Odorants in non-food products – Is there more to them than just their smell?

ANDREA BUETTNER[1,2]**, Jonathan Beauchamp**[2]**, Philipp Denk**[1,2]**, Miriam Strangl**[1,2] **and Christoph Wiedmer**[1,2]

[1] *Friedrich-Alexander-Universität Erlangen-Nürnberg, Professorship for Aroma Research, Emil Fischer Center, Department of Chemistry and Pharmacy, Henkestraße 9, 91054 Erlangen, Germany*
[2] *Fraunhofer Institute for Process Engineering and Packaging IVV, Giggenhauser Straße 35, 85354 Freising, Germany*

Abstract

Odours associated with contemporary products are encountered frequently on a daily basis, often with intense potency, yet their chemical nature has been barely investigated, to date. Several studies were performed to identify the substances that cause sensory defects in products that included children's toys, adhesives, and post-consumer plastic waste and their corresponding recycled polymers, which were analysed using odorant analytical techniques derived from the methods used in flavour research. A wide range of odorants were identified in these diverse matrices, with noticeable clustering of certain functional groups or substance classes. This chapter summarises previous findings according to the substance classes of the corresponding odorants and describes the analytical procedures employed for the targeted identification of odorants in polymer matrices.

Introduction

Contemporary products often emanate unusual or unpleasant smells that people are repeatedly confronted with in their everyday lives [1-6]. As with many undesirable smells, consumers report concerns over associated health risks, yet equally, an increasing number of consumers no longer react to such olfactory (warning) signals due to their (mis)belief that some smells, for example, 'plastic', are entirely normal and should not be a cause for concern. In many cases, such smells indeed might be simply harmless by-products of production processes that dissipate quickly after purchase, yet smells of other products can be caused by hazardous compounds. Conversely, however, odourless is not synonymous with harmless.

The continual development and global ubiquity of contemporary materials and associated products presents an increasingly pressing need to monitor and control their quality. In view of this it is interesting to note that the general issue of non-intentionally added substances (NIAS) has received increasing attention in product quality control screenings [7,8].

Recently, we published several studies that explored the odorous artefacts associated with modern materials and products, including those derived from woods, plastics, polymers, consumer waste regrinds, colouring agents, glues, adhesives and binders, and reported on how products of potential concern can be 'sniffed out' analytically. Knowledge of the underlying chemical structures of smells related to these products provides an essential basis to elucidate their formation pathways and is the main premise for developing targeted avoidance strategies and adapted sensor technologies for controlling for such substances. Furthermore, the analytical results provide the basis for risk assessment strategies for those who are exposed to such odorous emissions, not only consumers, but also people that regularly handle such products vocationally.

Experimental

Sensory evaluation

The descriptive analyses of the non-food samples under investigation were carried out by a trained sensory panel. The samples were presented individually in covered glass-vessels. The panel members were asked to open the lid of the vessel and note their perceived odour impressions. After a consensus decision of the odour attributes by the panel, the selected impressions were rated on a scale from 0 (not perceived) to 10 (very strongly perceived). Additionally, the overall intensities were evaluated together with the hedonic ratings. The intensity assessment was performed according to an in-house method based on the industrial standard EN ISO 13299:2016.

Isolation of the volatiles

The identification of odour-active compounds in the samples utilised a non-selective extraction method. Samples were dissolved in high purity dichloromethane and stirred vigorously at room temperature for 30 min. After filtration, the resulting solvent extract was subjected to distillation under high vacuum using solvent-assisted flavour evaporation (SAFE) [9]. This technique ensures a careful isolation of the volatile compounds due to the mild distillation conditions, whereby the temperature of the water bath is held at 50°C and the apparatus at 55°C and under high vacuum. The distillate was then concentrated by Vigreux distillation and micro-distillation [10].

Gas chromatography-olfactometry

The presence of odour-active compounds in the sample distillates was screened using gas-chromatography olfactometry (GC-O). An aliquot of each distillate was applied to the GC-system by the cold on-column technique. This injection technique avoids the formation of breakdown products and the generation of new odorants. At the end of the GC capillary, the effluent was split (1:1; v/v) to a flame ionisation detector (FID) and an odour detection port (ODP), at which a trained panellist determined the odour quality of the odorous regions in the eluent gas. A linear retention index (RI) for each odour-active region was calculated according to van den Dool and Kratz [11]. Experimental details are given in the corresponding publications [1-6].

Odour extract dilution analysis

Odour extract dilution analysis (OEDA) is used to screen for the most odorous components in a sample distillate and thereby provides a measure of the impact of individual odorants to the overall odour impression of the sample [12]. For this purpose, each distillate was volumetrically diluted stepwise with dichloromethane (1+2; v/v) resulting in different solutions corresponding to odour-dilution (OD) factors. An aliquot of each dilution step was analysed by GC-O.

Two-dimensional gas chromatography-mass spectrometry/olfactometry

Unambiguous identification of the constituent odorants of a sample extract was carried out by comparing the mass spectra (electron ionisation (EI) mode at 70 eV), RI, and odour quality with those of corresponding reference substances. This procedure was conducted using two-dimensional gas chromatography-mass spectrometry/olfactometry (2D-GC-MS/O). This system allows odorous portions that elute after separation in the first capillary to be cryo-trapped and subsequently transferred onto a second capillary column with different polarity to that of the first. This provides further separation of volatiles that co-elute from the first capillary column.

Results and discussion

Mono- and polyunsaturated carbonyl compounds

Carbonyl compounds are well known as aroma compounds in food, as are their mechanism of formation, such as for the unsaturated aldehydes (*E*)-non-2-enal or (*E,E*)-deca-2,4-dienal whereby the autoxidation of unsaturated fatty acids forms these fatty, cucumber or cardboard-like smelling compounds [13]. Diverse carbonyl compounds were identified in our recent investigations of non-food materials like toys, post-consumer packaging waste, and adhesives. (*E*)-Non-2-enal (fatty), (*Z*)-non-2-enal (fatty, green, musty), (*E,E*)-nona-2,4-dienal (fatty, peanut-like) and (*E,E*)-deca-2,4-dienal (fatty) were all found to be present in packaging waste and selected toys [1,2,4]. Other aldehydes included (*E*)-oct-2-enal (fatty, musty, peanut-like) in post-consumer packaging waste and toys [2,4], (*E,Z*)-nona-2,4-dienal (fatty) in diverse toys [1,2], and (*Z*)-dec-2-enal and (*E*)-dec-2-enal (fatty, metallic, and fatty, respectively) in packaging waste. Beside mono- and polyunsaturated aldehydes, some unsaturated ketones like the mushroom-like smelling oct-1-en-3-one [1,2,4] and hex-1-en-3-one with a glue-like odour [1,2] were additionally identified. Also, some epoxidised derivatives with metallic odorous attributes like *trans*-4,5-epoxy-(*E*)-non-2-enal [1] and *trans*-4,5-epoxy-(*E*)-dec-2-enal [1,2,4,5] were detected. All of these substances are likely to be formed by the degradation of fatty acids from trace contaminants, such as residual food matter in packaging waste or fatty acid-derived constituents such as fatty lubricants [14], which are used for the production of such materials.

Phenol, guaiacol and alkylated or halogenated derivatives

Phenol and guaiacol derivatives are classes of odorants that are ubiquitous in flora and fauna and are widely used as aromatising agents in the food and perfume industries [15,16], but they were also found to be present in modern plastic products. Phenol (typical phenolic odour), for example, was successfully identified in diverse aquatic toys and swimming aids [1], as well as in a plastic toy sword [6], and its derivative *p*-cresol (horse stable-like) was detected in a fancy-dress handbag for children [2], a toy sword [6], but also in adhesives, where the isomer *o*-cresol was also found to be present [5]. Another phenol derivative that was detected in several products was the leather-like smelling 3-ethylphenol [2,5,6], although its isomer 2-ethylphenol (phenolic odour) was only detectable in the toy sword sample [6]. The latter sample was found to additionally contain traces of 2-isopropylphenol (phenolic), 2-propylphenol (smoky), 3,5-dimethylphenol (phenolic), and 3- and 4-propylphenol (both leather-like, phenolic) [6]. In contrast, guaiacol (smoky) and the halogenated phenol derivative 2-bromophenol (medicinal, plaster-like) were only detected in acrylic adhesives.

The formation of these phenolic compounds in polymer matrices is not fully resolved, although their presence might relate to the use of phenolic antioxidants during the production of such products [17] and their formation during degradation. Nevertheless, other pathways, such as contaminated raw materials (e.g., pigments), might equally contribute to their presence.

Naphthalene and derivatives

Naphthalene is the smallest member of the polycyclic aromatic hydrocarbons (PAHs), a substance class that is commonly associated with health hazards due to the carcinogenic potential of these chemicals. In general, PAHs can be transferred into plastic products by contaminated raw materials such as extender oils or the pigment Carbon black [18].

Naphthalene contaminations in products are not only critical due to potential health hazards, but a secondary issue is the characteristic faecal or mothball-like odour that it can impart to the corresponding products. Polyvinyl chloride products, for instance, have been found to contain this compound, for example, with 74 mg/kg naphthalene detected in an inflatable plastic toy that had been investigated – and subsequently withdrawn from the market – due to its potent smell. It is worthy of note that the article in question was only sent to a specialised laboratory and analysed because its strange odour was noticed by a television crew, leading to media coverage on the issue [19]; as such, it is unlikely that this serendipitous finding is an isolated incident.

Methylnaphthalenes have also previously been responsible for product recalls, with a prominent case in 2010 when the Kellogg Company issued a voluntary recall of 28 million boxes of breakfast cereals in response to consumer reports of off-flavour and off-odour. This sensory defect could be traced back to hydrocarbon contaminations, including methylnaphthalene, in the wax paper liners of the cereal boxes. Unsurprisingly, neither the specific isomer nor the levels of 1- or 2-methylnaphthalene found in the tainted cereals have been made public [20].

These anecdotal examples give us an impression of the range of products in which contaminations of PAHs can occur, thus the detection of naphthalene and a variety of its derivatives in malodorous toys is unsurprising. Two of the products tested in our analyses – namely a fancy dress accessory handbag and a children's toy sword – were found to contain naphthalene as well as both 1- and 2-methylnaphthalene [2,6]. In addition, several dimethylnaphthalene isomers, namely 1,2- and 1,7-dimethylnaphthalene, were detected in both products [2,6]. The handbag additionally contained the isomers 1,4-, 1,5-, 1,6- and 2,6-/2,7-dimethylnaphthalene, as well as 2,3,5-trimethylnaphthalene, whereas 1,2-dihydronaphthalene and 2,6-diethylnaphthalene were present in the sword, and 3-methylisoquinoline was detected in both toys [2,6].

As mentioned above, naphthalene and both 1- and 2-methylnaphthalene exhibit faecal or mothball-like odours, and most of the aforementioned dimethylnaphthalene isomers exhibit similar odours. Surprisingly, the isomers 2,6- and 2,7-dimethylnaphthalene, as well as 2,6-diethylnaphthalene, exhibit anise-like odours, thus these results additionally provide new insights into structure-odour relations of these PAH compounds.

In addition to comprehensive molecular elucidation using classical and enhanced GC-MS approaches, often the absolute concentrations of such compounds within the sample matrix are not indicative of their emissions into the gas-phase, and consequently their exposure potential. GC-MS analyses can partially address this issue by the use of headspace gas sampling, but such methods are intermittent and provide only snapshots of emission profiles. In order to characterise the kinetics of release with higher resolution and accuracy, on-line chemical ionisation mass spectrometry in the form of proton-transfer-reaction mass spectrometry (PTR-MS) can be applied to follow the emissions of PAHs from such products [21]. Preliminary results (unpublished) from such PAH analyses on selected children's products revealed different release kinetics depending on the initial concentration in the material and nature of the material itself. Such insights assist in estimating risk assessment for exposure to affected products.

Terpenes and their oxidation products

Terpenes occur naturally in a large group of plants, bacteria, and in some insects, often as signalling molecules. Two biosynthetic pathways are involved in their formation,

the mevalonate pathway and the deoxylulose pathway, yet the formation of the building block isopentenylpyrophosphate (IPP) is common and fundamental in both. By coupling with another IPP unit, linear terpenes are formed and several changes by reactions such as cyclisation and hydrolysis lead to the large variety of terpenes [22, 23].

Terpenes have been used throughout the ages for a range of purposes, including perfumery and medical treatments such as aromatherapy. Resolving the underlying odorants of plants and resins such as frankincense is essential in this context in order to better understand the potential physiological benefits of their use. In the case of frankincense, several mono- and sesquiterpenes, often oxygenated, were found to be natural constituents of different varieties of the resin, specifically 1,8-cineole (eucalyptus odour), linalool (flowery, fresh, balsamic), verbenone (spicy, soup, bread), *trans*-carveol (mint, eucalyptus, green), carvone (mint, caraway, spicy), and thymoquinone (flatbread, black cumin) [24-26]. Furthermore, the hydrocarbon monoterpenes *α*-pinene (rosiny, pine), *β*-myrcene (geranium), *p*-cymene (solvent-like, fruity), limonene (citrus, soapy, fresh), the sesquiterpene hydrocarbons germacrene (fruity, woody, cherry), *α*-copaene (spicy, broth, woody) and the two oxygenated sesquiterpenes rotundone and mustakone were detected in frankincense samples.

As terpenes often exhibit flowery or fruity notes, they find application as fragrances, deodorants or masking ingredients in a variety of products including cosmetics, washing and cleaning agents. As the biosynthesis of these compounds are rare, terpenes used for such applications are typically produced by chemical synthesis. For example, *β*-ionone is routinely produced from citral and acetone via aldol condensation and cyclisation [27]. Besides toiletries and detergents, foods are often also rich in terpenes such as linalool and 1,8-cineol, especially spices [28]. This presents an issue for packaged foods, whose volatile compounds can migrate from the filling good into the packaging material, and indeed several terpenes have been identified to be present in plastic packaging waste and associated recycled materials [4], including, for example, β-ionone (violet-like) and *α*-isomethylionone (rosy). In the case of *β*-ionone, this compound is not only a common perfuming ingredient, but may also be formed by oxidative degradation in food containing carotenes [29].

Summary

Our analyses demonstrate that comprehensive state-of-the-art odorant analytical techniques – as routinely used in food science – are also a powerful tool to identify the odorants responsible for the intense smells of contemporary products. The odours of the analysed products were found to arise from diverse substances. Many of them, however, belong to the substance class of (poly-)unsaturated carbonyl compounds or derivatives of either phenol, guaiacol or naphthalene. Several odorants were also found to be terpenes or their derivatives. Depending on the substance, odorants might stem from contaminated raw materials or can be formed (as by-products) from contaminants or additives or via oxidation processes during production or storage.

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