

Characterization of odorous contaminants in post-consumer plastic packaging waste using multi-dimensional gas chromatographic separation coupled with olfactometric resolution

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Non-standard abbreviations: **2D-HRGC-MS-O** two-dimensional-high resolution gas chromatography-mass spectrometry/olfactometry, **AEDA** aroma extract dilution analysis, **FID** flame ionization detector, **FD** flavor-dilution, **GC-O** gas chromatography-olfactometry, **HRGC-O** high-resolution gas chromatography-olfactometry, **RI** retention index, **SAFE** solvent assisted flavor evaporation

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Abstract

The increasing world population with their growing consumption of goods escalates the issue of sustainability concepts with increasing demands in recycling technologies. Recovery of post-consumer packaging waste is one major topic in this respect. However, the contamination with odorous constituents today curtails the production of recycling products that meet the high expectations of both consumers and industry. To guarantee odor-free recyclates, the main prerequisite is to characterize the molecular composition of the causative odorants in post-consumer plastic packaging waste. However, targeted characterization of odorous trace contaminants amongst an abundance of volatiles is a major challenge, and requires specialized and high-resolution analytical approaches. For this aim, post-consumer packaging waste was characterized by sensory analysis and two-dimensional high resolution gas chromatography coupled with mass spectrometry and olfactometry. The 33 identified odorants represent various structural classes as well as a great diversity of smell impressions with some of the compounds being identified in plastics for the first time. Substances unraveled within this study provide insights into sources for odorous contamination that will require specific attention in the future in terms of screening and prevention in recycling products.

1 Introduction

Fifty-eight percent of food, beverages and non-food articles in Germany are packaged in plastic materials [1]. Thereby, according to a study of Consultic Marketing & Industrieberatung, published in 2016, 35% of the entire amount of produced plastics were used in the form of packaging materials in 2015 [2]. Overall, the consumption of these bulk goods resulted in 3.02 million tons of post-consumer plastic packaging waste in Germany in 2015 alone [2]. Almost half of this waste is supplied for energetic recovery by incineration [2]. Recovery by mechanical recycling, on the other hand, protects fossil resources by decreasing the consumption of raw materials used for the plastics production as well as the primary energy needed for their manufacturing [3]. Apart from that, recycling counteracts the greenhouse effect and the eutrophication and acidification of water resources [4].

Post-consumer waste generally comprises several components such as different types of polymers (e.g. polyethylenterephthalate, polystyrol), composite materials, and misleadingly depolluted non-plastic waste. The targeted separation of this complex mixture is an important premise to meet the high quality requirements of industrial production, and is likewise one of the main challenges in the management of closed loop recycling. While processes are targeted at improving the mechanical and other production-relevant properties of the recycled plastic materials, technical solutions to avoid or diminish odor-active compounds are just about to be thought after on a systematic basis [5]. Such odorous contaminants may stem from a variety of sources, and are primarily co-enriched in the course of the recovery of plastic polymers out of the heterogeneous waste material.

The potential sources of odorous contaminations may be manifold. The (mis-)usage of plastic packages as storage tanks for juices, household cleaners or motor oil may lead to migration of odorants and other contaminants from filling goods into the

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packaging material which then in turn contaminates the waste. For example, migration of D-limonene, an aroma impact compound of orange juice, into different plastic polymers has been demonstrated by Charara et al. (1992) [6]. Furthermore Huber and Franz (1997) studied volatile compounds in recycled polyethylene from bottles that were collected from household waste [7]. Amongst others, they analyzed well-known odor-active substances such as D-limonene and 1-dodecanol by means of GC coupled with a flame ionization detector (FID) or a MS detector [7].

Besides contamination and migration, residual byproducts such as monomers, oligomers or solvents, as well as environmental factors such as light, heat, oxygen and radiation can be major factors in the formation of malodorous taints of the waste [8]. Especially products of the hydrolysis and oxidative degradation of polymers and additives have been proposed to generate odor-active compounds [9]. Bravo et al. (1992) characterized odorants resulting from thermal oxidation of polyethylene [8]. Using GC with olfactometry detection (O), GC-FID and GC-MS, the authors successfully identified a total of 14 substances, namely saturated aldehydes such as octanal and nonanal, mono-unsaturated aldehydes such as (*E*)-non-2-enal and different ketones such as oct-1-en-3-one and hept-1-en-3-one [8].

In a later study, Tyapkova et al. (2009) analyzed odorants formed during γ -irradiation of polypropylene [10]. Thereby, application of high-resolution gas chromatography with olfactometry detection (HRGC-O) and 2-D-GC-MS-O led to the identification of odorous carboxylic acids such as acetic acid, butanoic acid and 2-/3-methylbutanoic acid. As the intensities of these compounds were increased in the γ -irradiated samples, it was assumed that the off-odor of γ -irradiated products is related to these substances [10].

A key long-term target of sustainable economy is to not only produce recyclates such as plastic bags, flower pots or beverage crates but also challenging products such as food packaging. According to European food legislation, however, such materials must not influence the organoleptic properties of the packaged goods, let alone contain any harmful substances that might migrate into the packaged goods [11]. To achieve packaging materials that are both optimized in terms of their general techno-functional but also their smell properties, optimized washing methods and manufacturing processes are needed. A key premise, however, for targeted avoidance or at least reduction of odorous contaminants is that their chemical structures are well known. However, to the best of our knowledge there are no comprehensive studies in the scientific literature reporting common odorous constituents and their sources and formation pathways in post-consumer plastic waste, and recovered polymers obtained therefrom. To close this gap, this study was designed to first evaluate post-consumer plastic packaging waste by means of sensory analysis. In parallel, characterization of the predominant odor-active compounds was carried out using HRGC–O as well as 2D-HRGC–MS–O. This specialized approach allows detection of highly odor-potent compounds even at trace level as well as of odorants co-eluting with other (odorless) components that may elapse unveiling when using conventional analytical techniques such as 1-D-HRGC–MS without olfactometric coupling [12, 13]. Accordingly, the aim of this study is to translate highly specialized analytical techniques that are well established in food aroma research into this novel area of research.

2 Materials and Methods

2.1 Description of the sample

The sample consisted of about 100 L of post-consumer packaging waste (pieces of approximately 1 cm², prewashed with water at elevated temperature, stored for a maximum of 1.5 years) representing typical household waste such as waste collected in the Yellow Bags by the Duales System Deutschland (so called "Green Dot"). The sample consisted of plastics and plastic composite materials only as metal packages and plastic non packaging material had already been sorted out.

2.2 Chemicals

The following chemicals were obtained from the suppliers given in parentheses:

(3*S*,5*R*,8*S*)-5-isopropenyl-3,8-dimethyl-3,4,5,6,7,8-hexahydro-1(2*H*)azulenone (rotundone) (Symrise, Holzminden, Germany); (3*E*)-4-(2,6,6-trimethylcyclohex-1-en-1-yl)-but-3-en-2-one (β -ionone) \geq 96%; (*E*)-non-2-enal \geq 97%, (*E*)-oct-2-enal \geq 94%, (*E,E*) deca-2,4-dienal \geq 85%; (*E,E*)-nona-2,4-dienal \geq 85%; 4-(4-hydroxyphenyl)-2-butanone (raspberry ketone) \geq 99%; 4-methylphenol (*p*-cresol) \geq 99%; dimethyltrisulfide \geq 98%; acetic acid \geq 99%; oct-1-en-3-one \geq 50%; octanal \geq 99%; 2-methylbutanoic acid \geq 98%; 3-hydroxy-4,5-dimethyl-furan-2(5*H*)-one (sotolone) \geq 97%; 3-isopropyl-2-methoxypyrazine \geq 97%; γ -decalactone \geq 98%; γ -dodecalactone \geq 97%; γ -nonalactone \geq 98%; (Aldrich, Steinheim, Germany); (*E*)-dec-2-enal \geq 95%; (*Z*)-dec-2-enal; (*Z*)-non-2-enal; 4-hydroxy-2,5-dimethyl-3-furanone (furaneol) \geq 99%; butanoic acid \geq 99,5%; nonanal \geq 95% (Fluka, Steinheim, Germany); 1-(3,4-dihydro-2*H*-pyrrol-5-yl)ethanone (2-acetyl-1-pyrroline) \geq 95%; (*trans*)-4,5-epoxy-(*E*)-dec-2-enal \geq 97% (aromaLAB, Freising, Germany); 4-hydroxy-

3-methoxybenzaldehyde (vanillin) \geq 99% (abcr, Karlsruhe, Germany); 1,2,7,7-tetramethylbicyclo[2.2.1]heptan-2-ol (2-methylisoborneol) (Sigma, Steinheim, Deutschland); 2,4,6-trichloroanisole \geq 98%; (LGC Standards, Wesel, Germany); 3,4,4 α β ,5,6 β ,7,8,8 α -octahydro-4 α ,8 α β ,9,9-tetramethyl-1,6-methanonaphthalen-1 β (2*H*)-ol (patchouli alcohol) \geq 98% (Biozol, Eching, Germany); 3-ethoxy-4-hydroxybenzaldehyde (ethylvanillin) \geq 98% (SAFC, Steinheim, Germany); 3-methyl-4-(2,6,6-trimethyl-2-cyclohexenyl)-3-buten-2-one (α -isomethylionone) \geq 99% (Sigma-Aldrich, Steinheim, Germany); 4,6,6,7,8,8-hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[*g*]isochromene (galaxolide) (fragrances International, Paris, France)

2.3 Solvent extraction of the sample

The volatiles of the waste material were extracted by stirring approx. 5 g of the sample in 200 mL dichloromethane in an iodine determination flask for 30 min. After filtration of the extract, non-volatile, dichloromethane-soluble matrix compounds were separated from the volatiles by means of solvent assisted flavor evaporation (SAFE) according to Engel et al. (1999) [14]. Thereby, the water bath of the distillation flask was thermostatted at 50°C whereas the water jacketing system for thermostating of the SAFE-apparatus was held at 55°C. Evaporated solvent and volatiles were collected in a flask cooled with liquid nitrogen. The obtained dichloromethane distillate was then thawed and concentrated to a total volume of 80 μ l at 50°C by using Vigreux distillation and microdistillation as described by Bemelmans [15].

2.4 High resolution gas chromatography with olfactometry

HRGC–O was performed with a TRACE GC Ultra (Thermo Fischer Scientific GmbH, Waltham, US) using the following capillaries: DB-FFAP (30 m x 0.32 mm, film thickness 0.25 μm ; J & W Scientific Agilent Technologies, Santa Clara, US) and DB-5 (30 m x 0.32 mm, film thickness 0.25 μm ; J & W Scientific Agilent Technologies, Santa Clara, US).

For the injection of the sample into the GC system the cool-on-column-technique (40°C) was applied. After 2 min the temperature of the GC containing the DB-FFAP capillary was raised at 10°C/min to 230°C whereas the temperature of the DB-5 capillary was raised at 8°C/min to 250°C. On both columns the final temperature was held for 5 min. The flow rate of the helium carrier gas was 2.2 mL/min. At the end of the capillary the effluent was split into two equal parts and transferred to a sniffing port and a FID by means of two deactivated but uncoated fused-silica capillaries (50 cm x 0.2 mm). FID and sniffing port were held at 250 and 270°C, respectively. The HRGC–O analyses were performed by at least three trained panelists (cf. Sensory Evaluation).

2.5 2-D high-resolution gas chromatography with mass spectrometry and olfactometry

The 2D-HRGC–MS–O system consisted of two CP 3800 GCs (Agilent Technologies, Santa Clara, US) in combination with a Saturn 2200 MS (Agilent Technologies, Santa Clara, US). The GCs were coupled with a Cryo-Trap System CTS 1 (Gerstel).

The first GC was equipped with a DB-FFAP capillary, the second GC contained a DB-5 capillary (column details see HRGC–O).

The application of the sample extracts to the GC system was performed at 40°C using the cool-on-column-technique. After 2 min the temperature of the first oven was raised at 8°C/min to 230°C and held for 5 min. By cryo-trapping (–100°C) and thermodesorption (250°C) the odorants were transferred onto the second oven. The temperature of this oven was raised at 8°C/min from 40°C to 250°C and held for 1 min. The flow rate of the helium carrier gas was 7.9 mL/min. At the end of the first capillary, the effluent was split into a sniffing port (290°C) and a FID (250°C). The effluent of the second GC was split again and the eluting compounds were transferred to the mass spectrometer as well as a sniffing-port (290°C).

Mass spectra in the electron impact (MS-EI) mode were generated at 70 eV ionization energy. A mass-to-charge ratio (m/z) range from 35 to 399 was chosen.

2.6 Identification of odorants

Identification of the odor-active compounds was based on the comparison of the odor quality, the retention indices (RI) [16] on both DB-5 and DB-FFAP capillaries and, if procurable, the mass spectral data, in comparison to those of authentic reference compounds.

2.7 Aroma extract dilution analysis

To find out which odorants were the most dominant ones, the flavor dilution factors (FD-factors) of the compounds were determined by means of aroma extract dilution analysis (AEDA) [17] from the following dilution series: the original extract (cf. Solvent extraction of the sample) was diluted stepwise (1 + 2) with dichloromethane. An aliquot of 2 μ l of the original extract (FD 1) and the dilutions with FD 3–2187 were then evaluated by means of HRGC–O using both DB-FFAP and DB-5 capillaries.

2.8 Sensory Evaluation

2.8.1 Panelists

The panel consisted of ten trained volunteers (two male, eight female; age 22–53) from the Fraunhofer IVV Institute (Freising, Germany). The panelists exhibited no known illness at the time of examination and their olfactory capabilities were trained and evaluated during weekly training sessions where panelists were tested for their ability of recognizing, naming and describing selected odorant solutions.

2.8.2 Sensory analyses

5 grams of the sample were presented to the panel in 200 mL wide necked amber bottles. For the descriptive evaluation the panelists were invited to list their ortho-nasal impressions. After collecting the main odor attributes (approval from more than half of the panelists), the panelists were asked to evaluate the intensities of these attributes on a scale from 0 (no perception) to 10 (strong perception). The median values of these ratings were plotted in a spider-web diagram. Furthermore, the

panelists were asked to rate the overall odor intensity of the sample on a scale from 0 (no perception) to 10 (strong perception).

3 Results and Discussion

3.1 Sensory Evaluation

In the course of the first phase of the sensory evaluation, the odor qualities fatty, spicy, woody and dusty were selected by the panel for the description of the sample. The odor profile of the sample, displayed in figure 1, shows that the most intense odor characteristic was the spicy odor with an intensity of 7.0. The attributes fatty and dusty were also rated as intense (intensities of 6.0, respectively). A woody odor was further recorded, but with a slightly lower intensity of 4.5.

The overall odor intensity of the sample was rated with a medium to high intensity with a median value of 6.0.

3.2 Characterization and identification of odor-active compounds in the waste sample

When analyzing the sample by means of HRGC–O, a total of 46 odorants was detected in the original extract (FD 1) on the DB-FFAP capillary. In the extract with the highest flavor dilution factor of 2187 six of these odor-active compounds were still perceived. Thereby, it is important to note that the intense odors did not correlate with the major FID peak signals, showing that trace compounds can be amongst the potent odor contributors, and that quantitative dominance of a substance does not necessarily correlate with smell impact (*cf.* Figure 2).

HRGC–O and 2D-HRGC–MS–O experiments were carried out to identify the most potent odorous compounds. In the course of these investigations, 33 odorants substances could be successfully identified based on their retention indices and odor qualities (*cf.* Table 1). Additionally, 21 of the 33 identified odorants could be unequivocally identified by comparison of the mass spectral data with those of original reference compounds as obtained by means of 2D-HRGC–MS–O. Among the detected compounds, the largest substance group consisted of unsaturated aldehydes. Thereby, fatty odors arose from (*E*)-oct-2-enal, (*Z*)-non-2-enal, (*E*)-non-2-enal, (*Z*)-dec-2-enal, (*E*)-dec-2-enal, (*E,E*)-deca-2,4-dienal and (*E,E*)-nona-2,4-dienal, whereas a metallic note was due to (*trans*)-4,5-epoxy-(*E*)-dec-2-enal. Furthermore, the soapy, citrus like smelling saturated aldehydes octanal and nonanal were identified. Compounds representing perfume-like or coconut-like smells belonged to the lactone group; these were γ -nonalactone, γ -decalactone and γ -dodecalactone. Apart from that, cheesy and vinegar-like smells could be traced back to acetic acid, butanoic acid and 2/3-methylbutanoic acid. β -Ionone and α -isomethylionone with a violet-like and rose-like impression, respectively, the black pepper-like smelling rotundone, 2-methylisoborneol and patchouli alcohol, both with a moldy odor, were potent odorants belonging to the group of (sesqui)terpenoid substances. Vanilla-like smells were due to ethylvanillin and vanillin. A further phenol derivative was *p*-cresol with a fecal, horse-stable-like odor. Other compounds were identified as the mushroom-like smelling oct-1-en-3-one and the raspberry-like smelling raspberry ketone. Moreover, 2-acetyl-1-pyrroline (popcorn-like), dimethyltrisulfide (garlic-like), 3-isopropyl-2-methoxypyrazine (cucumber-, green pepper-like), 2,4,6-trichloroanisol (corky), furaneol (caramel-like), sotolone (spicy, savory-like) and galaxolide (soapsuds, musk like) were successfully identified.

Overall, the highest FD-factor of 2187 was determined for (*trans*)-4,5-epoxy-(*E*)-dec-2-enal (metallic), patchouli alcohol (moldy), sotolone (spicy, savory-like), rotundone (black-pepper-like) and raspberry ketone (raspberry-like). The relative smell intensities of *p*-cresol (fecal, horse-stable-like), vanillin (vanilla-like), α -isomethylionone (rose-like), γ -nonalactone (coconut-like), and 2-methylisoborneol (moldy) were slightly lower, as expressed by their FD factor of 729.

When comparing the results of the sensory evaluation with the odor qualities of the identified compounds, noticeable analogies can be observed. The pronounced spicy note in the sample could be related to the presence of the potent spicy, savory-like smelling odorant sotolone, with a potential additional contribution of rotundone (black-pepper-like). The extremely high FD-factor of 2187 that was determined for both compounds indicates a high relevance of these odorants for the overall smell character of the sample, and is a likely explanation for the high ratings of the spicy impression during sensory evaluation of the sample. Furthermore, the fatty notes are likely to be elicited by the fatty smelling, unsaturated aldehydes. As a number of fatty smelling odorants of this substance class were found, synergistic or additive effects [18] may play a role for the strong perception of fatty odor.

On the other hand, characteristic attributes that might relate to other identified compounds with high FD-factors such as raspberry ketone (raspberry-like) or patchouli alcohol (moldy) were not mentioned in the sensory evaluation. A likely reason is that the perception of some odorants may be suppressed by other odorants when being presented as an odorant mix [19]. However, in view of a later odor removal strategy, such effects can be the reason that certain smell impressions suddenly appear that had not been observed before the cleaning procedure. Untargeted odorant removal might thereby just lead to a shift in aroma profile rather

than odor removal, as otherwise covered or masked odorants might suddenly play an olfactory role. Apart from that, it is also interesting to note that the woody and dusty odor impression described in the sensory analysis cannot be directly linked to the analytical results. In this respect it is important to note that wood smell is not represented by one odorant only but by a complex blend of diverse substances; accordingly, the complex mix of the sample investigated here might also evoke such an association [20]. Likewise is the term dusty a more general term rather than a smell character being associated to a single substance only [21]. On the other hand, combination of different odorants can result in new unexpected odor impressions which might also be happening in the investigated sample [22, 23].

The great variety of identified structures shows that there are numerous potential sources and processes that may be responsible for the odorants found in the analyzed sample. The carbonyl compounds, such as the unsaturated aldehydes and ketones, and the lactones, may stem from autoxidation of fatty acids in residual food materials as well as from fatty acid derivatives that are used as plastic additives such as lubricants [9]; these compounds may, depending on their qualitative and quantitative composition, cause diverse smell effects such as fatty, cardboard-like, and fishy impressions [24–26]. The lactones could, moreover, be formed as degradation products of lactones that are commonly used as heat stabilizers, whereas phenols such as *p*-cresol could stem from phenolic antioxidants [27]. In this context, it is important to note that alkylated phenols can elicit a range of odorous impressions, and are often characterized by relatively low odor thresholds [28]. Furthermore, it is worth mentioning that according to a report of Luger A. from the Institute for Consumer Products of the Lower Saxony State Office for Consumer Protection and Food Safety, Lüneburg, the identified odorants β -ionone, galaxolide

and α -isomethylionone are common smell ingredients in cosmetics and bodycare, as well as household products such as detergents [29]. Therefore, a migration of these substances into the packaging material or a contamination of the waste with product residues appears to be likely. Similar effects with filling products can be assumed regarding the identified (sesqui)terpenoids patchouli alcohol, rotundone and 2-methylisoborneol as formation of these odorants in plastic material is not described in the literature.

On the other hand, the occurrence of 2-methylisoborneol and 2,4,6-trichloroanisol as well as the carboxylic acids is often related to spoilage processes. For example, bacteria such as cyanobacteria and actinomycetes biosynthesize 2-methylisoborneol as volatile metabolite from sesquiterpenoid precursors [30, 31]. So far, the odorant has been particularly identified in water and fish [31–34]. Microbiological transformation may further lead to the generation of 2,4,6-trichloroanisol as some fungi are able to methylate the hydroxyl moiety of the contaminant 2,4,6-trichlorophenol into 2,4,6-trichloroanisol [35, 36]. Thereby it is likely that diverse fungal strains are not only present in paper packaging materials or wine where they may cause a moldy off-odor, but also in the analyzed post-consumer plastic packaging waste. Apart from that, acetic acid bacteria are known for their capability of transforming sugars and alcohols into organic acids [37]. Accordingly, the aforementioned odorants identified in the post-consumer plastic packaging waste in the course of this study are likely to stem from microbial bioconversion of organic residual material. Consequently, avoidance of bioorganic contaminations, together with early limitation of spoilage processes, appears to be one potential strategy to reduce odorous contamination, at least contamination with mold-related compounds.

4 Concluding remarks

The aim of the present study was the characterization of odorants in post-consumer plastic packaging waste. Thereby, sensory analyses confirmed a pronounced odor contamination of the sample. By means of targeted odorant analysis, numerous odorants were found to be involved in the smell of the sample and were successfully identified. Thereby, our studies showed that the causative odorants represent a broad range of diverse chemical structures. Likewise, they exhibit an array of different olfactory impressions. Amongst others, some fatty smelling, unsaturated aldehydes and saturated aldehydes with soapy, citrus-like smell impressions, as well as phenolic compounds and lactones were identified. While some of the detected odorants such as butanoic acid and 2/3-methylbutanoic acid have been identified in previous studies concerning plastics, other odorants like α -isomethylionone, galaxolide and patchouli alcohol have not been previously reported as odor-active compounds in plastic materials. Based on the knowledge of their chemical structures it can be assumed that migration of odorants from the filling products into the packaging material or contamination of the packaging material with these goods, as well as chemical degradation such as fat oxidation and microbial spoilage processes are likely sources of the identified odorants.

This study shows that targeted odor-chemical and sensory analyses are required to establish a fundamental understanding of the underlying odorous principles causing (offensively) smelling plastic packaging post-consumer waste. This knowledge aids future targeted development of improved purification methods and manufacturing processes.

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References

- [1] Schüler K., Umfassende Analyse statt Klein-Klein: Auf Einzelprodukte bezogene CO₂-Labels sagen nicht die ganze Wahrheit. *Lebensmittelzeitung* 2009, 03.
- [2] <http://www.plasticseurope.de/cust/documentrequest.aspx?DocID=67654> (last time accessed: January 11, 2017).
- [3] Hopewell J., Dvorak R., Kosior E., Plastics recycling: challenges and opportunities. *Phil. Trans. R. Soc. B.* 2009, 364, 2115-2126.
- [4] <https://www.gruener-punkt.de/fileadmin/layout/redaktion/mediathek/gruener-punkt-Nachhaltigkeitsbericht-2013-2014.pdf> (last time accessed: January 11, 2017).
- [5] Kitzberger C., Erema: RegrindPro - Quantensprung für das Recycling von Kunststoff-Mahlgut. *plasticker* 2016, 02.
<http://plasticker.de/fachwissen/showartikel.php?id=202&begriff=&backto=/fachwissen/fachartikel.php> (last time accessed: January 18, 2017)
- [6] Charara Z., Williams J., Schmidt R., Marshall M., Orange flavor absorption into various polymeric packaging materials. *J. Food Sci.* 1992, 57, 963-968.
- [7] Huber M., Franz R., Identification of migratable substances in recycled high density polyethylene collected from household waste. *J. High Resol. Chromatogr.* 1997, 20, 427-430.

- [8] Bravo A., Hotchkiss J. H., Acree T. E., Identification of odor-active compounds resulting from thermal oxidation of polyethylene. *J. Agric. Food Chem.* 1992, 40, 1881-1885.
- [9] Mayer F., Breuer K., Material odor–odoractive compounds identified in different materials—the surprising similarities with certain foods, possible sources and hypotheses on their formation. *Indoor Air.* 2006, 16, 373-382.
- [10] Tyapkova O., Czerny M., Buettner A., Characterisation of flavour compounds formed by γ -irradiation of polypropylene. *Polym. Degrad. Stabil.* 2009, 94, 757-769.
- [11] Regulation (EC) No 1935/2004 of the European Parliament and of the Council
- [12] Cortes H. J., Winniford B., Luong J., Pursch M., Comprehensive two dimensional gas chromatography review. *J. of Sep. Sci.* 2009, 32, 883-904.
- [13] Delahunty C. M., Eyres G., Dufour J.-P., Gas chromatography-olfactometry. *J. Sep. Sci.* 2006, 29, 2107-2125.
- [14] Engel W., Bahr W., Schieberle P., Solvent assisted flavour evaporation—a new and versatile technique for the careful and direct isolation of aroma compounds from complex food matrices. *Eur. Food Res. Technol.* 1999, 209, 237-241.
- [15] Bemelmans J. M. H., Review of isolation and concentration techniques. Progress in flavour research. Applied Science Publisher, London 1979, pp. 79-98.
- [16] Van den Dool H.; Kratz P. D., A generalization of the retention index system including linear temperature programmed gas—liquid partition chromatography. *J. Chromatogr. A* 1963, 11, 463-471.
- [17] Grosch W., Evaluation of the key odorants of foods by dilution experiments, aroma models and omission. *Chem. Senses* 2001, 26, 533-545.

- [18] Guadagni D., Buttery R. G., Okano S., Burr H., Additive effect of sub-threshold concentrations of some organic compounds associated with food aromas. *Nature* 1963, 200, 1288-1289.
- [19] Laska M.; Hudson, R., A comparison of the detection thresholds of odour mixtures and their components. *Chem. Senses* 1991, 16, 651-662.
- [20] Bauer P., Identifizierung geruchsaktiver Substanzen in Kiefernholz. state examination, Friedrich-Alexander-Universität Erlangen-Nürnberg, 2016.
- [21] Elsharif S. A., Buettner A., Structure-odor relationship study on geraniol, nerol and their synthesized oxygenated derivatives. *J. Agric. Food Chem.* 2016.
- [22] Buettner A.; Schieberle P., Evaluation of key aroma compounds in hand-squeezed grapefruit juice (*Citrus paradisi* Macfayden) by quantitation and flavor reconstitution experiments. *J. Agric. Food Chem.* 2001, 49, 1358-1363.
- [23] Buettner A.; Schieberle P., Characterization of the most odor-active volatiles in fresh, hand-squeezed juice of grapefruit (*Citrus paradisi* Macfayden). *J. Agric. Food Chem.* 1999, 47, 5189-5193.
- [24] Czerny M., Buettner A., Odor-active compounds in cardboard. *J. Agric. Food Chem.* 2009, 57, 9979-9984.
- [25] Sandgruber S., Buettner A., Comparative human-sensory evaluation and quantitative comparison of odour-active oxidation markers of encapsulated fish oil products used for supplementation during pregnancy and the breastfeeding period. *Food Chem.* 2012, 133, 458-466.
- [26] Sandgruber S., Buettner A. Sensory and molecular characterization of the aroma profiles of fish oil supplements. Proceedings of the 13th Weurman Flavour Research Symposium 2013, pp. 245-249.

- [27] Voigt J., *Die Stabilisierung der Kunststoffe gegen Licht und Wärme*. Tenth Edition, Springer, Berlin 1966
- [28] Czerny M., Brueckner R., Kirchhoff E., Schmitt R., Buettner A., The influence of molecular structure on odor qualities and odor detection thresholds of volatile alkylated phenols. *Chem. Senses* 2011, 26, 539-553.
- [29]
http://www.laves.niedersachsen.de/download/40953/Bericht_ueber_Messungen_des_Einsatzes_von_Duftstoffen_in_Wasch-_und_Reinigungsmitteln.pdf (last time accessed: January 11, 2017)
- [30] Gerber N. N., A volatile metabolite of actinomycetes, 2-methylisoborneol. *J. Antibiot.* 1969, 22, 508-509.
- [31] Izaguirre G., Hwang C. J., Krasner S. W., McGuire M. J., Geosmin and 2-methylisoborneol from cyanobacteria in three water supply systems. *Appl. Environ. Microbiol.* 1982, 43, 708-714.
- [32] Persson P.-E., Sensory properties and analysis of two muddy odour compounds, geosmin and 2-methylisoborneol, in water and fish. *Water Res.* 1980, 14, 1113-1118.
- [33] Mahmoud M. A., Buettner, A., Characterisation of aroma-active and off-odour compounds in German rainbow trout (*Oncorhynchus mykiss*). Part I: Case of aquaculture water from earthen-ponds farming. *Food Chem.* 2016, 210, 623-630.
- [34] Nakamura S., Sakui N., Tsuji A., Daishima S., Determination of 2-methylisoborneol and geosmin in aqueous samples by static headspace-gas chromatography-mass spectrometry with ramped inlet pressure. *J. Sep. Sci.* 2005, 28, 2511-2516.

[35] Tindale C. R., Whitfield F. B., Levingston S. D., Nguyen T., Fungi isolated from packaging materials: Their role in the production of 2, 4, 6-trichloroanisole. *J. Sci. Food Agr.* 1989, 49, 437-447.

[36] Álvarez-Rodríguez M. L., López-Ocana L., López-Coronado J. M., Rodríguez E., Cork taint of wines: role of the filamentous fungi isolated from cork in the formation of 2, 4, 6-trichloroanisole by O methylation of 2, 4, 6-trichlorophenol. *Appl. Environ. Microbiol.* 2002, 68, 5860-5869.

[37] König H., Uden G., Fröhlich J., Biology of Microorganisms on Grapes, in Must and in Wine. Acetic Acid Bacteria. Springer, Berlin 2009.

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Figure captions

Figure 1: Odor profile of the investigated sample. Data are displayed as median values of the sensory evaluation (ten panelists: eight female, two male).

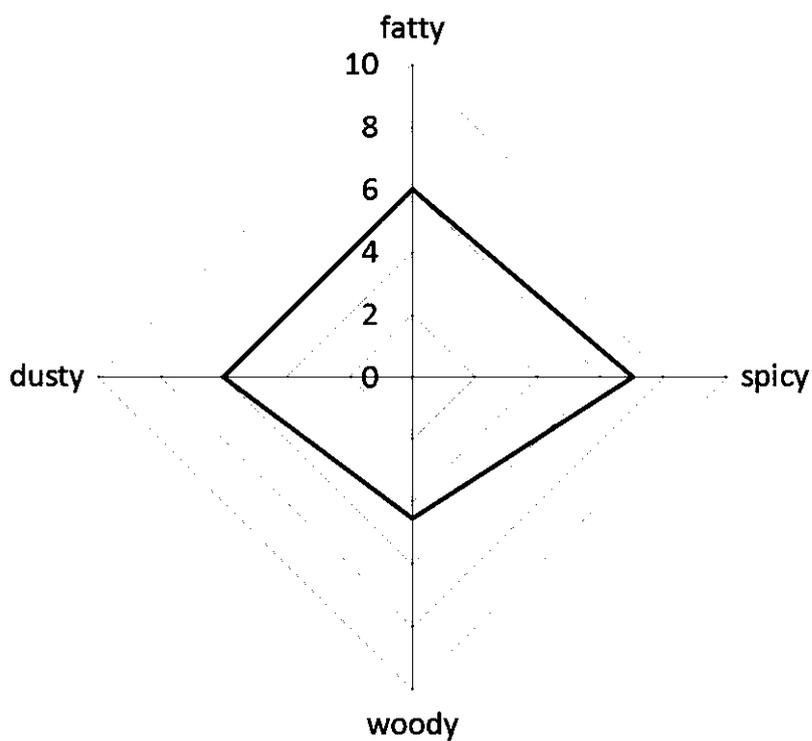


Figure 2: FID chromatogram of the extract corresponding to FD1 on the DB-FFAP column analyzed by means of HRGC–O. Presented are the retention times of the odorants with FD factors of 2187 and 729.

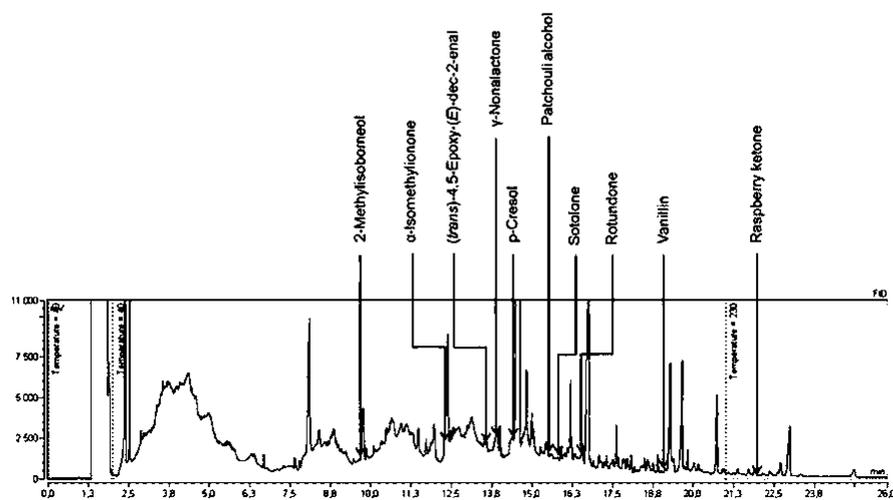


Table 1. Characterization of odor-active compounds by means of AEDA on dichloromethane solvent extracts of the waste sample. Given are the FD factors of the compounds (according to their elution on capillary column DB-FFAP) together with the respective odor qualities and retention indices.

No.	Odorant	Odor quality ^a	FD-factor ^b	RI ^c -value on	
				DB-	DB-5
1	Octanal ^d	Citrus-like	81	1281	1003
2	Oct-1-en-3-one ^f	Mushroom-like	27	1296	982
3	2-Acetyl-1-pyrroline ^f	Popcorn-like	9	1326	921
4	Dimethyltrisulphide ^d	Garlic-like	243	1365	968
5	Nonanal ^e	Soapy, citrus-like	9	1381	n.d.
6	(<i>E</i>)-Oct-2-enal ^d	Fatty, musty	81	1418	1060
7	3-Isopropyl-2-methoxypyrazine ^f	Cucumber-like, green pepper-like	81	1426	1097
8	Acetic acid ^e	Vinegar-like	27	1448	n.d.
9	(<i>Z</i>)-Non-2-enal ^f	Fatty, musty	27	1504	1147
10	(<i>E</i>)-Non-2-enal ^d	Fatty	81	1529	1164
11	2-Methylisoborneol ^f	Moldy	729	1579	1196
12	(<i>Z</i>)-Dec-2-enal ^f	Fatty	9	1596	1249
13	Butanoic acid ^d	Cheesy	81	1620	811
14	(<i>E</i>)-Dec-2-enal ^d	Fatty, metallic	9	1630	1261
15	2/3-Methylbutanoic acid ^f	Cheesy, Sweaty	81	1668	866
16	(<i>E,E</i>)-Nona-2,4-dienal ^e	Fatty	81	1695	n.d.
17	2,4,6-Trichloroanisol ^f	Corky	243	1795	1338
18	(<i>E,E</i>)-Deca-2,4-dienal ^d	Fatty	9	1803	1318
19	α -Isomethylionone ^e	Rose-like	729	1838	n.d.
20	β -Ionone ^d	Violet-like	243	1935	1480
21	(<i>trans</i>)-4,5-Epoxy-(<i>E</i>)-dec-2-enal ^d	Metallic	≥ 2187	2006	1379
22	γ -Nonalactone ^e	Coconut-like	729	2017	n.d.
23	4-Hydroxy-2,5-dimethylfuran-3(2H)-one ^f	Caramel-like	9	2028	1066
24	<i>p</i> -Cresol ^d	Fecal, horse-stable-like	729	2083	1078
25	γ -Decalactone ^e	Perfume-like	27	2139	n.d.
26	Patchouli alcohol ^d	Moldy	≥ 2187	2161	1664
27	3-Hydroxy-4,5-dimethylfuran-2(5H)-one ^f	Spicy, savory-like	≥ 2187	2194	1114
28	Rotundone ^d	Black pepper-like	≥ 2187	2253	1712
29	Galaxolide ^d	Soapsuds-like, musk-like	243	2300	1852
30	γ -Dodecalactone ^f	Perfume-like	9	2370	1665
31	Ethylvanillin ^e	Vanilla-like	243	2540	n.d.
32	Vanillin ^d	Vanilla-like	729	2575	1400
33	Raspberry ketone ^f	Raspberry-like	≥ 2187	2990	1555

a) Odor quality perceived at the sniffing port

b) Flavor-dilution factor (FD) on capillary DB-FFAP according to [17]

c) Retention index (RI) on capillaries DB-FFAP and DB-5 according to [16]

d) The compound was identified by comparison of odor quality, retention index on both capillaries and mass spectrum (MS-EI), obtained by 2D–HRGC–MS/O analysis, with the properties of the reference compound.

e) The compound was identified by comparison of odor quality, retention index on capillary DB-FFAP and mass spectrum (MS-EI), obtained by 2D–HRGC–MS/O analysis, with the properties of the reference compound.

f) The compound was identified by comparison of odor quality and retention indices on capillaries DB-FFAP and DB-5 with the properties of the reference compound.

n.d. not determined