan Wendel from EURO-MOULDERS for their invaluable contributions, fruitful discussions, and guidance throughout the research project. The project was supported by the European Association of Flexible PU Foam Blocks Manufacturers (EUROPUR) and the European Association of Manufacturers of Moulded PU Parts for the Automotive Industry (EURO-MOULDERS).

Supplementary Materials

Additional information on GC instruments. Table S1: glossary. Table S2: list of odorants identified in the PU samples. Tables S3–S17: AEDA results obtained with the DB5 column. Tables S18–S32: AEDA results obtained with the DB5 column. Table S33: internal standards, quantifier ions, and calibration lines used for quantitation. Figures S1–S15: time-concentration plots of acetaldehyde and propanal. (*Supplementary Materials*)

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